

# Alteration of Mancos Shale by Synthetic Hydrofracturing Fluid

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## Research Motivation

Shale gas produced through hydrofracturing has changed the energy perspective in the United States. Shale gas extraction is complicated by the fast decline in wellbore production, and requires re-stimulation and drilling new wells. Understanding mineralogical composition of an altered layer of shale (we used Mancos shale in this study) will provide insight whether methane transport through these altered zones is affected compared to the unaltered material.

## Research Objectives

Our goal is to conduct an integrated experimental and modeling study to fundamentally understand methane partitioning in the nanopores of mudstone matrices. We examined methane transport from low-permeability matrices to fracture networks induced by hydraulic fracturing that control gas-in-place and well production.

## Method

The alteration of Mancos shale in hydrofracturing fluid in Parr digestion vessels for 1–2 months at 90°C (Figure 1). Additional experiment–pure clay minerals (illite and illite/smectite) were reacted under the same conditions to deduce whether clay mineral dissolution occurs under these conditions.

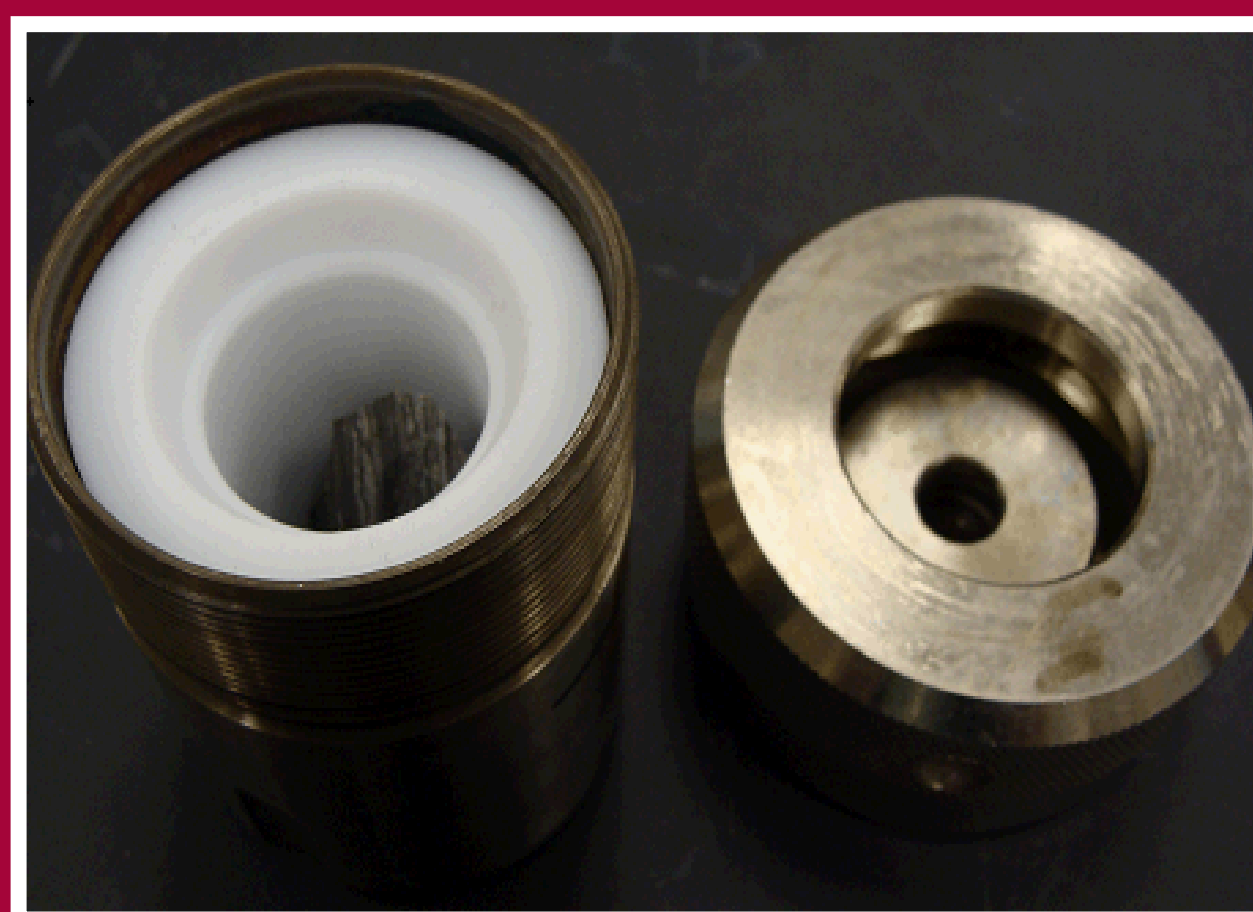


Figure 1: Alteration of Mancos shale under hydrothermal conditions

Characterization– X-ray diffraction (XRD)– powder and micro-XRD, and micro-X-ray fluorescence mapping (micro-XRF). Analysis of liquids for major anions and cations–ion chromatography (IC), and for trace metals by inductively coupled plasma mass spectrometry (ICP-MS).

Synthetic hydrofracturing fluid: 0.1% Polyacrylamide; 0.05% Sodium polyacrylate; 0.1% Sodium chloride; 0.02% Methanol; 0.01% Hydrochloric acid; 0.007% Tetrakis (hydroxymethyl) phosphonium sulfate.

Geochemical modeling: The Geochemist's Work Bench (GWB) Path of Reaction Modeling (Bethke, 1998), is used to interpret geochemical data. The initial aqueous composition is hydrofracturing fluid and reactants are the minerals detected in Mancos shale. Reacting minerals and kinetic rate constants are listed in Table 1, and input fluid composition – in Table 2.

## Future Work

- We will perform methane adsorption measurements on Mancos shale in both native and altered by hydrofracturing fluid states
- We will use longer reaction times and more aggressive types of hydrofracturing fluids and characterize alteration zones on shale using micro X-ray Fluorescence and micro-X-ray Diffraction.
- Finalize geochemical model to take into account complexation.

## Results–Mineralogical Changes

### Micro-XRF maps

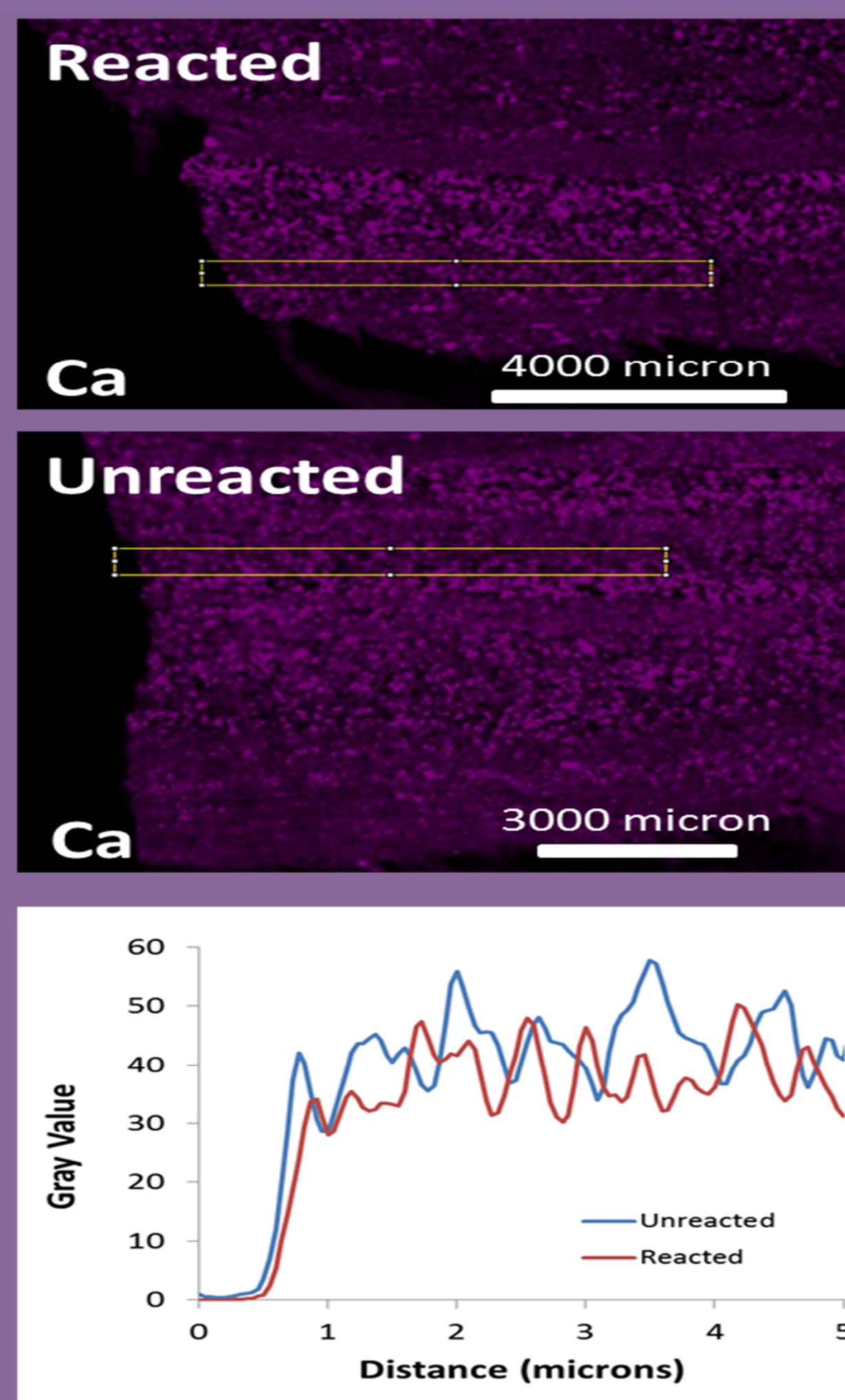


Figure 2: Micro-XRF mapping

### Bulk XRD

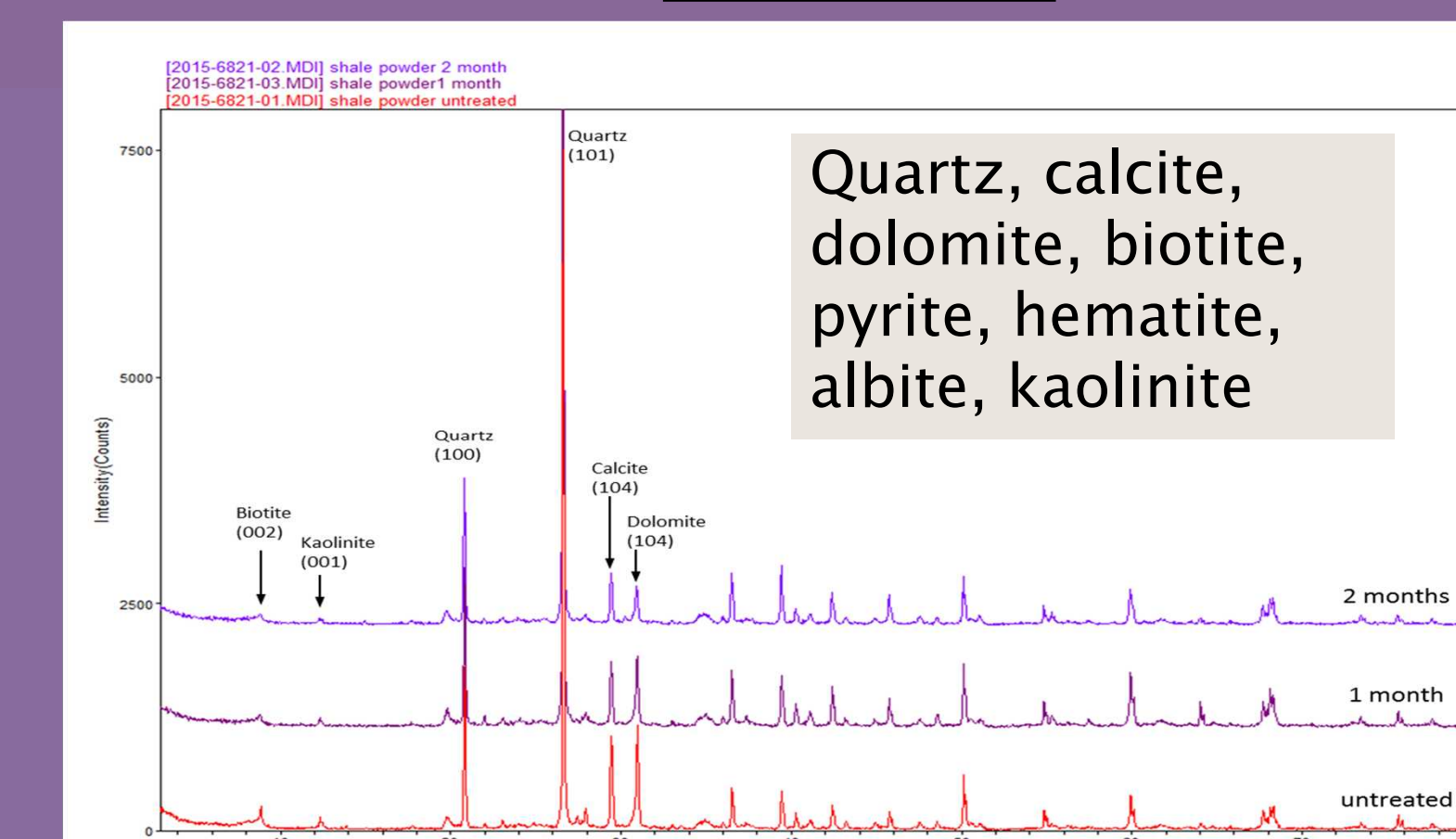


Figure 3: XRD results

Calcium, barium, strontium, magnesium, manganese, silica, sodium, chloride and sulfate were released from Mancos shale after reaction with hydrofracturing fluid. Altered zones on shale surface after 2 months of reaction are thin – likely, within a few microns (Figure 2). The XRD patterns normalized to the 100% peak for quartz indicate that the dolomite, calcite, biotite, and kaolinite peaks decrease in intensity relative to the quartz peaks with increased treatment time (Figure 3). Dissolved aluminum did increase in the illite/smectite reactor but not in the pure illite reactor; indicating smectite is more soluble in these conditions. However, no dissolution of illite and illite/smectite was observed. Understanding mineralogical composition of the altered layer will provide insight whether methane transport through these zones will be affected compared to the unaltered material.

## Results– Geochemical Modeling

Table 1

Mineral	Specific surface area*, cm <sup>2</sup> /g	Solid to fluid ratio, g/L	Kinetic rate constant log (mol/cm <sup>2</sup> sec)
Quartz	8.3	53.7	-17
Calcite	8.3	3.3	-8
Dolomite	8.3	5.1	-12
Muscovite	8.3	1.3	-14
Kaolinite	8.3	0.7	-14
Albite	8.3	1.3	-15.6
Pyrite	8.3	0.7	-14.6

Table 2

Input	
pH	3.98
Na <sup>+</sup>	430 mg/L
Cl <sup>-</sup>	700 mg/L
SO <sub>4</sub> <sup>2-</sup>	21 mg/L
SiO <sub>2</sub> (aq)	370 mg/L
Temperature	90 °C
Reaction time	60 Days

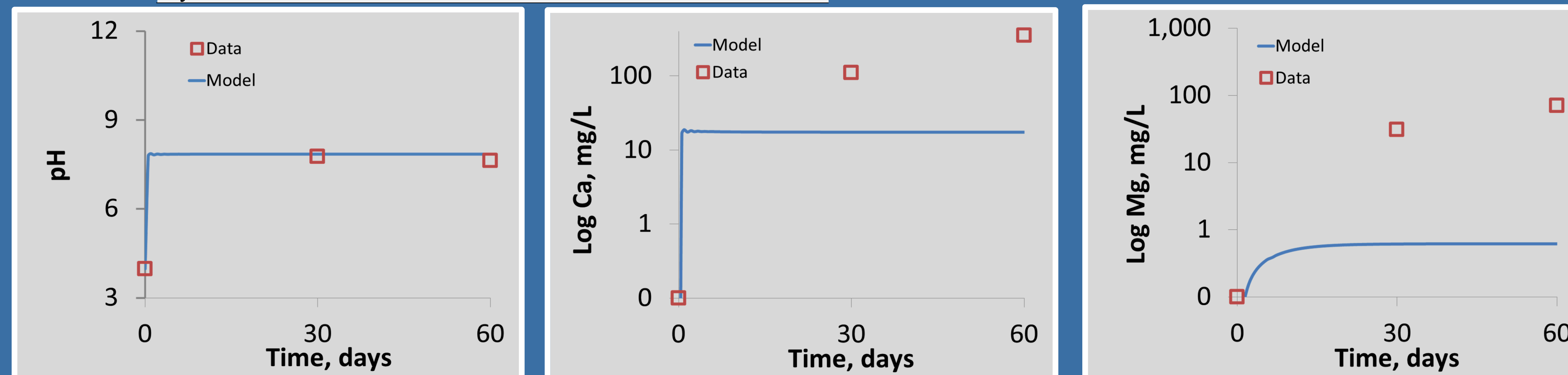


Figure 4: Geochemical models

Preliminary geochemical models (Figure 4) predict dissolution of calcite, and dolomite, and corresponding rise in pH. Geochemical model under-predicts calcium and magnesium concentration, as it does not account for the formation of the polyacrylate–alkaline earth metal complexation.

### References:

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