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## **Impact of geochemical interactions between hydraulic fracturing fluid and Whitby Mudstone on mineralogy and fracture permeability**

Maartje E. Houben (1), John Kaszuba (2), Auke Barnhoorn (3), and Suzanne J.T. Hangx (1)

(1) Department of Earth Sciences, Utrecht University, Budapestlaan 4, 3584 CD Utrecht, The Netherlands, (2) Department of Geology & Geophysics and School of Energy Resources, 1000 E. University Ave., University of Wyoming, Laramie, Wyoming 82071 USA, (3) Faculty of Civil Engineering and Geosciences, Stevinweg 1, 2628CN Delft, the Netherlands

Development of unconventional shale oil and gas reservoirs combines mechanical and chemical stimulation in horizontal wells that extend for hundreds to thousands of meters within organic-rich formations. Chemical imbalance between the shale and injected fluids, a mixture of water, chemical additives, and proppants, potentially drives geochemical reactions that may alter mechanical properties of the rock. Simultaneously, induced fracturing may drive physical changes that alter geochemical water-rock interactions. Coupling and feedback mechanisms between geochemical and geomechanical processes are poorly understood in these dynamic systems.

We examine how a mechanically-induced fracture network may alter geochemical reaction pathways between shale and stimulation fluid used in hydraulic fracturing and the impact this may have on (fracture) permeability. Therefore, we studied two fractured samples taken from the Mulgrave Shale member of the Whitby Mudstone (Early Jurassic, UK). The Mulgrave Shale member consists of fissile, bituminous, dark grey mudstone with TOC values of 4-15%. One sample was cleaved along the bedding plane, while the second sample was deformed in direct shear to induce multiple fractures, with a surrounding damage zone. For both samples we measured argon gas permeability before and after fracturing, as well as performed CT-imaged to capture the intact and fractured microstructure.

Both fractured shales were subsequently reacted with stimulation fluid at 10 MPa and 100°C for approximately 2000 hours. The fluid was an acidic (pH = 2.1), NaCl water (ionic strength = 0.07 mol/kg) containing mmol/kg quantities of Ca, Mg, HCO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. The fluid also contained two additives typically used in hydraulic fracturing, KCl (10 mmol/kg) as a clay stabilizer and acetic acid (3.3 mmol/kg) to inhibit precipitation of Fe oxyhydroxides. Furthermore, Cs (1 mmol/kg) was added to improve CT-imaging of fluid penetration into the fractures and shale matrix. During batch reaction, the reaction fluid was sampled regularly to monitor reaction progress.

Post-reaction, we again imaged the samples using CT and measured permeability. Fluid analysis showed that pH increased from 2.1 to about 6 after 1000 hours of reaction in both shales, but pH increased slightly more rapidly by reaction in the shale with the damage zone. Total dissolved inorganic carbon evolved in similar fashion in both experiments and did not readily distinguish between the two styles of fracturing induced in the Whitby Mudstone. In this contribution, we will present the results of the permeability and mineralogical evolution of these samples in more detail.