MODELING CO_2–H_2S–WATER–ROCK INTERACTIONS IN WILLISTON BASIN CARBONATES UNDER RESERVOIR CONDITIONS

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This work reports results that were obtained during a series of laboratory experiments and numerical modeling of geochemical reactions performed by the Plains CO_2 Reduction (PCOR) Partnership. The PCOR Partnership represents more than 80 public and private sector partners located in nine states and four Canadian provinces in the heartland of North America. It is one of seven regional partnerships that make up the Regional Carbon Sequestration Partnership Program managed within the U.S. Department of Energy's Office of Fossil Energy and implemented through the National Energy Technology Laboratory. The main goal of these experiments was to determine the chemical kinetics of mineral dissolution and precipitation caused by carbon dioxide or sour gas injection into a Williston Basin (North Dakota, USA) formation for storage or enhanced oil recovery (EOR).

In order to simulate these geochemical reactions, core samples were collected from the Mississippian Madison Group, a carbonate-dominated group of formations in the Williston Basin. Also, several pure mineral samples (e.g., magnesite, magnetite, etc.) were obtained from commercial vendors and utilized as kinetic indicators. Samples in a form of powder and solid core plugs were exposed for a period of 4 weeks to pure supercritical carbon dioxide (CO_2) and a mixture of supercritical CO_2 (67.3 mol%) and hydrogen sulfide (32.7 mol%) at 2250 psi (155 bar) and 158°F (70°C) in 10 wt% NaCl synthetic brine conditions.

The mineralogy of the Madison Group samples was determined utilizing x-ray diffraction (XRD), x-ray fluorescence, and QEMSCAN® analytical techniques, and integrative mineralogical analysis was performed utilizing linear program normative analysis. This analysis demonstrated the presence of ankerite, anorthoclase, anhydrite, calcite, cristobalite, dolomite, halite, hematite, kaolinite, illite, pyrite, and quartz in the Madison Group samples. The reactive surface area analysis was performed with ArcGIS software, where QEMSCAN data was processed, in order to determine the pore geometry.

After exposure, XRD and QEMSCAN analysis of reaction products was also performed. Some minerals displayed high reactivity with acid gas, including the conversion of anhydrite to gypsum. Other samples showed high reactivity while exposed to pure CO_2; for instance, the pyrite was completely dissolved in brine and precipitated as a siderite and hematite later in a course of the experiment; the hematite was dissolved in brine and partially reprecipitated or converted in siderite; and the dolomite partially was converted to calcite and magnesium carbonate. In turn, the alteration of porosity and permeability of rocks as a result of dissolution and precipitation of minerals was observed. Moreover, a comparison of reactivity of the powdered samples against core plugs was conducted: it appeared that powdered samples reacted at comparable rates with solid rock samples. Furthermore, the fluid analysis also reported presence of Fe, K, Ca, Mg, and Si after exposure to CO_2 and sour gas water.

The results of the laboratory experiments were compared with numerical modeling that was performed with the Geochemist's Workbench, PHREEQC, and CMG software packages, where the thermodynamic database was adjusted with SUPRCRT92 code. The kinetic formula from Lasaga was altered in order to fit the observed mineral dissolution and precipitation patterns. For instance, it was discovered that calculations based on the Pitzer thermodynamic database provide better accuracy in predictions not only numerically but also conceptually. Overall, after adjusting thermodynamic databases and tweaking the kinetic parameters, such as reactive surface area, etc., the kinetic modeling and 3-D reactive transport modeling are in good correlation with the laboratory observations. The results of this work were utilized to understand geochemical interactions during EOR operations at the Northwest McGregor oilfield (Williston Basin, North Dakota, USA), where 440 tons of carbon dioxide was injected in order to determine the effects of CO_2 on the productivity of the reservoir, wellbore integrity, overall reservoir properties, etc.