

An experimental and modelling study on H₂SO₄-rock-brine reactions under varying conditions

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Flue gas from coal fire plants is by enlarge dominated by CO₂ but may contain low concentrations of SO₂. The geological storage of CO₂-SO₂ as an impurity is likely to cause enhanced brine acidification through the formation of sulphuric acid. Potential secondary effects are more extensive mineral dissolution and precipitation. Batch reactor experiments were conducted and geochemically modelled to improve our understanding of SO₂-rock-brine reactions under well-defined conditions so to enhance our ability to geochemically model CO₂-SO₂ storage. Sedimentary rock samples from the Western Canada Sedimentary Basin, Canada, and the Surat Basin, Australia, were reacted with synthetic brine in short-term reactor experiments of 30d duration. The brine was acidified with H₂SO₄, an aqueous proxy of SO₂, and was sampled throughout the experiment. Temperature, starting pH and sample particle size were varied to investigate their impact on reaction rates. The experimental results show that an addition of H₂SO₄ induces reactions that are strongly dependent on the mineralogy. Reaction rates were increased at lower pH, higher temperature and/or smaller sample particle size. Mineral phases participating in the reactions were identified by integrating the experimental results into kinetically controlled reaction path models using Geochemist's Workbench. The experimental data were modelled in two time intervals. Within the first 48h rapid changes were observed due to sample fines, which have a greater reactive surface area. The following 28d showed lower reaction extent and fit models with smaller reactive surface areas. In all cases the modelling provided a good fit to the experimental data. Carbonate minerals acted as significant buffers of pH, with decreasing reactivity observed from calcite to dolomite then siderite. By fitting the models to the experimental data calcite was identified as a dissolving mineral phase showing a change of up to 0.2 wt%. Further, the modelling results suggest that nearly an equal amount of gypsum precipitated. For the less reactive silicate phases the models indicate dissolution (e.g. 0.07 wt% chlorite) and in some cases precipitation (e.g. 2*10⁻⁴ wt% SiO₂) taking place. The models will be extended to longer time frames to investigate long term effects to up to 100 years.