# Following the reactions of hydration, dissociation and oxidation of $SO_2$ in saline brines by Raman spectroscopy

C. OSTERTAG-HENNING[1]

[1]Federal Institute of Geosciences and Natural Resources, Stilleweg 2, D-30665, Hannover, (correspondence: christian.ostertag-henning@bgr.de)

The fate of impurities in $CO_2$ being co-injected into geological storage sites containing saline brines has been investigated in numerous experiments and modelling studies. The results were contradicting, some authors stated, that $SO_2$ has no significant effect on the reservoir [1] as no significant mineral dissolution or precipitation would be induced, others put forward the hypothesis, that $SO_2$ would induce significant mineral dissolution and hence changes in porosity/ permeability in the vicinity of the injection borehole [2] or that $SO_2$ would rapidly be converted to sulfate and then precipitated, decreasing permeability [3]. The main differences result from assumptions on the chemical reactions relevant in the subsurface, e.g. whether disproportionation of $SO_2$ to $H_2SO_4$ and $H_2S$ is occuring in the reservoir.

Besides the scarcity of solubility data of $SO_2$ in saline brines at in situ temperature and pressure conditions one crucial shortcoming in todays geochemical modelling attempts is the lack of kinetic data on the reactions hydration or dissolution of $SO_2$, its dissociation in saline brines, its possible disproportionation and redox reactions as oxidation by dissolved ions and on mineral surfaces at in situ pressures and temperatures.

To study these reactions with Raman spectroscopy, a dedicated system was developed with four optical heads connected by fibre optics to the spectrometer. These heads allow the parallel acquisition of spectra and hence detection of sulfur species (and its isotopomers) at four locations in a gas-liquid-mineral surface system contained in a fluid flow pathway made of quartz glass. And it allows unravelling of different fast reactions: in addition to the hydration and dissociation, the diffusion of individual species and redox reactions with dissolved ions or gases added at one location in the system. These observations help to address open questions about the kinetics of reactions of $SO_2$ in the subsurface during the ongoing $CO_2$ injection and delinates the partitioning of $SO_2$ from the $CO_2$ into the saline brine.

[1] Bacon *et al.* (2009) Energ. Proc. **1**, 3283. [2] Kummerow & Spangenberg (2011) *Geochem. Geophys. Geosys.* **12**, Q05010. [3] Pearce *et al.* (2016) *Appl. Geochem.* **72**, 59.