



## **The fractionation of Fe and Cu between brine and CO<sub>2</sub> at up to 130 °C and 8.4 MPa, with implications for metal mobilization in CO<sub>2</sub> storage reservoirs**

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In order to better understand the long-term effects of CO<sub>2</sub> storage in saline aquifers, there has been increasing interest in the mobilization of metals in brine-CO<sub>2</sub> systems, in the context of both permanent mineral trapping and the potential spreading of contaminants. Owing to the fact that the brine is a stronger solvent than CO<sub>2</sub> for polar metal complexes, previous studies have focused primarily on brine-reservoir rock interactions (e.g., Gunter et al., 1997; Wigand et al., 2008), and the role of CO<sub>2</sub> as a separate solvent has yet to be considered. While CO<sub>2</sub> may not be a strong solvent, even ppm-level metal concentrations represent a considerable amount of mobilization in reservoirs that are host to millions of tonnes of CO<sub>2</sub>, so a quantitative evaluation of this process is desirable.

To this end, we have conducted an experimental investigation of vapour-liquid equilibria in the systems FeCl<sub>3</sub>-NaCl-CO<sub>2</sub>-H<sub>2</sub>O and CuCl<sub>2</sub>-NaCl-CO<sub>2</sub>-H<sub>2</sub>O at 60-130°C and 6.5-8.5 MPa. The experiments were carried out in a large-volume autoclave loaded with a solution containing 20 wt% NaCl and either 100 ppm Fe or 1000 ppm Cu, as well as pressurized CO<sub>2</sub>. Paired samples of brine and CO<sub>2</sub> were extracted from separate capillary lines at successive pressure-temperature intervals, and analyzed for Fe and Cu using ICP-AES. The CO<sub>2</sub> samples were found to contain concentrations of 0.5 to 2.0 ppm Fe and 0.5 to 6.7 ppm Cu, which generally displayed a positive correlation with fluid density. Given the relatively small degree of metal fractionation into the CO<sub>2</sub> as compared to the brine, the concentrations in the brines remained constant at 100 ppm Fe and 1000 ppm Cu. From these data, it can be seen that the Fe and Cu concentrations in the CO<sub>2</sub> are approximately 1% and 0.1% of those in the brine, respectively.

Considering the metal concentrations typical to brines that have reacted with CO<sub>2</sub> and sandstone (20-200 ppm Fe, 1 ppm Cu; e.g., Gunter et al., 1997; Wigand et al., 2008), these results suggest that a plume of injected CO<sub>2</sub> could contain up to 0.2-2 ppm Fe and 0.001 ppm Cu. At a hypothetical injection site used to store 10 Mt of CO<sub>2</sub>, this would lead to the mobilization of 20 t of Fe and 0.01 t of Cu. Further, as the dissolution of Fe and Cu is chemically similar to that of other metals such as Pb and Zn, the relocation of significant quantities of additional metals may also be expected. The potential consequences of these results for long-term CO<sub>2</sub> storage include the precipitation of metal carbonate minerals in shallower, more distal regions of the aquifer and the transferral of metals to adjacent aquifer systems.

### **References**

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