



Leaching of organic acids from macromolecular organic matter by non-supercritical CO₂

P. Sauer, C. Glombitza, and J. Kallmeyer

Institute of Earth- and Environmental Science, University of Potsdam, Potsdam, Germany

The storage of CO₂ in underground reservoirs is discussed controversially in the scientific literature. The worldwide search for suitable storage formations also considers coal-bearing strata. CO₂ is already injected into seams for enhanced recovery of coal bed methane. However, the effects of increased CO₂ concentration, especially on organic matter rich formations, are rarely investigated.

The injected CO₂ will dissolve in the pore water, causing a decrease in pH and resulting in acidic formation waters. Huge amounts of low molecular weight organic acids (LMWOAs) are chemically bound to the macromolecular matrix of sedimentary organic matter and may be liberated by hydrolysis, which is enhanced by the acidic porewater. Recent investigations outlined the importance of LMWOAs as a feedstock for microbial life in the subsurface [1]. Therefore, injection of CO₂ into coal formations may result in enhanced nutrient supply for subsurface microbes.

To investigate the effect of high concentrations of dissolved CO₂ on the release of LMWOAs from coal we developed an inexpensive high-pressure high temperature system that allows manipulating the partial pressure of dissolved gases at pressures and temperatures up to 60 MPa and 120°C, respectively. In a reservoir vessel, gases are added to saturate the extraction medium to the desired level. Inside the extraction vessel hangs a flexible and inert PVDF sleeve (polyvinylidene fluoride, almost impermeable for gases), holding the sample and separating it from the pressure fluid. The flexibility of the sleeve allows for subsampling without loss of pressure.

Coal samples from the DEBITS-1 well, Waikato Basin, NZ ($R_0 = 0.29$, TOC = 30%), were extracted at 90°C and 5 MPa, either with pure or CO₂-saturated water. Subsamples were taken at different time points during the extraction. The extracted LMWOAs such as formate, acetate and oxalate were analysed by ion chromatography. Yields of LMWOAs were higher with pure water than with CO₂-saturated water, revealing a suppressing effect of CO₂. Both extractions had higher yields than those reported for soxhlet extraction [2].

LMWOAs found in the extraction fluid may not just result from hydrolysis but also from different secondary reactions. It was suggested that oxalate in aqueous extracts of coals is a result of the decomposition of 1,2-dihydroxy-carboxylic acids [3]. We assume that for oxalate (and maybe for other LMWOAs as well) the extraction yield is not only affected by hydrolysis but also by secondary reactions, which may be inhibited or suppressed in the presence of CO₂ in the extraction medium. During soxhlet extraction the sample only gets into contact with freshly distilled water, not with an acidic fluid. This may explain the lower yields.

REFERENCES

- [1] Glombitza et al. (2009). *Org. Geochem.*, 40, 175-183.
- [2] Vieth et al. (2008). *Org. Geochem.*, 39, 985-991.
- [3] Bou Radd et al. (2000). *Fuel*, 79, 1185-1193.