

Towards the geochemical tricorder: Trends and needs in subsurface geochemical sensor systems for energy recovery and carbon management

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Chemical and fluid property analysis of reservoir fluids extracted from reservoirs under *in situ* reservoir conditions (ISRC) is a holy grail of reservoir geochemistry. This is especially important in heavy oil fields where the petroleum often will not flow at native ISRC and is equally important in sampling fluids from CO₂ storage programs to provide monitoring capabilities. Great advances in our ability to sample and characterize reservoir fluids that flow under ISRC have been made in the last decade with dynamic well testing systems coupled to optical spectrometers leading the way currently. While developments have been dramatic and successful, current tools cannot provide the molecular information necessary for many organic or inorganic geochemical applications. Given our capabilities to send advanced analytical instrumentation across the solar system it is surprising that more sophisticated instrumentation is not used a mere few kilometers below our feet! We anticipate that reservoir geochemistry associated with carbon management and downhole sensors for CO₂ and storage reservoir water chemistry to be a large research and development area in the next decade as monitoring and verification of the quantities of large volume carbon dioxide storage programs becomes routine.

We summarize our own attempts to develop instrumentation for direct sampling and geochemical or fluid property analysis of reservoir fluids (oils, waters, gases) *in situ* and describe key technical boundaries to be crossed in terms of sensor technologies and proxy methods for determination of key flow and geochemical properties of hydrocarbon and aqueous fluids associated with energy recovery and CO₂ storage activities. We describe new approaches to sampling and assessing oil viscosity appropriate for *in situ* analysis in heavy oilfields and define *in situ* sensor specifications for performing reservoir geochemical applications such as permeability barrier detection and production allocation in petroleum reservoirs.

Chemistry of Li-Na-K-OH-H₂O brines up to high concentrations and temperatures

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Lithium interest for industrial production has been increasing during the last few years. This alkali metal is of primary importance in the battery production for electricity storage, in vehicles and electronic devices. Because of very high solubility of lithium in water, the chemical behaviour of lithium minerals is mainly described in binary aqueous systems [1, 2] or at standard temperature [3-5]. Indeed, the chemistry of highly saline aqueous solutions is highly non-ideal and very complex. Its characterization requires specific approaches. The ion-specific interactions model developed by Pitzer [6] is particularly well suited for dealing with ionic strengths ranging from low up to very high salinities, *i.e.* above several tens of moles per kg of water.

In this work, we studied the Li-Na-K-OH-H₂O chemical system, and determined the relevant Pitzer interaction parameters using the procedure developed by André *et al.* [7]. In the binary LiOH-H₂O system, this set of parameters allows the description of the phase diagram for temperatures ranging from 0 to 240°C and for salinities up to saturation, *i.e.* up to 8 mol/kgw. In the ternary LiOH-KOH-H₂O and LiOH-NaOH-H₂O systems, phase diagrams can be satisfactorily described up to 30 mol/kgw, and 100°C, and up to 20 mol/kgw, and 150°C, respectively.

The set of parameters determined in this study should allow the description of the chemical behaviour of the quaternary LiOH-KOH-NaOH-H₂O system over a wide range of salinities and temperatures. The model presented here is a first step towards the possibility for optimizing the lithium extraction processes from natural hypersaline brines, geochemical resources, and industrial waste aqueous solutions.

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