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Radiolysis: Kinetics, equilibria and feedbacks in the gas-fluid-rock system for the production and preservation of molecular hydrogen.

CHRISTIAN OSTERTAG-HENNING

Federal Institute for Geosciences and Natural Resources

The production of molecular hydrogen (H_2) by splitting of water molecules with energy from ionizing radiation is important in different contexts: On a human timescale in nuclear reactors, on millennial timescales in high-level nuclear waste repositories, and on geologic timescales as a process forming naturally occurring hydrogen on Earth and elsewhere in the universe. Many studies use a simplified approach to model the amount of H_2 produced in a system over a given timespan by extrapolating published radiolysis yields of moles H_2 per mass of water and received energy radiation dose. This approach neglects the finding of near-equilibrium molarities or "self-limitation" of the reaction in a closed system (e.g. Bjergbakke et al, 1989) and hence yields unrealistic high amounts of H_2 produced by radiolysis especially over long timescales. The "self-limitation" is an outcome of the chemical reaction network including back-reactions (oxidation) after the incipient H2 production in a closed system. Contrary to a limitation of H_2 molarities by oxidation in this network, an increase of H_2 molarities may result if chemical species usually oxidizing H_2 or atomic H are sequestered by reactions with redox active ions in the aqueous phase, on the mineral surfaces.

To study these reactions in detail and parametrize a reaction network including both the initial physical processes of the radiolysis and the following chemical reaction network, a series of more than 300 irradiation experiments were carried out. In the experiments with pure water, the aqueous fluid to gas phase ratio was varied. In addition, the redox system of the fluid was adjusted by adding dissolved reduced sulfur or oxidized carbon species, or reactive mineral surfaces of pyrite, siderite or olivine were present.

The constructed kinetic reaction network model implementing mass transfer between the gas and aqueous fluid phase is validated against published models in e.g. Facsimile, and applied for different scenarios on the human to geologic timescale from the pore scale to rock units in sedimentary basins with implications for the amount of natural H_2 generation in the subsurface by this reaction network.

Bjergbakke, E., et al. (1989). *Radiochimica Acta*, *48*, 65–71.