CHEMICAL FORMS AND SORPTION OF RADIOCARBON IN GEOSPHERE

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BACKGROUND

Radiocarbon (^{14}C) is one of the key radionuclides when assessing the radiation doses to humans and biota due to the final disposal of spent nuclear fuel. It is formed mainly by the neutron activation reaction $^{14}N(n,p)^{14}C$ and is present in spent nuclear fuel, Zircaloy cladding and metal parts of the reactor.

The main uncertainty in assessing the behaviour of radiocarbon in geosphere is its speciation. The prevailing forms of carbon in groundwater are dissolved carbon dioxide and methane. Of these forms methane is not retained in the bedrock, but dissolved carbon dioxide can be sorbed. The sorption mechanisms studied in this project are the carbon isotope exchange between groundwater and fracture calcite and adsorption onto cationic iron (hydr)oxide surfaces.

This project aims in developing understanding of the chemical behaviour of radiocarbon. The project began in 2013 and is planned until the end of the KYT2018 program.

SORPTION BY ISOTOPE EXCHANGE

In groundwater at solubility equilibrium with calcite ($CaCO_3$), calcite is precipitated and dissolved at equal rates. Therefore, no change in the concentration of the (bi)carbonate or calcite ions in groundwater occur. In such system, radiocarbon in dissolved carbon dioxide can also be precipitated and form a solid solution with fracture calcite in the reaction

$CaCO_3$ (calcite) + $H^{14}CO_3^-$ (aq) ↔
$Ca^{14}CO_3$ (calcite) + HCO_3^- (aq)

where the radiocarbon forms a solid solution with fracture calcite.

The batch experiments completed in 2014 show that the isotope exchange exponentially decreases the activity of radiocarbon in solution. The decrease is faster with increasing calcium concentration of the groundwater but reaches a constant rate at calcium concentrations higher than 10 mM. An example of the decrease of the activity in saline groundwater can be seen in Figure 1. The half-life of the isotope exchange as a function of calcium concentration is presented in Figure 2. These results show that the radiocarbon in dissolved carbon dioxide can be retained from the bedrock especially in brackish and saline groundwaters in contact with calcite.

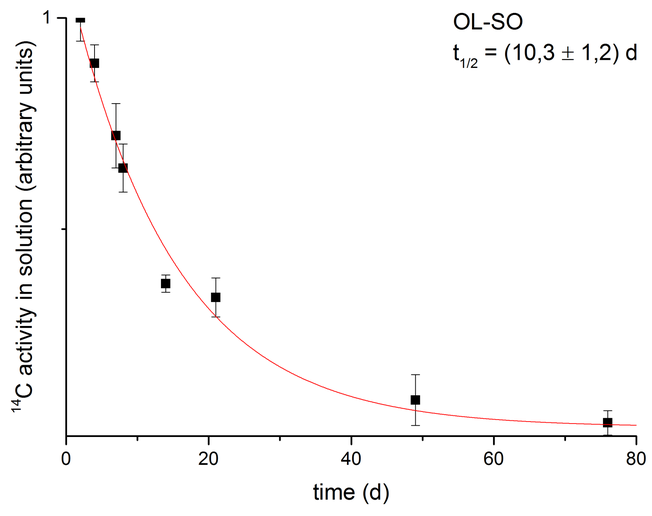

Figure 1. The decrease of the activity of radiocarbon in saline groundwater in contact with calcite, fitted exponential function and the half-life of the isotope exchange.

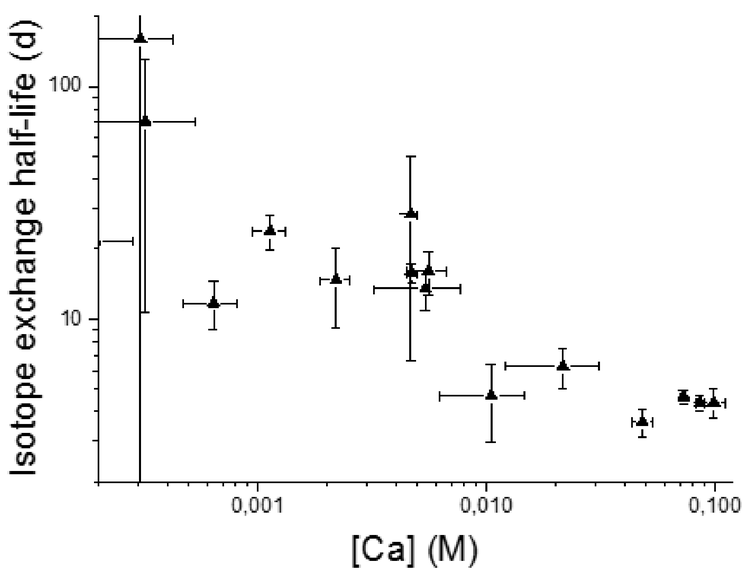

Figure 2. The half-life of the isotope exchange between solution and calcite phase as a function of the calcium concentration of the solution.

SPECIATION OF RADIOCARBON

The speciation of radiocarbon is being studied by simulating the conditions at repository depth where the radiocarbon is expected to be present as methane and at the sulphate-rich layer where the methane is expected to oxidize to carbon dioxide. The knowledge of the speciation of radiocarbon is important as the sorption of it depends on the chemical form of it.

In speciation studies gas chromatography and mass spectrometry are employed to monitor the speciation and the isotopic composition of carbon in solution. A scheme of the analysis method is shown in Figure 3.

PUBLICATIONS 2013-2014

- 4 conference presentations (2 poster and 2 oral presentations)
- 1 Master's Thesis (Sami Kallio)
- 1 Bachelor's Thesis (Shenelle Ghulam)

In addition, a scientific article is being written on the carbon isotope exchange between groundwater and fracture calcite.

ACKNOWLEDGE-MENTS

The project has received funding from the Finnish Research Programme on Nuclear Waste Management (KYT2014) in 2013 and 2014.

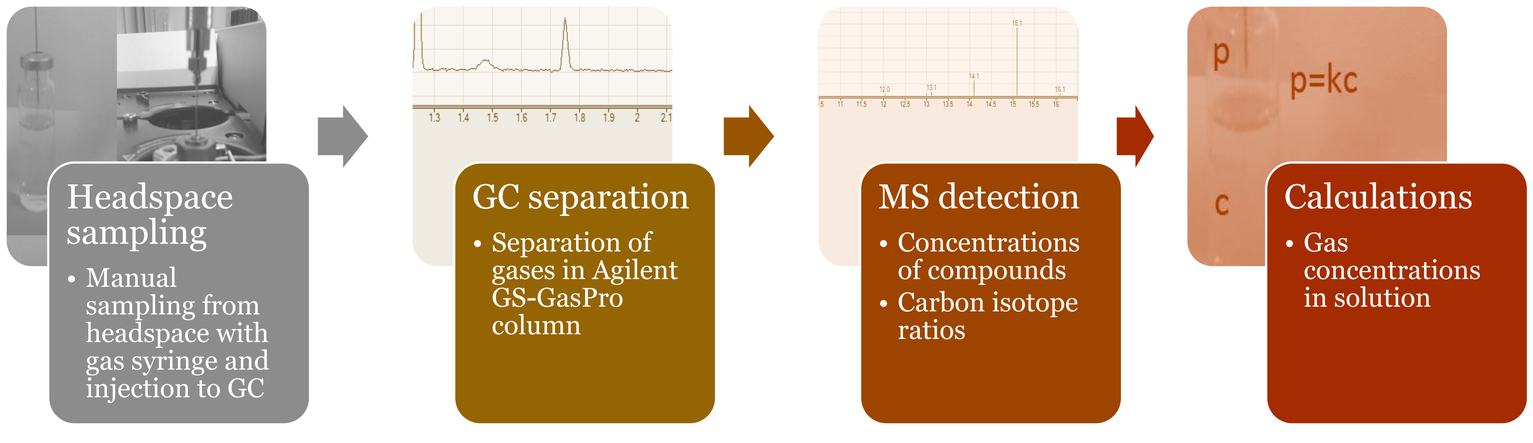

Figure 3. The analysis of the carbon species and their isotope ratios.

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