Janne Lempinen
Jukka Lehto
Laboratory of Radiochemistry
Department of Chemistry
University of Helsinki
Finland

SORPTION OF RADIOCARBON ON GOETHITE, HEMATITE AND MAGNETITE

BACKGROUND

Radiocarbon (^{14}C) is a top-priority radionuclide in terms of the long-term safety of the disposal of spent nuclear fuel. There is little knowledge on its speciation in geosphere if released from the repository, but it is expected to be present in groundwater as dissolved inorganic carbon or light hydrocarbons. For the inorganic fraction of the radiocarbon released to the geosphere, sorption mechanisms such as carbon isotope exchange with calcite mineral and sorption on the surface hydroxyl groups of iron minerals can be considered.

Of the iron minerals, hematite and goethite have an isoelectric point (IEP) above neutral pH, which favours the sorption of anionic species at the pH range of 7 – 9 in groundwaters. Sorption of inorganic radiocarbon on magnetite is not expected as its IEP is lower than 6.5. This study describes sorption of radiocarbon on the minerals as a function of pH and ionic strength.

SORPTION ISOTHERMS

The sorption isotherms were determined by batch experiments using ^{14}C-labelled DIC on synthetic minerals at pH 8.2, achieved by using 10 mM TRIS buffer. The sorption on magnetite was only detectable at the low DIC concentrations below 1 mM, whereas soprtion on goethite and hematite showed Langmuir type behaviour reaching the maximum sorption at DIC concentration of 3 mM.

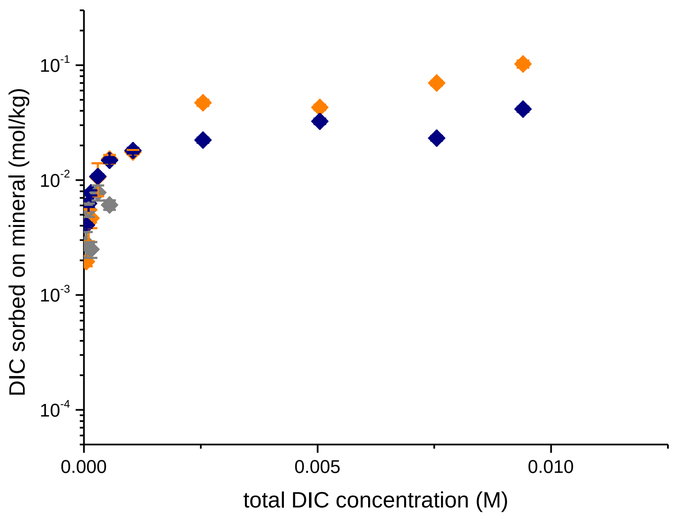

Figure 1. Sorption isotherms of ^{14}C-labelled DIC on hematite (◆), goethite (◆) and magnetite (◆).

The constants for the Langmuir adsorption isotherms for goethite and hematite were calculated from a linear fit of the sorbed amount (q) and equilibrium concentration (c) of DIC to the equation

$$\frac{1}{q} = \frac{1}{q_0 K_L} \times \frac{1}{c} + \frac{1}{q_0}$$

The sorption capacity (q_0) and equilibrium constant (K_L) are given in Table 1.

Mineral	q_0 [mol/kg]	K_L [L/mol]
goethite	0.020 ± 0.002	5450 ± 540
hematite	0.030 ± 0.004	2630 ± 280

Table 1. Sorption capacity (q_0) and equilibrium constant (K_L) of sorption of DIC onto hematite and magnetite.

EFFECT OF pH AND IONIC STRENGTH

To determine the effect of pH of the solution, experiments at DIC concentration of 5×10^{-5} M were performed throughout the pH range 6.5 – 12. pH of the samples was adjusted by adding hydrochloric acid or sodium hydroxide. Figure 2 shows the distribution coefficient of DIC between the minerals and solution. It is evident that the sorption decreases as a function of pH and is negligible at pH values greater than 8. This can be explained by the decrease in positive surface charge of the minerals as the pH increases.

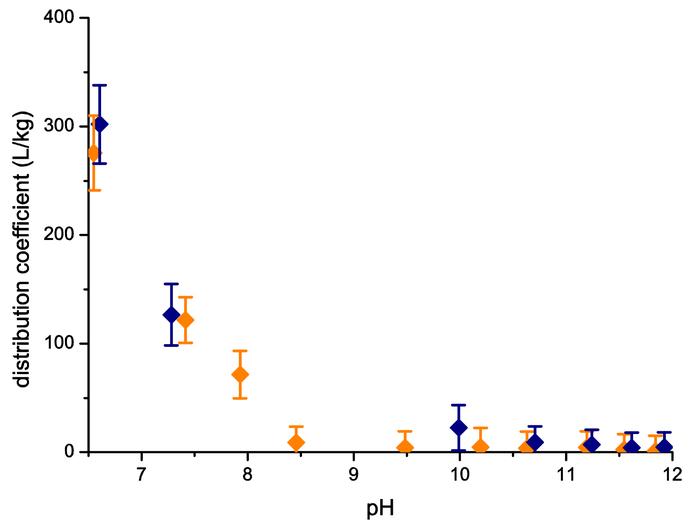

Figure 2. The distribution coefficient of DIC between hematite (◆)/goethite (◆) and solution as a function of pH.

The effect of ionic strength was studied by addition of sodium chloride into the solutions. The added concentrations were 10 mM and 100 mM. Figure 3 shows the effect of the ionic strength on the sorption of DIC on hematite. The figure shows decrease in the sorption with increasing sodium chloride concentration, which is due to the chloride ions competing for sorption sites with bicarbonate ions. Similar sorption behaviour as a function of ionic strength of DIC was also observed on goethite.

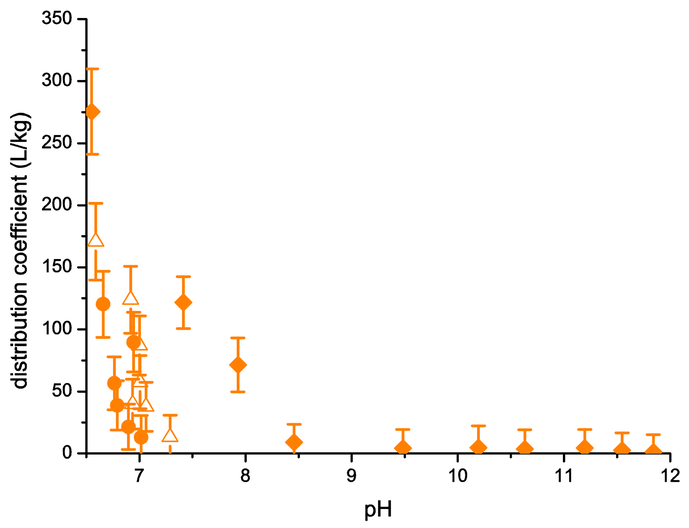

Figure 3. The distribution coefficient of DIC between hematite and solution with no added NaCl (◆), 10 mM NaCl (△) and 100 mM NaCl (●).

CONLUSIONS

- Dissolved inorganic radiocarbon is slightly sorbed onto goethite and hematite but not on magnetite
- The sorption is pH dependent: sorption decreases with increasing pH but is significant only in the pH range of 6.5 – 8
- Chloride ions in solution decrease the sorption of DIC by competing for sorption sites
- Goethite and hematite minerals in bedrock can inhibit the transport of radioactive DIC, but to a lesser extent in groundwaters with high chloride ion concentration

ACKNOWLEDGE-MENTS

This research has been funded by Finnish Research Programme on Nuclear Waste Management (KYT2018).

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI
MATEMAATTIS-LUONNONTIETEELLINEN TIEDEKUNTA
MATEMATISK-NATURVETENSKAPLIGA FAKULTETEN
FACULTY OF SCIENCE