Available online at www.sciencedirect.com

ScienceDirect

Physics and Chemistry of the Earth 32 (2007) 539–551

PHYSICS and CHEMISTRY of the EARTH

www.elsevier.com/locate/pce

On the mobility and potential retention of iodine in the Callovian–Oxfordian formation

C. Tournassat [a,*], E.C. Gaucher [a], M. Fattahi [b], B. Grambow [b]

[a] *BRGM, Environment and Process Division, 3 Avenue Claude Guillemin, F-45060 Orléans Cedex 2, France*
[b] *SUBATECH, Ecole des Mines de Nantes, UMR 6457, F-44307 Nantes Cedex, France*

Received 12 July 2005; received in revised form 25 November 2005; accepted 30 December 2005

Abstract

Iodide sorption experiments were conducted on clay stone samples originating from the Callovian–Oxfordian formation under experimental conditions as close as possible to *in situ* conditions. The total natural iodine content of the formation is shown to be very constant throughout the formation, ranging from 2 to 3 ppm. This range is in agreement with a past iodine accumulation in the marine organic matter of the sediment before and during deposition, and early diagenesis. At variance with total iodine, the leached iodine concentrations are variable. If leached iodine is considered to represent porewater solute iodine, its concentration can be calculated and ranges from 0 (below detection limit) to ~60 μmol/L and represents 0–25% of the total iodine. The reason for this variability is not understood. Sorption isotherms were determined either for natural $^{127}I^-$ solutions or for $^{131}I^-$ spiked $^{127}I^-$ solutions, with concentrations ranging from 10^{-9} to 10^{-3} mol/L at solid to liquid ratios from 10 to 200 g/L. No or little sorption was encountered, K_d values being in the range 0–0.5 L/kg with statistical and analytical error bands being greater than the K_d values, with the exception of one experiment at low solid to liquid ratio (10 g/L), showing significant K_d values of ~25 L/kg. In sorption experiments with natural $^{127}I^-$ and at the lowest added iodide concentrations ($<10^{-6}$ mol/L) an apparent negative K_d was obtained due to the iodide content in the solid porewater that was leached once the solid was suspended. The low affinity of iodide for argilite is thus confirmed. However, based only on these results and given the extent of the error bands, one cannot discard a limited iodide uptake. Literature data on iodide diffusion on similar rock materials have already shown that iodide does not behave like chloride. The retention mechanism of radio-iodide is discussed in the light of the present results and diffusion data. A model involving isotopic exchange between the natural iodine content of the geological formation and radio-iodine allows all of the results to be described. Not all the iodine in the formation appears to participate in isotopic exchange reactions with the solution. A quantification of the isotopically labile fraction of iodine would allow the effect of isotopic exchange on radio-iodide migration throughout the Callovian–Oxfordian formation to be assessed and predicted.

Keywords: Iodine; Callovian–Oxfordian; Diffusion; Retention; Isotopic exchange

---

1. Introduction

Iodine 129 is an important radioactive pollutant, contributing to potential future radiation doses resulting from radioactive waste disposal in deep host-rock formations, due to its ubiquity in these wastes, its long half-life period (approximately 16 million years) and its high mobility in most rocks and sediments. This high mobility is linked to the anionic nature of dissolved iodine species and its consequent low affinity for sorption on typically negatively charged mineral surfaces.

This study aims at characterising the iodine retention capacity of the Callovian–Oxfordian clay stone in the framework of the ANDRA research program on radionuclide behaviour in its underground research laboratory (URL). Iodine retention has been studied on numerous minerals, sediments and soils over the last few decades. However, discrepancies or even apparently contradictory results between these studies preclude a reliable prediction

---

[*] Corresponding author. Tel.: +33 2 38 64 47 44; fax: +33 2 38 64 30 62. *E-mail address:* c.tournassat@brgm.fr (C. Tournassat).

1474-7065/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.pce.2005.12.004

of the retention of iodine as a function of the thermodynamic conditions and the mineral/organic content of the sample.

There is good evidence and a consensus of opinion on the absence of iodide uptake on carbonates, quartz, chlorite, montmorillonite and muscovite (e.g. Muramatsu et al., 1990; Ticknor and Cho, 1990; Fuhrmann et al., 1998; Kaplan et al., 2000). However, some other mineral phases present in the Callovian–Oxfordian (e.g. Gaucher et al., 2004) are more problematic. For instance, iodide at trace concentration has been shown to sorb efficiently onto pyrite surfaces. However, Fuhrmann et al. (1998) have demonstrated by XANES spectroscopy, that the uptake mechanism is only valid for the IO_3^- solute ion, but not for the I^- ion, I^- being repelled from pyrite surfaces. Based on these results, Fuhrmann et al. have suggested that iodine tracer, introduced as I^-, could oxidise to form IO_3^- in sorption experiments, provided that no reducing agent is used. The case of illite, one of the main mineral components of clay stone, is even more problematic than the case of pyrite. Kaplan et al. (2000) have shown that illite efficiently retains trace amounts of radioactive $^{125}I^-$ tracers. The derived K_d are pH dependent and range from 46 L/kg at pH 3.6 to 22 L/kg at pH 9.4, for an iodine concentration of $\sim 10^{-12}$ mol/L and a solid to liquid ratio of 1:10 g/mL. In the same publication, they reported negative K_d values for montmorillonite and interpreted them as an indication of an anion exclusion phenomenon. Given the structural similarities, the difference in the iodide sorption properties of illite and montmorillonite are not easily explained. The hypothesis of illite charged edge surface sorption is not entirely satisfactory because montmorillonite is expected to present more or less the same sites on its edge surfaces. Hence, the explanation for iodide uptake on illite needs to be confirmed. Finally, organic matter could be considered as a potential sorbing phase for iodine (Yamaguchi et al., 2006 and references therein). Although little data indicate significant sorption of iodide on pure minerals or organic matter, literature references showing high iodide retention on soils and sediments are very common. This retention behaviour can be linked to the effect of organic matter towards iodine. Iodine uptake on soils and sediments is affected by the pH value. Iodine uptake is furthered by acidic pH (e.g. Yoshida et al., 1992; Fukui et al., 1996; Kaplan, 2003). However, some studies stand in contradiction to this simple observation (e.g. Bird and Schwartz, 1997). The relationship pH/adsorption has often been linked to the presence of positive charges on the mineral/organic surfaces at low pH. This hypothesis has been verified for well characterised minerals like iron(III) oxihydroxides (e.g. Benes, 1979). The redox state of iodine in solution (i.e. mainly iodide, I^-, or iodate, IO_3^-) is also a key parameter. Yoshida et al. (1992), Fukui et al. (1996) and Muramatsu et al. (1990) have demonstrated that iodate uptake is even more pronounced than iodide uptake, on the same soils and sediment samples. At iodine trace concentration, the conversion of iodide into iodate, and conversely, occurs during iodide, and iodate, sorption experiments on soils (Muramatsu et al., 1990; Fukui et al., 1996). These redox conversions may be due to reactions on mineral surfaces, to reactions with O_2 from the atmosphere and to biologically induced reactions. Microbial activity seems to be the most important factor favouring iodine uptake on soils and sediments. Sample pretreatments by autoclaving (Muramatsu and Yoshida, 1999), heating (Whitehead, 1973; Lieser and Steinkopff, 1989; Muramatsu et al., 1990; Fukui et al., 1996), irradiation (Muramatsu et al., 1990; Bird and Schwartz, 1997; Devivier et al., 2004), H_2O_2 washing (Whitehead, 1973; Lieser and Steinkopff, 1989) or antibiotic introduction (Bird and Schwartz, 1997) lead to a dramatic decrease (or disappearance) of iodide and iodate uptake, iodide being more affected than iodate. Mixing fresh soil or sediment with the treated one restores their iodine uptake capacity (Muramatsu and Yoshida, 1999). Furthermore, isolating the soils or sediments from oxygen (e.g. using an N_2 atmosphere glove-box) leads to a disappearance of the iodine uptake. Placing the samples in air restores this uptake (Bird and Schwartz, 1997). Conversely, a soil accumulates iodine in the presence of oxygen and releases this iodine in anoxic and reductive conditions (Muramatsu and Yoshida, 1999; Yamaguchi et al., 2006). In agreement with these laboratory experimental results, Price and Calvert (1973, 1977) have shown that marine iodine rich sediments are associated with oxygenated deposit areas, whereas iodine poor sediments are associated with redox reductive deposit areas.

In the light of this literature data, it appears that iodine uptake by a soil or sediment is mainly due to microbial activity. Mineral phases may also contribute to the uptake but seem to highly depend on the redox state of iodine, i.e. iodide I^- vs. iodate IO_3^-. In the redox condition prevailing in a deep clayey formation waste disposal, iodine should be present as iodide (I^-). The Callovian–Oxfordian clay stone is constituted by mineral phases that are known not to sorb iodide (e.g. carbonates, quartz, chlorite, montmorillonite, etc.) but also by mineral phases showing contradictory results as a function of the studies (e.g. illite and pyrite) and organic matter. Organic matter is then expected to be the main sink for iodide there. However, recent studies in abiotic and reductive conditions have demonstrated that humic substances do not sorb iodine in the I^- form but only in the I_2/I_3^- form (Reiller and Moulin, 2003). Bacterial activity is not considered to take place to a significant extent in compacted clay stone. Thus, it has been necessary to conduct iodine sorption experiments under thermodynamic and biological conditions as close as possible to the conditions prevailing in the *in situ* Callovian–Oxfordian conditions. Batch sorption experiments were conducted with stable and radioactive iodide solutions in abiotic, anoxic and reductive conditions on Callovian–Oxfordian rock samples, with iodine concentrations ranging from 10^{-9} to 10^{-3} mol/L. The results relative to these sorption experiments are compared to the distribution of natural