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Studying the migration behaviour of selenate in Boom Clay by electromigration

Thomas Beauwens, Pierre De Cannière, Hugo Moors, Lian Wang, Norbert Maes*

SCK-CEN, Belgian Nuclear Research Centre, Waste and Disposal—R&D Geological Disposal, Boeretang 200, B-2400 Mol, Belgium

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Abstract

For the disposal of high-level waste (HLW) in a deep geological formation as Boom Clay, safety assessment studies have shown that long lived ^{79}Se is one of the more critical fission products. Therefore, the knowledge of its migration properties (diffusion, retention) through the geological barrier (Boom Clay) is of paramount importance. The migration behaviour of selenium strongly depends on its speciation. Under reducing conditions, selenide would be the dominant species and selenium migration would mainly be controlled by the low solubility of Se(−II)-bearing minerals. However Se species are often found in redox disequilibrium and more oxidized species might also coexist. Therefore, the study of selenate migration requires attention, as it might be the most mobile selenium species in the host rock. Electromigration experiments performed with a ^{75}Se-labeled selenate in Boom Clay indicate a high mobility for this species. The apparent diffusion coefficient (D_{app}) of selenate in Boom Clay is estimated from electromigration experiments performed under different electric fields. Using two independent approaches, the value of D_{app} for selenate is shown to fall in the range from 1.7×10^{-11} to 6.2×10^{-11} m^2 s^{-1}. Moreover, no reduction of selenate in Boom Clay was observed.

Keywords: Electromigration; Diffusion coefficients; Selenium; Speciation; Boom clay; Radioactive waste

1. Introduction

Among the fission products present in high-level radioactive waste (HLW), ^{79}Se certainly deserves more attention: this radioelement of long half-life is present in sufficiently large amount in irradiated nuclear fuel to give a significant contribution to the dose rate to man once it escapes from the engineered barrier system. The half-life of ^{79}Se is uncertain but comprised in the range 65000 years to 1.1 MY (Singh, 2002; Jiang et al., 2002).

As a redox-sensitive element, selenium can exist under four different oxidation states. Elemental selenium ($Se_{(0)}$) and metal–selenide minerals (such as $FeSe_2$) are stable at low redox potentials and are poorly soluble. The aqueous species in reducing conditions is Se(−II), the speciation of which is dominated by HSe^- at $pH>3.8$ (Elrashidi et al., 1987). Under mildly reducing conditions, Se(+IV) is

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* Corresponding author.
E-mail address: nmaes@sckcen.be (N. Maes).

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the main aqueous species and present as $HSeO_3^-$ at acidic to neutral pH, or SeO_3^{2-} at alkaline pH. Except for $MnSeO_3$ at acidic pH, metal selenite minerals are too soluble to persist in soils (Elrashidi et al., 1987), and selenite concentration is mainly governed by adsorption processes (Bar-Yosef and Meek, 1987). Under oxidizing conditions, Se(+VI) is the dominant species, either as $HSeO_4^-$ or SeO_4^{2-}, depending on pH conditions, and may reach high concentration due to the high solubility of Se(+VI) solid phases. Selenate adsorption is low under most pH conditions (Masscheleyn et al., 1990). Compared to selenite, selenate sorption onto apatite and iron oxides was always found lower in the same conditions (Duc et al., 2003). It is therefore important to study its migration behaviour in the framework of High-Level Radioactive Waste disposal. Selenium is also known to form complexes with organic matter (Bueno and Potin-Gautier, 2002). The long-term migration behaviour of ^{79}Se will depend on geochemical conditions prevailing in the host rock surrounding the repository.

According to thermodynamic calculations performed under the reducing conditions imposed by pyrite and organic matter in Boom Clay (the reference host rock in Belgium), selenium is expected to be present under reduced forms. This is well illustrated by a Pourbaix diagram (Fig. 1). In situ, the pH of Boom Clay interstitial water (BCW, mainly $NaHCO_3$ 0.02 mol/l; Dierckx, 1997; Maes et al., 2002) is equal to 8.2, and the redox potential ranges from −0.2 to −0.4 V (vs. SHE). Under these conditions, selenium concentration (and thus mobility) should be limited by the low solubility of minerals such as $FeSe_2$ or $Se_{(0)}$.

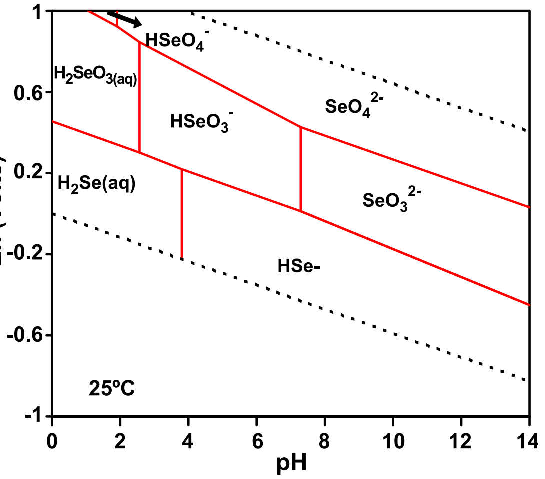

Fig. 1. Pourbaix diagram for selenium in Boom Clay Water. Code: the Geochemist's Workbench® 3.1. Thermodynamic database: LLNL's thermo.com.v8.r6+.dat.

However, it is difficult to know when the thermodynamic equilibrium between the radionuclides present in the waste packages and the surrounding geological environment will be established. Kinetics of selenium redox reaction are slow (Foster et al., 2003). Se species are often found in redox disequilibrium and oxidized species might persist in reducing environments. Selenite concentration in reducing conditions representative for Boom Clay will be governed by sorption followed by a reduction–precipitation mechanism, while selenate is likely not sorbed nor easily reduced (Bruggeman et al., 2002). The study of selenate migration in Boom Clay requires thus a higher priority, as it might be the most mobile selenium species in the host rock.

Selenate reduction in sediments is thought to be a very slow process in the absence of reducing bacteria. Field tracer tests performed with selenate in a sewage-contaminated zone showed the conservative behaviour of selenate under reducing conditions (Davis et al., 1993). Evidences of fast abiotic pathways for the reduction of selenate towards elemental selenium were found in laboratory experiments with synthetic minerals of well-known composition, such as FeS (Yllera de Llano et al., 1996), or sulfate-interlayered green rust $Fe(II)_4Fe(III)_2(OH)_{12}SO_4 \cdot 3H_2O$ (Myneni et al., 1997), but their involvement in field situations was questioned (Oremland et al., 1998). It has recently been shown that selenate reduction by green rust exerts much more isotopic fractionation than bacterial reduction (Johnson and Bullen, 2003), so that it is possible to distinguish both mechanisms in field situations.

The reduction of selenate by pyrite was assumed to explain the incomplete selenium recovery observed at the outlet of granite columns (Yllera de Llano et al., 1996). However, selenium sorption experiments in reducing conditions imposed by pyrite showed neither sorption nor reduction of selenate for more than 60 days, while selenite concentration decreased due to reduction in the meantime (Bruggeman et al., 2002).