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Supplementary information for the manuscript entitled:

Retentium of selenium by calcium aluminate hydrate (AFm) phases under strongly-reducing radioactive waste repository conditions

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1. Redox speciation of selenium under alkaline conditions

Predominance diagrammes in the pH range 10 < pH < 14 show that the selenium speciation is dominated by Se(IV) under moderately reducing conditions, whereas Se(0), Se_x^{2-} (x=2, 3, 4) and HSe^- dominate the redox speciation under strongly reducing conditions.[1]

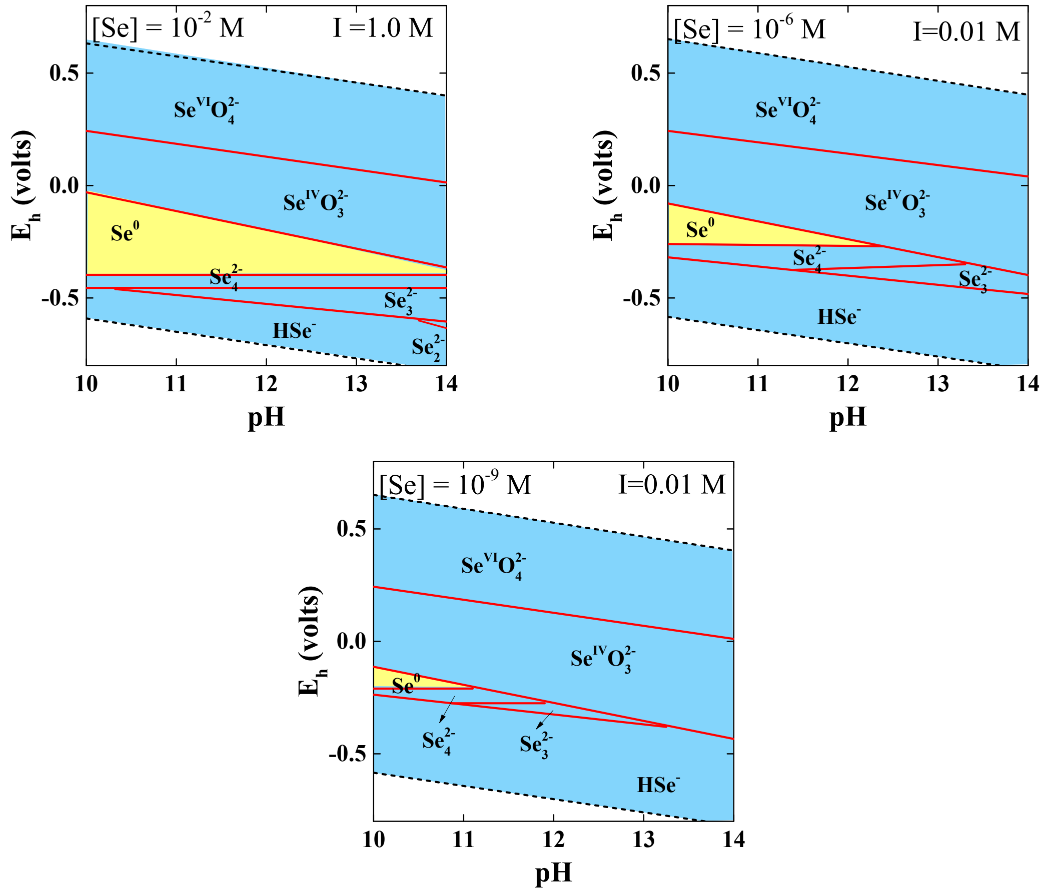

Figure S1: Predominance diagrams of Se in the pH and E_h regions relevant for the cementitious near field of a low- and intermediate level nuclear waste repository, calculated for three different total Se concentrations. Calculations were performed using the code Medusa[2] with thermodynamic data for Se included in the NEA thermodynamic database[1] considering three total Se concentrations: [Se] = 10^{-2} M, 10^{-6} M and 10^{-9} M.

2. Reduction of Se(IV) to Se(-II)

NaHSe (Se(-II)) solutions were obtained by electrochemical reduction of 10^{-2} M Na_2SeO_3 (Se(IV) solutions in 1.0 M NaOH. with the help of a standard three electrode electrochemical cell coupled with a VMP3 multichannel potentiostat (Bio-Logic, France) in constant potential mode (E_h = -1.29 V (SHE)). Hyperalkaline conditions (pH ≥ 14) were applied to avoid precipitation of Se(0) which is considerably slowing down the reduction. The risk for alkaline glass corrosion under such harsh experimental conditions excludes the use of materials made of glass and ceramic frits in the electrochemical cells. Furthermore, special leak-free reference electrodes need to be employed to avoid AgO precipitation.The electrochemical cell consists of a home-made polyacryl container, a high surface area reticulated vitreous carbon (RVC) working electrode (BASi, USA), a platinum (Pt) wire as counter electrode (BASi, USA) and a leak-free Ag/AgCl reference electrode embedded in peek (eDAQ, Australia) (Figure 1a and b). The counter electrode was kept isolated from the cell solution in a separate compartment made of polyacryl, within the electrochemical cell (Figure 1b). Electrical contact was made through an alkali-resistant perfluorinated cation-exchange membrane (Nafion® 117, DuPont, USA)[7].

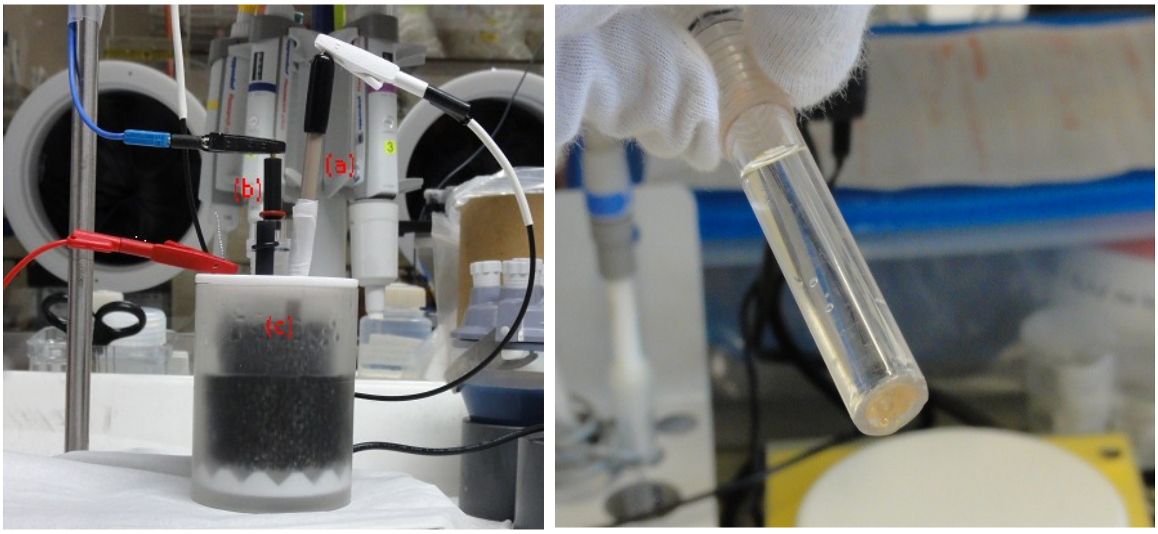

Figure S2. Left: Electrochemical cell with (a) leak-free reference electrode, (b) auxiliary electrode and (c) reticulated vitreous carbon electrode (black material in the poly-acrylic container). Right: Detailed image of polyacryl compartment with Nafion membrane, containing the auxiliary electrode.

UV-Vis spectrometry (Cary 6000i, Agilent Technologies, Santa Clara, USA) allows identification of the reduced Se species (HSe^- and Se_x^{2-}) in solution and was used to follow the evolution of the reduction process and to confirm the completeness of the reduction reaction (Figure S3 and S4). HSe^- and a series of polyselenides absorb strongly in the near-UV region whereas Se(0), SeO_3^{2-} and SeO_4^{2-} lack any absorbance. The spectral characteristics and the absorbance maxima of the reduced Se species are listed in a paper by Licht and Forouzan [3]. UV-Vis spectra were recorded using Hellma Suprasil™ quartz cuvettes with a path length of 1.0 cm. Absorbances were recorded using single wavelength scans between 230 nm and 550 nm at a scan rate of 600 nm/min, a wavelength interval of 0.5 nm and a spectral band with of 2 nm.

UV-Vis spectra recorded during the reduction process showed that the formation of HSe^- (peak max. at a wavelength, $\lambda = 245$ nm) is preceded by the appearance of different polyselenides (Se_4^{2-}, Se_3^{2-} and Se_2^{2-}) accompanied by clear changes in the colour of the solution (Figure S3 and S4). The colourless Se(IV) solution turns orange /red indicating increasing amounts of poly selenide species, and returns to a colourless solution when all Se is reduced to HSe^-. Figure S3 includes UV-Vis spectra after 1 day, 2 days and 5 days reduction.

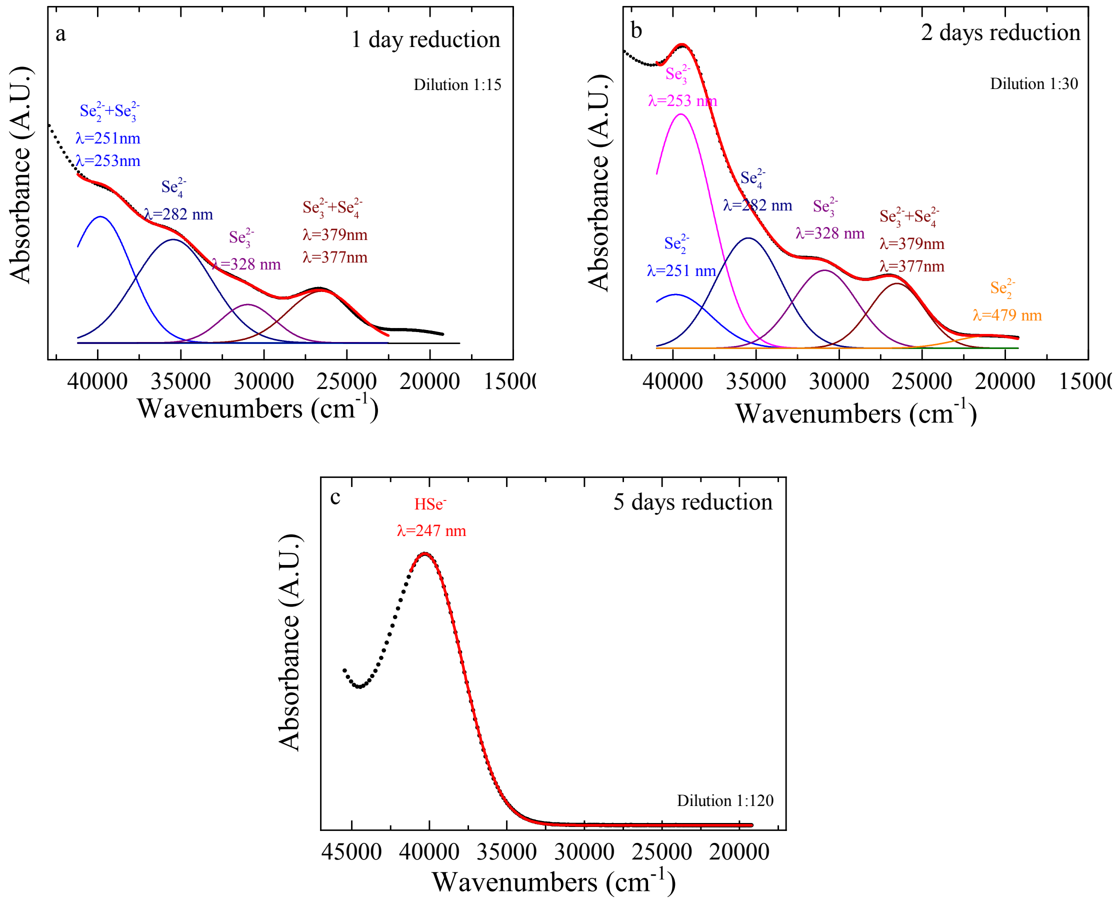

Figure S3. UV-Vis spectra at different stages of the Se(IV) to Se(-II) reduction process in 1 M NaOH. [Se_{tot}] = 10^{-2} M. a) Sample after 1 day reduction. b) sample after 2 days reduction. c) sample after 5 days reduction

This reduction process is accompanied by clear changes in the colour of the solution: (Figure S4).

Figure S4. Aliquots of Se solution during the reduction process. The colour of the solution indicates the stage of the process.

3. Stabilisation of the selenium redox state with hydrazine (N_2H_4)

To stabilize Se in the (-II) redox state, 10^{-2} M hydrazine (N_2H_4) was added to all experiments to preserve reducing conditions[4, 5]. N_2H_4 is a strong reducing agent as reflected by the reduction potential for the following reaction in basic solution[6]:

$$N_2(g) + 4H_2O(aq) + 4e^- \Leftrightarrow N_2H_4(aq) + 4OH^-(aq) \qquad E_h^0 = -1.15\ \mathrm{V} \qquad (1)$$

4. Se redox speciation and oxidation kinetics

Thermodynamic calculations indicate that a 10^{-2} M N_2H_4 solution in 0.01 M NaOH in equilibrium with a glovebox atmosphere containing 1 atm N_2 should provide a redox potential (E_h) of ~-1.0 V, well within the stability field of HSe^- (Figure S1). Preliminary test experiments, however, revealed that a hydrazine concentration of 10^{-2} M is not capable of completely stabilizing the –II redox state of Se in a 10^{-3} M HSe^- solution in 0.01 M NaOH. The measured E_h values in this solution were found to be -0.51±0.03 V (SHE) which is well above the theoretical value of -1.0 V assuming that the redox couple N_2/N_2H_4 would control the E_h in the system, but still within the theoretical stability field for HSe^-. The redox potential was found to remain constant over a period of 18 days. UV-Vis spectra, however, show that the measures taken to prevent oxidation (i.e., inert atmosphere with O_2 concentrations below 0.1 ppm and addition of 10^{-2} M hydrazine) were not sufficient to suppress Se(-II) oxidation completely over a time period of 18 days (Figure 6a). This is in contrast to the observations made by Landesmann et al. [7]. Note however that the latter authors only verified the redox potential to confirm the –II redox state of Se. The UV-Vis spectra shown in Figure 6 further suggest that the fraction of Se oxidized depends on the total HSe^- concentration in solution:

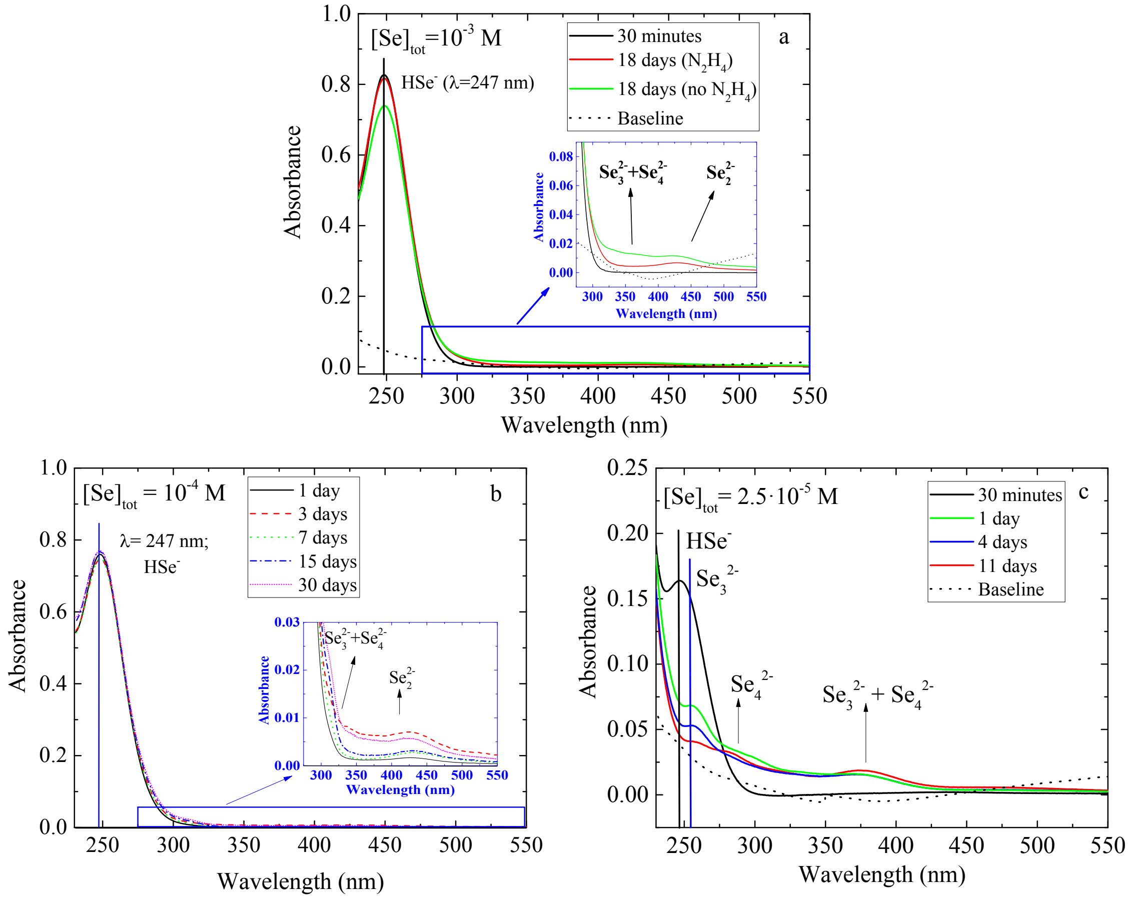

Figure S5: Oxidation kinetics of Se(-II) solutions in 0.01 M NaOH in the presence of 10^{-2} M N_2H_4 (except when specified in the figure). Dependence on $[Se]_{tot}$. a) Dilution factor = 10. b) Dilution factor = 1. c) Dilution factor = 1.
Baselines are added as a reference. All spectra are baseline-corrected.

HSe^- solutions containing 10^{-3} M HSe^- or 10^{-4} M HSe^- show only minimal oxidation after 18 days and 30 days equilibration in the glove box with only very small polyselenide bands visible in the wavelength range 250 nm < λ < 550 nm. In a $2.5\cdot10^{-5}$ M HSe^- solution, virtually all the HSe^- has been oxidized after 11 days equilibration in the glovebox and the UV-Vis spectrum is dominated by polyselenide bands. The absorbance of the polyselenide peaks is however too weak to allow quantification. Note that the UV-Vis spectra do not provide information about the amounts of Se(0) and SeO_3^{2-} formed as these redox species do not absorb light in the UV-Vis region. E_h values measured in the 10^{-3} M HSe^- solution in 0.1 M NaOH remained constant at a value of -0.51 ± 0.03 V (SHE) over the entire observation period whereas the E_h value of the $2.5\cdot10^{-5}$ M HSe^- solution decreased from a value of -0.41 V (SHE) after 1 day to -0.27 V (SHE) after 11 days indicating the measured redox potential is controlled by Se redox species and not by N_2H_4 and providing further evidence that Se oxidation has taken place. The present oxidation tests thus show that solutions containing HSe^- concentrations below 10^{-4} M under alkaline conditions are very sensitive to oxidation even though extensive precautions were taken to reduce the presence of oxygen to a minimum.

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