Reduction and Solubility Behaviour of Selenium under Boom Clay Conditions

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Summary

Theoretically selenium (Se) is expected to be present as Se/FeSe/FeSe₂ under the reducing conditions implied by the pyrite (FeS₂) presence in Boom clay. This theoretical equilibrium situation is experimentally investigated from oversaturation (starting from SeO₄²⁻/SeO₃²⁻) and from undersaturation (starting from Se⁰ and Se²⁻ (FeSe, ...) precipitates). Upon introduction of SeO₄²⁻ to Boom clay, no considerable sorption or reduction was seen to occur over short experimental measuring periods. Its migration behaviour is therefore assumed to be (initially) almost unretarded. As association with Boom clay organic matter is highly unlikely. Upon reduction of SeO₃²⁻ in the presence of FeS₂, a precipitate with a solubility of approximately 3 ×10⁻⁹ M was observed (probably crystalline Se⁰). In the presence of organic matter or Boom clay minerals, the kinetics of reduction are decreased and an association with Boom clay organic matter was found to exist, probably attributable to a stabilisation of Se colloids (which are formed upon reduction of SeO₃²⁻) by the organic colloids present in solution. These colloids are not expected to be mobile within the clay formation. SeO₃²⁻ migration is expected to be retarded, because of sorption onto FeS₂ and clay minerals. Through chemical reduction and electro-deposition, different reduced Se solid phases (amorphous Se⁰, crystalline Se⁰, metal selenides) were formed with different experimental solubilities ranging from 10⁻¹⁰ M to 10⁻⁷ M. Upon equilibration with Boom clay organic matter, no interaction was observed. It remains unclear if HSe⁻ species can interact with solid phases present in Boom clay.

1. Introduction

Theoretically selenium (Se) is expected to be present as Se/FeSe/FeSe₂ under the reducing conditions implied by the pyrite (FeS₂) presence in Boom clay. This theoretical equilibrium situation was experimentally investigated from oversaturation (starting from SeO₄²⁻/SeO₃²⁻) and from undersaturation (starting from Se⁰ and Se²⁻ (FeSe, ...) precipitates).

Firstly, a new method based on ion chromatography of radiolabelled ⁷⁵Se solutions followed by gamma-ray counting was developed to accurately measure selenium species with different degrees of oxidation (selenate (SeO₄²⁻) and selenite (SeO₃²⁻)) in solution, in absence of organics. The identification of reduced selenium species (HSe⁻, Se⁰) had to be done indirectly. The new method of analysis allowed to detect Se species concentrations as low as 10⁻¹⁰ M (Bruggeman et al., 2002).
2. Results

1) the case for SeO$_4^{2-}$ addition

Upon contacting SeO$_4^{2-}$ with pyrite (FeS$_2$), the solid phase responsible for the reducing conditions in Boom clay, no considerable sorption or reduction was seen to occur over short experimental measuring periods (60 days). This indicates that 1) SeO$_4^{2-}$ is not sorbed onto FeS$_2$, nor Fe oxides; 2) SeO$_4^{2-}$ reduction is very slow, which is in agreement with soil science literature. Its migration behaviour is therefore assumed to be (initially) almost unretarded. Although these systems did not contain any humic substances (HS), interaction of SeO$_4^{2-}$ with Boom clay organic matter (OM) is highly unlikely.

Migration parameters for selenate were determined by electromigration (Trancom -II, 2004) and showed no retardation.

2) the case for SeO$_3^{2-}$ addition

In systems where SeO$_3^{2-}$ was contacted with FeS$_2$ (in the absence of HS) a steady decrease in time (60 days) of SeO$_3^{2-}$ concentrations was observed, until a final concentration in solution (centrifugation 31000 g, 20 nm cut-off) of approximately $3 \times 10^{-9}$ M was reached (figure 1). However, even after two months, equilibrium was not attained in many samples. All investigated systems were shown to obey to one single rate law, which was found to be first-order in selenium and FeS$_2$, and inversely proportional to the square root of the FeS$_2$ occupancy by selenium. These findings indicate that SeO$_3^{2-}$ reduction occurs through sorption onto FeS$_2$ and that a Se precipitate with a solubility of $3 \times 10^{-9}$ M was formed. This precipitate was probably crystalline Se$^0$, based on the measured solubility and the X-Ray Diffraction (XRD) evidence from chemically and electro-chemically reduced Se solid phases.

The above method was then extended to similar FeS$_2$ systems, but now a HS containing Boom clay extract was used as background electrolyte. In these batches, total Se concentrations decreased in time with the same rate as if no organic matter were present, but remained constant after 14 days equilibration time. At this point, the supernatant consisted mainly of SeO$_3^{2-}$, but a small part of the total Se in solution (< 10%) was associated with the organic matter. Th is “equilibrium” condition corresponded to a sorption mechanism for SeO$_3^{2-}$ with a log $K_D$ value of 3.49±0.01 L/kg. After the setting of this sorption “equilibrium”, SeO$_3^{2-}$ concentrations were seen to decrease only at a very slow rate, while Se concentrations associated with organic matter stayed constant or even increased. After 90 days in the systems with initial SeO$_3^{2-}$ concentration of $10^{-6}$ M, up to 25% of total Se in solution was observed to be associated with organic matter, while in the systems with initial SeO$_3^{2-}$ concentration of $5 \times 10^{-6}$ M this percentage was only 2% - 17%. At the end constant $K_D$ values were obtained for free Se (log $K_D = 3.57\pm0.01$ L/kg) in solution.
In a third, long-term experiment, the speciation of Se was studied in Boom clay suspensions starting from oversaturation with $^{75}$SeO$_3^{2-}$. In order to eliminate all possible O$_2$ interactions with the Se systems, various centrifuge tubes containing $^{75}$SeO$_3^{2-}$ and Boom clay were submerged into a larger container with Boom clay suspension. Systems were prepared using two solid-to-liquid ratios (0.05 and 0.21 kg/L), as well as two $^{75}$SeO$_3^{2-}$ concentrations ($5 \times 10^{-6}$ M and $10^{-6}$ M). These systems were allowed to equilibrate up to 9 months (figure 2).

Upon addition of $^{75}$SeO$_3^{2-}$ to Boom clay suspensions, it was shown that initially, a distribution of Se between the solid and the liquid phase was seen to exist, attributable to the (inner-sphere) sorption of selenite onto broken edges of the clay particles. After a certain time (depending on the system studied) two “stable” concentrations of $^{75}$SeO$_3^{2-}$ were seen to exist: one being $1.4(\pm 0.2) \times 10^{-7}$ M and the other being $2.4(\pm 0.2) \times 10^{-8}$ M. These two concentrations were (remarkably enough) identical to the plateau values of SeO$_3^{2-}$ observed in the experiment described for systems containing pyrite and HS. Hereafter, in some systems (after 3 months’ equilibration time) $^{75}$SeO$_3^{2-}$ concentrations in solution again lowered towards $3 \times 10^{-9}$ M, corresponding to the experimental solubility observed in experiments using FeS$_2$ as a reductant. The amount of solid phase in the systems seemed to be the critical parameter for the reaction kinetics in the samples. In all systems $^{75}$Se concentrations in solution tended to decrease, but the system with lowest initial Se conc. and largest solid/liquid ratio attained equilibrium most rapidly. Thus, adsorption of SeO$_3^{2-}$ onto the clay minerals seemed to act as a competitor for the reduction of SeO$_3^{2-}$ by FeS$_2$.

A part of the $^{75}$Se in all the Boom clay systems was also found to be associated with dissolved organic matter. This amount was initially low (10% - 30% relative to the total Se solution concentration), but remained constant (although slightly decreasing) throughout the experiment, in contrast with the decreasing SeO$_3^{2-}$ concentrations. Thus, after nine months, the largest part (40% - 75%) of selenium in
solution was found to be associated with organic matter, probably attributable to a stabilisation of Se colloids (which are formed upon reduction of $\text{SeO}_3^{2-}$) by the organic colloids present in solution.

![Graph](image_url)

Figure 2: $\text{SeO}_3^{2-}$ concentration in solution (mol/L) vs. Se concentration on the Boom clay solid phase (mol/g) for the long-term experiment to study the Se speciation under Boom clay geochemical conditions. The figure shows how $\text{SeO}_3^{2-}$ concentrations in solution initially decreased to two “plateau” values (of $1.35 \times 10^{-7}$ M and $2.4 \times 10^{-8}$ M), and that only after three months’ equilibration time, $\text{SeO}_3^{2-}$ concentrations in the systems with highest solid-to-liquid ratio again lowered towards the previously observed experimental Se “solubility” value of $3 \times 10^{-9}$ M.

The previous distribution experiments predict a retardation of $\text{SeO}_3^{2-}$, because of sorption onto FeS$_2$ and clay minerals. Migration experiments with $\text{SeO}_3^{2-}$ (Trancom-II, 2004) showed a very complex diffusion pattern which is due to the presence of fast migrating (non-interacting) oxidised $\text{SeO}_4^{2-}$ and by slow sorption-precipitation processes to reduced Se forms (Se colloid – organic matter colloid associations will be filtered in Boom clay).

3) the case for reduced Se solid phases addition

Following the observation that Se(+IV) (and Se(+VI)) reduction to the expected Se $^{2-}$ equilibrium species in laboratory FeS$_2$ systems is a slow kinetic process, a second set of experiments was set up in which reduced Se solid phases were prepared in order to study the Se solubility from undersaturation. Several methods were considered and investigated for the reduction of Se oxyanions to more reduced forms: 1) chemical reduction by the use of powerful reducing agents ($\text{N}_2\text{H}_4$, Na$_2$S, FeS, Zn, Fe) ; 2) electro-reduction ; 3) isotopic exchange between FeSe and $^{75}$Se spike.

Several chemical reduction systems were prepared with inactive Se and providing promising results, with rapid formation of (amorphous red and crystalline black) elementary selenium (Se $^0$) using Na$_2$S and H$_4$N$_2$ as reductants, and (possibly) metal-selenide phases using Na$_2$S+Fe, Fe and Zn as reductants. These phases were checked by XRD measurements (diffractograms of metal-selenide phases were not
conclusive). After these preliminary experiments, several systems were set up to prepare reduced $^{75}$Se solid phases starting from $^{75}$SeO$_3^{2-}$ and using different chemically reducing solutions. After a washing step, all systems were contacted with Synthetic Boom clay Water (SBCW, ~ $10^{-2}$ M NaHCO$_3$), to measure the experimental solubility (after 12 days) of the prepared $^{75}$Se reduced solid phases. Analytical results of the systems where $^{75}$Se was chemically reduced, showed that the measured solubility was dependent on the specific reducing environment used, and thus on the respective solid phase formed. $^{75}$Se concentrations in solution (after centrifugation, cut-off ~20 nm) showed three ranges of experimental solubilities, which could be coupled to the previously made visual observations and XRD measurements of inactive Se solid phases. It was therefore proposed that the following solid phases were formed, with decreasing respective solubility: $\text{Se}^0$ (amorphous) [Se] = $2.2 \times 10^{-8}$ M ($-9.1 \times 10^{-8}$ M), $\text{Se}^0$ (crystalline) [Se] = $1.5 \times 10^{-9}$ M ($-8.1 \times 10^{-9}$ M), $M_x \text{Se}_y$ (amorphous) [Se] = $4.8 \times 10^{-10}$ M ($-9.7 \times 10^{-10}$ M) ($M = \text{Fe, Zn}$).

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<thead>
<tr>
<th>Se precipitate</th>
<th>Colour</th>
<th>Solubility</th>
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<tbody>
<tr>
<td>Amorphous $\text{Se}^0$</td>
<td>Red</td>
<td>$\sim 2.2 \times 10^{-8}$ M</td>
</tr>
<tr>
<td>Crystalline $\text{Se}^0$</td>
<td>Black</td>
<td>$\sim 2.0 \times 10^{-9}$ M</td>
</tr>
<tr>
<td>Metal selenide (Zn, Fe)</td>
<td>Black</td>
<td>$\sim 4.8 \times 10^{-10}$ M</td>
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Electro-reduction of inactive SeO$_3^{2-}$ with the help of a galvano-potentiostat was also successfully tested, with solid Se phases precipitating on the surface of metallic (Pt, Ni) scraps present in solution. Visual observation and XRD measurements on this precipitate allowed to identify amorphous and crystalline Se$^0$ as the solid phases being formed. Equilibration of the metal scraps with electro-deposited $^{75}$Se in SBCW showed indeed the formation of 2 different solid phases, having measured experimental solubilities (after 12 days, centrifugation cut-off ~20 nm) of approximately $8.0 \times 10^{-8}$ M ($-2.0 \times 10^{-7}$ M) and $4.0 \times 10^{-9}$ M ($-5.3 \times 10^{-9}$ M).

Isotopic exchange of $^{75}$SeO$_3^{2-}$ in FeSe was also tried, and disappearance of $^{75}$Se counts from solution was observed. After one and a half year of equilibration, a reddish precipitate became noticeable, probably amorphous $^{75}$Se. Since this pointed to a simple reduction of $^{75}$SeO$_3^{2-}$ and no evidence of isotopic exchange was observed, these batches were not used in further experiments.

Upon equilibration of the synthetically prepared $^{75}$Se solid phases with Boom clay humic substances, no interaction with organic matter was observed. The dominating effect is therefore solubility.

The same systems (on the one hand different chemically reduced $^{75}$Se solid phases, on the other hand electro-deposited $^{75}$Se) were also contacted with Boom clay suspensions (2 solid-to-liquid ratios, 0.05 kg/L and 0.21 kg/L) and allowed to equilibrate up to two months. $^{75}$Se concentrations in solution ranged from $5.8 \times 10^{-10}$ M to $2.22 \times 10^{-8}$ M, which was overall lower than the concentrations observed in batch experiments where the same $^{75}$Se solid phases were contacted with SBCW. This probably means that either reduced $^{75}$Se species interact with the Boom clay solid phase (and systems are kinetically not yet in equilibrium), or that during centrifugation, co-precipitation of reduced Se colloids by the clay particles present in the samples occurred. However, no relation with the organic matter concentration was found, thus providing no evidence for HSe$^-$ complexation with Boom clay HS. Neither was any specific relationship observed with the amount of solid Boom clay phase for the total $^{75}$Se concentration.
3. Conclusion

Concluding, except for $\text{SeO}_4^{2-}$, the Se transport mechanism in the far field is expected to be dominated by the solubility of a reduced Se solid phase. An association with HS is possible, but not likely to enhance the experimental solubility due to the ultrafiltration effect of the clay formation.

4. Acknowledgement

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References
