**Retention of Anionic Species on Granite: Influence of Granite Composition - 12129**

Katerina Videnska[1*], Vaclava Havlova[2]

[1] Institute of Chemical Technology, Prague, Czech Republic, 16628; e-mail: videnskk@vscht.cz

[2] Nuclear Research Institute Rez, Rez, Czech Republic, 25068

## ABSTRACT

Technetium (Tc-99, $T_{1/2}$ = $2.1 \cdot 10^5$ yrs) and selenium (Se-79, $T_{1/2}$ = $6.5 \cdot 10^4$ yrs) belong among fission products, being produced by fission of nuclear fuel. Both elements can significantly contribute to risk due to their complicated chemistry, long life times, high mobility and prevailing anionic character. Therefore, knowledge of migration behaviour under different conditions can significantly improve input into performance and safety assessment models.

Granite is considered as a potential host rock for deep geological disposal of radioactive waste in many countries. Granitic rocks consist usually of quartz, feldspar, plagioclase (main components), mica, chlorite, kaolinite (minor components). The main feature of the rock is advection governed transport in fractures, complemented with diffusion process from fracture towards undisturbed rock matrix.

The presented work is focused on interaction of anionic species ($TcO_4^-$, $SeO_4^{2-}$, $SeO_3^{2-}$) with granitic rock. Furthermore, the importance of mineral composition on sorption of anionic species was also studied. The batch sorption experiments were conducted on the crushed granite from Bohemian Massive. Five fractions with defined grain size were used for static batch method. Mineral composition of each granitic fraction was evaluated using X-ray diffraction. The results showed differences in composition of granitic fractions, even though originating from one homogenized material. Sorption experiments showed influence of granite composition on adsorption of both $TcO_4^-$ and $SeO_3^{2-}$ on granitic rock. Generally, Se(IV) showed higher retention than Tc(VII). Se(VI) was not almost sorbed at all. Fe containing minerals are pronounced as a selective Se and Tc sorbent, being reduced on their surface. As micas in granite are usually enriched in Fe, increased sorption of anionic species onto mica enriched fractions can be explained by this reason. On the other hand, fractions enriched in feldspar did not show increased sorption affinity to Tc and Se [1].

## INTRODUCTION

Selenium and technetium occur in various oxidation states depending on environment redox conditions. Technetium exists in reducing environment in the form of specie Tc(IV) and in oxidizing environment as Tc(VII) specie $TcO_4^-$. Poorly soluble forms of technetium are expected (oxo- or hydroxo- compounds or carbonate species) under reducing conditions of nuclear waste deep geological repository. All the species of Tc(IV) are only slightly soluble that implies possible sorption in geologic systems. Migration of Tc(IV) into the environment is not usually expected. But in the presence of oxygen the insoluble Tc(IV) compounds oxidize to soluble Tc(VII). The anion $TcO_4^-$ shows high mobility and solubility compared to the Tc(IV) technetium compounds. $TcO_4^-$ is considered to be highly mobile non-sorbing radionuclide. Possible Tc(VII) immobilisation process is reduction on to Tc(IV) in the presence of reducing agents. The reductive agents may be metals – iron, copper, zinc, chrome, tin etc.

Selenium is one of the redox-sensitive elements. In aqueous solutions it can occur in three oxidation states (-II, +IV, +VI). Specie occurrence and solubility depend on redox conditions of the environment. Se(-II) occurs in reducing environment, Se(IV) and Se(VI) species can be

expected under oxidation environment. In anoxic environment the presence of minerals containing iron (e.g. iron sulphide) can lead to reduction of Se(IV). Resulting Se(0) and ferroselite (FeSe$_2$) are formed [2]. Under oxidizing conditions selenite Se (IV) can be retained by sorption on Fe(II)-containing minerals, selenate is under these conditions very mobile [3,4].

Granite is considered as a potential host rock for deep nuclear waste repository in number of countries. Sorption of anion species on granite has been studied in many works. The comparison of technetium sorption under aerobic and anaerobic conditions has shown that the sorption of TcO$_4^-$ anions was very low under aerobic conditions (K$_D$ = 0 – 0.01 m$^3$/kg). Under anaerobic conditions retention of Tc increased due reduction o Tc(VII) to Tc(IV) (K$_D$ = 0.1 – 1 m$^3$/kg) [5]. Comparison of sorption distribution coefficient of SeO$_3^{2-}$ under various conditions has shown that under aerobic conditions the distribution coefficient is lower (K$_D$ = 0.004 m$^3$/kg) than in anaerobic conditions (K$_D$ = 0.04 m$^3$/kg) [1].

The objective of the work presented was to study of sorption of technetium and selenium anions on crushed granite. The sorption experiments were conducted with various granite size fractions under aerobic conditions, using synthetic granitic water as a solution. Moreover, influence of different mineral composition of each size fraction was taken into account. Special focus was paid to content of Fe containing minerals as possible selective anion specie sorbents.

**METHODOLOGY**

**Solid phase and liquid phase**

Granitic rock was sampled from the bore core, originating from the depth 97.5-98.7 m at (Melechov massive, Centre Bohemian Massive, Czech Republic). The core was crushed and sieved into defined size fractions: fraction A: grain size smaller then 0.063 mm, fraction B: grain size 0.063-0.125 mm, fraction C: grain size 0.125-0.63 mm, fraction D: grain size 0.63-0.8 mm, fraction E: grain size bigger then 0.8 mm. Each fraction was analysed by RTG diffraction (diffractometer Philips X'Pert System). Mineralogical compositions of granitic fractions are shown in Table I. Synthetic granitic water was used as solution for tracer preparation; its chemical composition is shown in Table II. All chemicals were of analytical grade.

Table I. Mineralogical composition of granitic fractions (in weight %)

| Minerals | Fraction A | Fraction B | Fraction C | Fraction D | Fraction E |
|---|---|---|---|---|---|
| Quartz | 27 | 30 | 32 | 31 | 29 |
| Orthoclase | 37 | 32 | 31 | 31 | 37 |
| Plagioclase | 23 | 20 | 18 | 24 | 22 |
| Mica | 8 | 12 | 14 | 10 | 8 |
| Chlorite | 5 | 6 | 5 | 4 | 4 |

Table II. Composition of synthetic granitic water (in mg/L)

| Component | Concentration |
|---|---|
| Na$^+$ | 10.6 |
| K$^+$ | 1.8 |
| Ca$^{2+}$ | 27 |
| Mg$^{2+}$ | 6.4 |
| Cl$^-$ | 42.4 |

| | |
|---|---|
| $SO_4^{2-}$ | 27.7 |
| $NO_3^-$ | 6.3 |
| $HCO_3^-$ | 30.4 |
| $F^-$ | 0.2 |

**Sorption experiments**

The static batch method was used in order to study sorption of tracers on solid material. All batch experiments were conducted in laboratory under atmosphere and were performed in duplicate at 25 ± 1 °C.

The radioactive tracer $NH_4^{99}TcO_4$ was used for sorption experiments with $TcO_4^-$. Reaction mixtures were prepared by mixing 0.7 g granitic fraction and 7 mL of synthetic granitic water (representing granitic massive ground water composition in Czech Massive). 100 µL of $NH_4^{99}TcO_4$ (Lacomed s.r.o Rez, Czech Republic, c = 0.0111 mol/L, A = 740 kBq/mL) was then added to reaction mixtures. Reaction mixtures were shaken and after an appropriate time the liquid and solid phase were separated by centrifugation (10 min, 4000 rpm). β-activity of Tc-99 was determined in liquid phase. The sorption kinetics of Tc-99 onto granite were measured at time intervals varying from 2 days to 3 months [6, 7].

Stable $Na_2SeO_3$ and $Na_2SeO_4$ were used for sorption experiment with selenium. Reaction mixtures were prepared by mixing 0.3 g granitic fraction and 9 mL liquid phase. Liquid phase was synthetic granitic water containing defined amount of selenium. Concentration of $Na_2SeO_3$ or $Na_2SeO_4$ in synthetic granitic water was $2 \cdot 10^{-5}$ mol/L. These mixtures were shaken for 1 week and sampled after 1, 2, 3, 5 and 7 days. Samples were centrifuged (10 min, 4000 rpm) and selenium concentration in liquid phase was determined using inductively coupled plasma mass spectrometry (ICP-MS) [8]. The blank test without granitic fraction in solution was conducted following the same procedures.

 Eh, pH and specific conductivity were also measured in liquid phases.

**β-activity measurement**

The β-activity of Tc-99 was measured with an SPF 35 plastic scintillation detector. 1 mL of aqueous phase was pipette on the Petri dish and dry under the IR lamp and afterwards was measured the β-activity of Tc-99 [9].

**ICP-MS measurements**

The determination of selenium was performed using an ICP-MS technique (spectrometer Elan DRC-e, Perkin-Elmer, Concord, Canada). The most abundant isotope Se-80 was used for the measurement and the spectral interferences due to $^{40}Ar_2^+$ were removed by methane as reaction gas and germanium served as the internal standard. Before measurement the samples were diluted (1 + 9) by 0.28 mol/L $HNO_3$ solution (Suprapur®, Merck, Darmstad, Germany) and spiked by germanium solution to obtain final concentration 500 µg/L Ge. Calibration solution (0, 100, 200 and 500 µg/L Se respectively) were prepared by dilution of stock solution 1000 mg/L (Analytika Prague, Ltd.) and were also spiked by internal standard [10].

**Sorption distribution coefficient determination**

Sorption distribution coefficients $K_D$ were calculated from measured concentrations and activities respectively. Sorption distribution coefficients of selenium were defined as follows:

$$K_D = \frac{(c_0 - c) \cdot V}{c \cdot m} \quad (m^3/kg), \qquad \text{(Eq. 1)}$$

where $K_D$ is the distribution coefficient, $c_0$ is the initial concentration of selenium in solution (mol/L), c is the concentration of selenium in liquid phase after sorption (mol/L), V is liquid volume (L) and m is solid mass (kg).

Sorption distribution coefficients of technetium were calculated by the following formula:

$$K_D = \frac{(A_0 - A) \cdot V}{A \cdot m} \quad (m^3/kg), \qquad \text{(Eq. 2)}$$

where $K_D$ is the distribution coefficient, $A_0$ is the initial activity of technetium in solution ($min^{-1}$), A is the activity of technetium in liquid phase after sorption ($min^{-1}$), V is liquid volume ($m^3$) and m is solid mass (kg).

**RESULTS**

**Granitic fraction composition**

Granitic fractions of defined grain size were analyzed by XRD diffraction analysis. Generally, the majority of mineral phase in the granite are quartz and feldspar (plagioclase and orthoclase). Minor phases are chlorite, mica and kaolinite. However, XRD results revealed that granitic fractions differed from each other, even though being prepared from one homogenized crushed rock material. Granitic fractions A and E contained the highest concentration of orthoclase and also contained the lowest concentration of minor minerals as chlorite and mica. On the contrary, fraction B and C contained in comparison lower concentrations of orthoclase and plagioclase and higher concentration of mica. Mica containing iron in its structure can play an important role in the sorption of namely redox species, contribution to redox state changes that can lead to specie immobilisation (including Tc and Se).

**Sorption of $TcO_4^-$ on granite**

Sorption experiments with technetium took three months. The sorption distribution coefficients ($K_D$) obtained by batch tests are displayed in Table III. The highest values of $K_D$ were achieved for granitic fractions B and C. The results have shown that technetium sorption increased until 14 days of experiment when $K_D$ reached the highest values ($K_D$ = 0.0086 $m^3/kg$). Further on, desorption process followed, resulting in $K_D$ decrease down to 0.0035 $m^3/kg$ (fraction B) and to 0.0072 $m^3/kg$ (fraction C). Similar patter was observed for other fractions.

Tab. III The distribution coefficients of Tc-99 obtained by sorption experiments

| Contact time | Distribution coefficient ($m^3/kg$) | | | | |
|---|---|---|---|---|---|
| | **Fraction A** | **Fraction B** | **Fraction C** | **Fraction D** | **Fraction E** |
| **2 days** | < 0.0001 | 0.0062 | 0.0023 | 0.0004 | < 0.0001 |
| **3 days** | 0.0003 | 0.0076 | 0.0032 | 0.0002 | 0.0006 |
| **9 days** | 0.0008 | 0.0086 | 0.0058 | 0.0006 | 0.0007 |
| **14 days** | 0.0003 | 0.0062 | 0.0085 | < 0.0001 | 0.0001 |
| **31 days** | < 0.0001 | 0.0033 | 0.0086 | < 0.0001 | < 0.0001 |

| | | | | | |
|---|---|---|---|---|---|
| **63 days** | < 0.0001 | 0.0032 | 0.0072 | < 0.0001 | < 0.0001 |
| **94 days** | 0.0006 | 0.0035 | 0.0072 | 0.0002 | 0.0003 |

**Sorption of selenium on granite**

The sorption experiment with selenite Se(IV) and selenate Se(VI) lasted one week. The sorption distribution coefficients of selenite and selenate are listed in Table IV and Table V. The highest value of $K_D$ of selenite was achieved for granitic fraction B which contained 12% of mica minerals. $K_D$ values increased slowly in the first four days of experiment (increase from 0.0232 $m^3$/kg to 0.0603 $m^3$/kg). However, after 7 days $K_D$ got sharply increased reaching up to one order higher values than at the beginning of the experiment ($K_D$ = 0.1629 $m^3$/kg for fraction B). Sorption experiments with selenate showed high mobility of selenate anion and very low sorbing behaviour. The $K_D$ values were very low and the presence of mica in granite composition did not influence $K_D$ values (see Table V). Similar trend as for Tc was observed: $K_D$, even though one order lower than for Se(IV) increased slightly with time, but after 2 days decreased even under detection limit.

Tab. IV The distribution coefficients of selenite obtained by sorption experiments

| Contact time | Distribution coefficient ($m^3$/kg) | | | | |
|---|---|---|---|---|---|
| | **Fraction A** | **Fraction B** | **Fraction C** | **Fraction D** | **Fraction E** |
| **0.2 days** | 0.0053 | 0.0052 | 0.0022 | 0.0049 | 0.0308 |
| **1.2 days** | 0.0124 | 0.0232 | 0.0037 | 0.0012 | 0.0001 |
| **2.9 days** | 0.0222 | 0.0400 | 0.0112 | 0.0163 | 0.0032 |
| **4.0 days** | 0.0246 | 0.0603 | 0.0153 | 0.0045 | 0.0004 |
| **7.1 days** | 0.0314 | 0.1629 | 0.0615 | 0.0058 | 0.0325 |

Tab. V The distribution coefficients of selenate obtained by sorption experiments

| Contact time | Distribution coefficient ($m^3$/kg) | | | | |
|---|---|---|---|---|---|
| | **Fraction A** | **Fraction B** | **Fraction C** | **Fraction D** | **Fraction E** |
| **0.3 days** | 0.0035 | 0.0042 | 0.0031 | 0.0032 | 0.0028 |
| **1.0 days** | 0.0037 | 0.0044 | 0.0024 | 0.0015 | 0.0004 |
| **2.0 days** | 0.0023 | 0.0051 | 0.0020 | 0.0018 | 0.0003 |
| **3.9 days** | < 0.0001 | 0.0016 | < 0.0001 | < 0.0001 | < 0.0001 |
| **7. days** | < 0.0001 | 0.0021 | 0.0027 | < 0.0001 | < 0.0001 |

**DISCUSSION**

Sorption experiments with anionic species were performed on five granitic fractions that appear to differ in mineral composition due to selective enrichment of mica and chlorite minerals during sieving.

The results of sorption experiments with Tc-99 showed that resulting sorption distribution coefficients can be influence by mineral composition of solid phase. Fraction B and C contained the highest concentration of mica minerals (approx. 13%), resulting in the highest $K_D$ for these fractions. Distribution coefficient of Tc-99 sorption in granitic fraction C was the highest after nine days of contact phases ($K_D$ = 0.0085 $m^3$/kg) and for fraction B after 14 days of contact phases ($K_D$ = 0.0086 $m^3$/kg). $K_D$ values of Tc-99 for the other fractions were lower. Those results are in

consistency with [11, 12] that presumed, that surface mediated reduction of Tc(VII) on Fe(II) bearing minerals can be expected to be the dominating reaction path in natural systems.

Sorption experiments with selenite Se(IV) partly showed the similar trend as in the case of Tc-99: selective sorption for phases, enriched in Fe rich minerals. Even though mica are not explicitly reported as preferential Se sorbent, Fe phases (pyrite, iron oxide, hematite) are widely reported [13, 14, 15]. The highest values of $K_D$ were achieved for granitic fraction B ($K_D$ = 0.1629 $m^3$/kg) and C ($K_D$ = 0.0615 $m^3$/kg), in both cases after 7 days of sodium selenite contact with granite. The presence of Fe bearing minerals in granitic rocks raised sorbed amount of anionic species on granite for both Se(IV) and Tc(VII) tracers , even though Se (IV) showed high sorption than Tc(VII). Selenate Se(VI) did not exhibit a lot of sorption as expected. On the other hand, fractions enriched in feldspar did not exhibit increase tracer sorption.

Nevertheless, the sorption process for Se(IV) on granite fraction B and C continued even after 7 days (see Tab. III) in contrary with Se(VI) and Tc(VII) behaviour. The increase might be caused by migration of Se(IV) into mice sheet silicate interlayer, the process well know for Cs [13, 14, 15, 16 etc]. Here on Fe sites in mica interlayers, Se(IV) might be reduced and immobilized from further migration. However, not clear proof for such a process was found so far. Moreover, no clear conclusions of sorption process for all three tracers can be drawn out from the batch sorption results presented. The most common reported sorption processes for all three anionic species are either surface complexation [20], precipitation [11, 12, 13] or even ion exchange [15], however still not fully clearly identified.

Further research is planned, namely focused on identification of surface sorption processes and preferential sorbents within granitic material.

**REFERENCES**

1.  Carbol, P., Engkvist, I. (1997). Compilation of radionuclide sorption coefficients for performance assessment. SKB rapport R-97-13, Swedish Nuclear and Waste Management Co, Stockholm, Sweden.

2.  Jan, Y.-L., Wang, T.-H., Li, M.-H., Tsai, S.-C., Wei, Y.-Y., Teng, S.-P. (2008). Adsorption of Se species on crushed granite: A direkt linkage with its internal iron-related minerals. Applied Radiation and Isotopes, 66, 14-23.

3.  Piqué, Á., Grandia, F., Sena, C., Arcos, D., Molinero, J., Duro, L., Bruno, J. (2010). Conceptual and numerical modelling of radionuclide transport in near-surface systems at Forsmark. SKB rapport R-10-30, Swedish Nuclear and Waste Management Co, Stockholm, Sweden.

4.  Buckau, G., Kienzler, B., Duro, L., Montoya, V. (2007). 2nd Annual Workshop Proceedings of the Integrated Project „Fundamentals Processes of Radionuclide Migration" – 6th EC FP IP FUNMIG. Technical Report TR-07-05, Swedish Nuclear and Waste Management Co, Stockholm, Sweden.

5.  Baston, G.M.N., Berry, J.A., Brownsword, M., Cowper, M.M., Heath, T.G., Tweed, C.J. (1995). Sorption of uranium and technetium on bentonite, tuff and granodiorite. Material Research Society Symposium – Proceedings, 353, 989-996.

6.  Vinšová, H., Jedinákova-Křížová, V., Kolaříková, I., Adamcová, J., Přikryl, R., Zeman, J. (2008). The influence of temperature and hydravion on the sorption properties of bentonite. Journal of Environmental Radioaktivity, 99, 415-425.

7.  Vinšová, H., Jedinákova-Křížová, V., Ožanová, M. (2009). Interaction of ^{99}Tc onto bentonite and influence of Fe(II) and (Ca, Mg) ion exchange in its interlayers. Journal of Radioanalytical and Nuclear Chemistry, 281, 75-78.

8.  Jan, Y.-L., Tsai, S.-C., Jan, J.-C., Hsu, C.-N. (2006). Additivity of the distribution ratio of Cs and Se on bentonite/quartz sand mixture in seawater. Journal of Radioanalytical and Nuclear Chemistry, 267, 225-231.

9.  Vinšová, H., Večerník, P., Jedinákova-Křížová, V. (2006). Sorption characteristics of ^{99}Tc onto bentonite material with different additives under anaerobic conditions. Radiochimica Acta, 94, 435-440.

10. Eichler Š., Mestek, O. (2011). Speciační analýza selenu s využitím HPLC a ICP/MS pro výzkum distribuce selenu v bariérách jaderného úložiště. Chemické listy, 105, 24-26.

11. Cui, D., Eriksen, T.E., 1996a. Reduction of pertechnetate by ferrous iron in solution: influence of sorbed and precipitated Fe(II). Environmental Science and Technology 30 (7), 2259– 2262.

12. Cui, D., Eriksen, T.E., 1996b. Reduction of pertechnetate in solution by heterogeneous electron transfer from Fe(II)-containing geological material. Environmental Science and Technology 30 (7), 2263– 2269.

13. Duc M., Lefevre G., Fedoroff M., Jeanjean J., Rouchaud J.C., Monteil-Rivera F., Duminceau J., Milonjic S. (2003) Sorption of selenium anionic species on apaptites and iron oxides from aqueous solutions. Journal of Environmental Radioactivity 70, 61_72.

14. Rovira M., Gimenez J., Martimez M., Martimez-Llad X., de Pablo J., Martí V., Duro L. (2008) Sorption of selenium(IV) and selenium (VI) onto natural iron oxides: Goethite and hematite. Journal of hazardous materials 150, 279-284.

15. Naveau A., Monteil-Rivera A., Guillon E., Dumonceau E. (2007) Interaction of aqueous selenium -II and IV with metallis sulfide surfaces Environ,.Sci.Technol. 41 5376-5382.

16. Sawhney  B. (1972). Selective sorption and fixation of cations by clay minerals: a Review. Clay and Clay minerals, 20, 93-100.

17. Evans D.,  Alberts J., Clark A. (1983). Reversible fixation of cesium Q37 leading to mobilization from rerservoir sediments. Geochimica at Cosmochimica Acta, 47, 1041-1049.

18. Comans R. N. et al. (1989). Mobilization of radiocesium in pore water of lake sediments. Nature, 339, 367-369.

19. Comans R. Hockley D. (1992). Kinetics of cesium sorption on illite. Geochimica at Cosmochimica Acta, 56, 1157-1164.

20. Dong Suk Han, Batchelor B., Abdel-Wahab. A. (2011). Sorption of selenium(IV) and selenium(V I) onto synthetic pyrite (FeS$_2$): Spectroscopic and microscopic analyses. Journal of colloid and interface science, 10.1016/j.jcis.2011.10.065.

**ACKNOWLEDGEMENTS**