FIXATION OF ANIONIC FORMS OF RADIOACTIVE CONTAMINANTS ON NATURAL SORBENTS

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Abstract

Ability of bentonite to sorb inorganic anions was investigated to predict transport of radioactive anionic forms throught the backfill material in nuclear waste repository to the biosphere. It is generally known that bentonite materials show an excellent cation-exchange capacity and on the other hand a poor uptake of anions.

The aim of our work has been to find out the conditions suitable for the technetium and iodine sorption under oxidizing conditions which occured in the form of anions. For model experiments perrhenate was selected as an analogue of pertechnetate in non-active experiments, due to its similar chemical behaviour.

The effect of the addition of different materials (e.g. activated carbon, graphite, Fe^{2+} ions and Fe) to bentonite, solid : aqueous phase ratio and a pH value on the sorption of studied anions uptake and on the Kd values were investigated.

Electromigration and polarography methods were used for the determination of the redox state of anion forms of technetium, iodine and rhenium in the aqueous phase and for the determination of Kd values. Acquried results were compared with data obtained by radiometric detection. The kinetics of sorption was described by a mathematical model to predict long - term behaviour of studied systems.

Introduction

The radionuclides of ^{99}Tc and ^{129}I are the fission products of nuclear fuel. The chemical behaviour of technetium in the near field interaction of nuclear waste repository is of considerable interest because of the long half-life of the nuclide Tc-99 and its relatively large abundance in nuclear waste ($T_{1/2} = 2.13.10^5$ years, fission yield ca. 6 %). The salts of Tc(VII), which is the stable oxidation state under non-reducing conditions, are in general very soluble. On the other hand, the Tc(IV) hydrous oxide, $TcO(OH)_2$ or $TcO_2.nH_2O$ (n = 1-2), which are formed under reducing conditions, are only sparingly soluble i.e. Tc(IV) is the desirable oxidation state in a nuclear waste repository. However, in the presence of oxygen, both hydrous $TcO_2.nH_2O$ and crystalline TcO_2 are found to be oxidized and dissolved as TcO_4^-, more or less rapidly. Vice versa, the TcO_4^- ion is sorbed or reduced on "various material" i.e. activated carbon, metal (Cu, Zn, Fe) or $Na_2S_2O_4$, Na_2S, NaH_2PO_4, FeS. In the presence of sulfide, technetium forms insoluble Tc_2S_7. The reaction rate on the iron filings may be explained by a combination of the reductive precipitation and/or adsorption on iron filings or (hydr)oxide surfaces[1-4].

It can be seen immediately from the Eh-pH plot for iodine[5] that at low total concentration values of iodine (10^{-10} - 10^{-6} mol/L) and at low redox potential I^- is the only stable specie. I_2 is stable in acid solutions at relatively high redox potential, whereas IO_3^- anion is formed in alkaline solutions at higer

redox potentials. IO_3^- ion is stable with respect to dispropotionation in both acid and alkaline solutions. Species of iodine in the oxidation state +1 (e.g. HOI) are unstable, in particular in acid and neutral solutions and those in the oxidation state +7 (e.g. IO_4^-, H_5IO_6 or $H_3I_2O_6^-$) are formed only at very high redox potentials Eh and can therefore also be neglected[5-6].

Methods

Several analytical methods were used for the determination of concentration and activity of pertechnetate and iodine and for the identification of individual species of iodine and technetium:

Capillary electrophoresis with the direct UV detection was selected for the determination of concentration of perrhenate. Illustrative electrophoregram of analysis perrhenate is shown in Fig.1. Electrophoretic experiments were performed in untreated fused-silica capillary [39 cm long (30 cm to the detector) X 75 μm I.D.] purchased from Composite Metal Services (The Chase Hallow, Worcester, UK) mounted in the CAPEL 105 capillary electophoresis system (Lumex, St. Petersburg, Russia). Before analysis the capillary was conditioned by sequentially washing with water (5min), 0.1 mol/L HCl (5min), 0.1 mol/L NaOH (5min), water (5min). Conditions of analysis were as following: background electrolyte- 40 mmol/L Britton - Robinson buffer, pH = 4.7, direct UV detection, λ = 214 nm, U = -10kV, hydrodynamic injection: 30s / 15mbar.
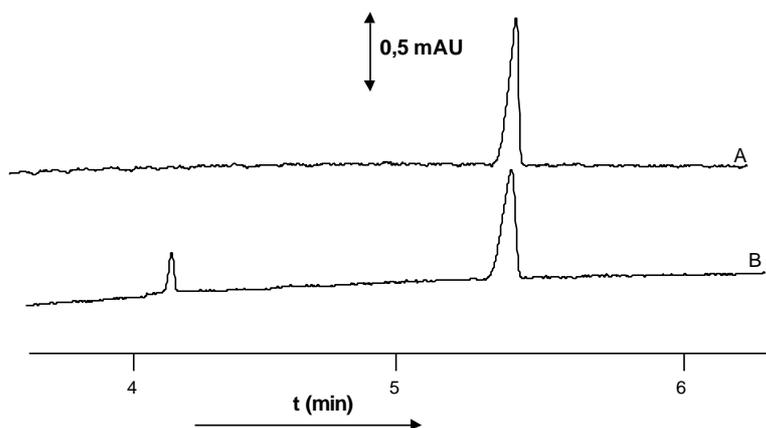

Fig.1:. Illustration electrophoregram of analysis of perrhenate
A-0.1 mmol/L $KReO_4$; B-bentonite leachate, conditions of measurment: BGE: 40 mmol/L Britton-Robinson buffer, U = -10kV, λ = 214 nm, hydrodynamic injection 30s / 15mbar

Capillary isotachophoresis with the conductivity detection was used for the separation of individual forms of iodine (I^- and IO_3^-). The experiments of capillary isotachophoresis (ITP) were carried out in a CS capillary electrophoretic analyzer EA 100 (Labeco, Spišská Nová Ves, Slovakia) with one pre-separation column. Pre-separation column (FEP, 90 mm lenght X 0.8 mm I.D.) was equipped with conductivity detection. Current in this column was set at 150 μA. Fig. 2 shows the isotachopherogram of separation of individual forms of iodine. Determination of these forms of iodine was provided in the electrolyte system shown in the table 1.

Table 1: System of electrolytes for the cITP

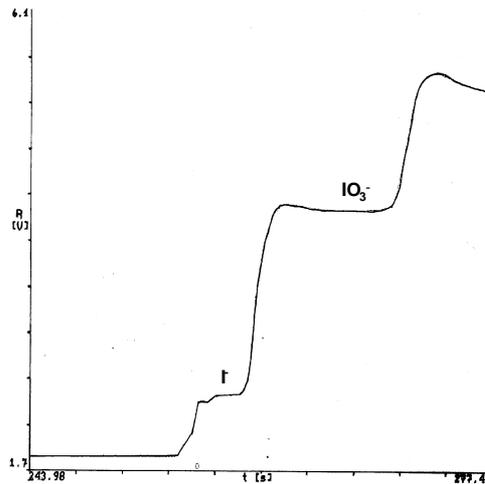|	
Leading electrolyte	5 mmol/L $Cd(NO_3)_2$
Terminating electrolyte	5 mmol/L tartaric acid

Fig.2 : Illustrative isotachoforegram of separation I⁻ and IO₃⁻

Terminating elelctrolyte: 5 mmol/L tartaric acid; Leading electrolyte: 5 mmol/L Cd(NO₃)₂;
c(I⁻) = c(IO₃⁻) = 0.2 mmol/L

Confirmation of individual forms of technetium in bentonite leachate was made by diference pulse polarography. The experiments diference pulse polarography were carried out in a polarograph PA4 with 3 electrodes connection. The conditions of measurment was: duration time of drop 1s, speed of polarization 5mV/s, modulation amplitude 50 mV. Pertechnetate can be reduced to the lower oxidation states in three steps as it is illustrated in Fig. 3. First step is the reduction of Tc(VII) to Tc(IV), second one corresponds to the Tc(IV) - Tc(III) change and the third one is the Tc(III) - Tc(0) reduction step. Due to the low concentration of $^{99}TcO_4^-$ during the experiments it was possible to observe polarographic peaks corresponding to Tc(VII) - Tc(IV) and Tc(III) - Tc(0) steps.
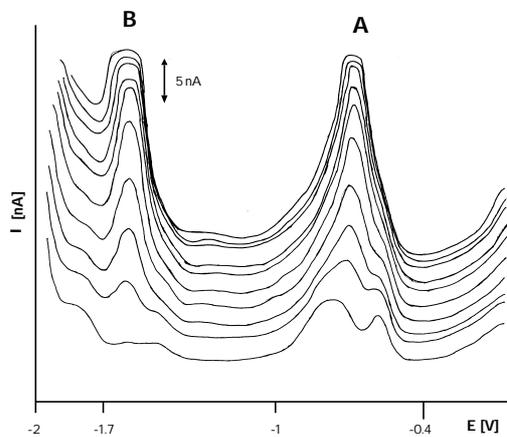

Fig.3 : Illustrative polarogram of bentonite leachate
1 - background electrolyte (1mol/L sodium citrate + 0.1 mol/L NaOH); 2 - 10 the kinetics of sorption of $^{99}TcO_4^-$ on the bentonite (1 - 8 days); A - reduction Tc(VII) - Tc(IV); B - reduction Tc(III) - Tc(0)

Experimental
Bentonite type R (locality Rokle, 4 km from Kadan town, Czech Republic), on the grain size 0.315 - 0.8 mm was used for the sorption experiments. Several bentonite mixtures with different additives e.g. activated carbon, iron filing, FeSO₄, graphite were tested for the uptake of studied anions ($^{99}TcO_4^-$, ^{125}I, ReO₄⁻). Two types of synthetic ground water- bentonite and granitic water were tested for the accurate description of processes in the depository of radioactive waste.   Reaction

mixtures were prepared by mixing of 0.7 g bentonite R with selected additive and 7 mL of synthetic ground water. These mixtures were labelled by 100 μL of ^{125}I, $^{99}TcO_4^-$ and ReO_4^- respectively. Reaction mixtures modified in this way were shaken and after the appropriate time the liquid and solid phase were separated by centrifugation. Eh, pH, specific conductivity, activity and individual species of studied elements were determined in the bentonite leachates.

Results and discussion

Kinetic of sorption

The sorption yield of studied anions was less than 25% on the bentonite and bentonite mixtures with graphite and $FeSO_4$. The values of Kd on these solid phases are summarized in table 2. The uptake of studied anions is insignificant under these conditions.

Table 2: The Kd values of ^{125}I, $^{99}TcO_4^-$ and ReO_4^- for the different solid phases

Solid phase	Kd (mL/g)		
	ReO_4^-	$^{99}TcO_4^-$	^{125}I
Bentonite	0.1 - 0.9	0.1 - 2.7	0.68 - 0.72
Bentonite + Fe (10:1)	347.8 - 398.9	248.1 - 347.1	---
Bentonite + activated carbon (10:1)	10.3 - 36.1	4900 - 5540	35.3 - 40.3
Bentonite + FeSO$_4$ (10:1)	2.5 - 3.6	---	2.51 - 3.10
Bentonite + graphite (10:1)	0.9 - 1.1	---	---

The sorption yield of studied anions (^{125}I, $^{99}TcO_4^-$, ReO_4^-) was higher than 75% after 1 day of the contact with the bentonite and Fe mixtures and activated carbon (Fig. 4). The sorption of $^{99}TcO_4^-$ and ReO_4^- on the iron filings depends on their concentration. The main mechanism of uptake of studied anions on activated carbon and iron filings is sorption (confirmed by DPP and cITP).
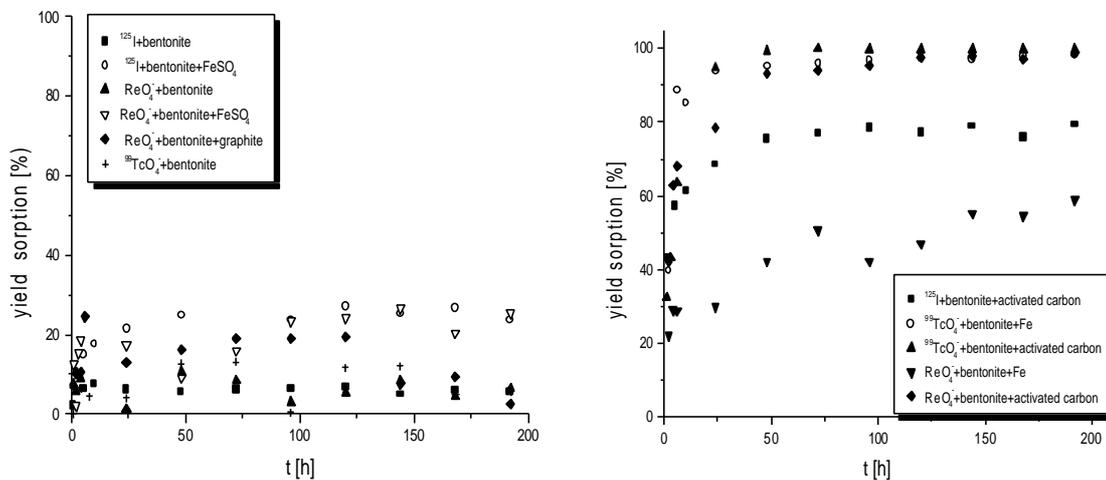

Fig.4: Kinetics sorption of studied anions on the different bentonite mixtures
Solid phases: bentonite, bentonite mixtures with Fe, graphite, $FeSO_4$ and activated carbon;
liquid phases: bentonite and granitic water, $c(ReO_4^-) = 0.1$ mmol/L, $c(^{99}TcO_4^-) = 2.66 \cdot 10^{-12}$ mol/L, $c(^{125}I) = 1.53 \cdot 10^{-12}$ mol/L

Effect of pH value on the sorption of studied anions

It is generally known that bentonite possess a great bufferring capacity in the wide interval of pH values[7-8]. The equilibrium pH after 8 days contact of phases was established on the value 8.5 - 9 for the initial pH of reaction mixture 2 - 9 (Fig.5). Due to this fact nearly the same values of the yield sorption of studied anions were obtained in this interval of equlibria pH values.
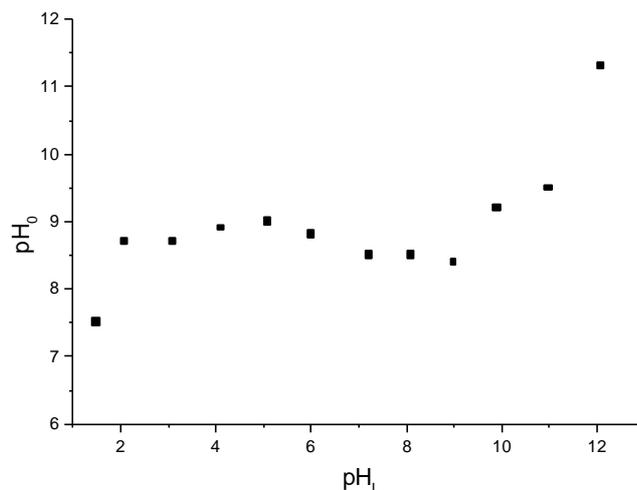
Fig. 5: Bufferring capacity of bentonite
Solid phase: bentonite + activated carbon 10:1, liquid phase: bentonite water, c (KReO$_4$) = 0.1 mmol/L, initial 1.5 - 12, contact of phases 8 days
pH$_0$ – equlibrium pH after 8 days of contact of phases, pH$_I$ – initial pH

Determination of the optimum ratio of bentonite:Fe and bentonite:activated carbon on sorption ReO$_4^-$ ions
Yield sorption of perrhenate, higher than 90%, was found for the ratio bentonite : Fe in interval 2:1 - 4:1. Sorption yield of perrhenate was lower than 90 % in bentonite mixture which contained less amount of iron filings. The optimum ratio bentonite : activated carbon was in interval 5:1 - 25:1 (Fig.6). The results of non-active experiments were utilized for the sorption of ^{99}TcO$_4^-$ and ^{125}I.
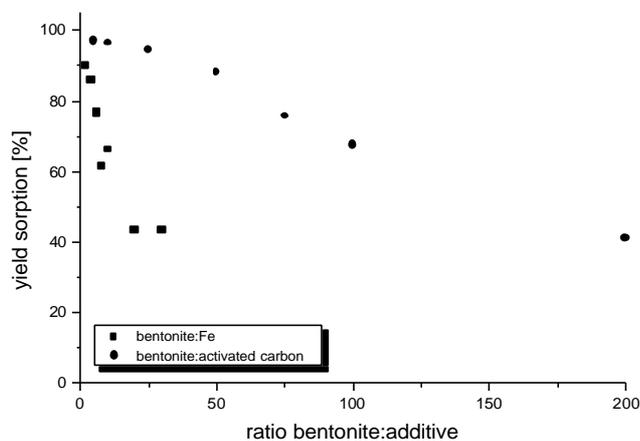

Fig.6: Dependence sorption yield of ReO$_4^-$ for the different ratio bentonite : Fe and bentonite : activated carbon
Ratio of bentonite : Fe 2:1 - 30:1 and bentonite : activated carbon 5:1 - 200:1, liquid phase: bentonite water, c (KReO$_4$) = 0.1 mmol/L, contact of phases 8 days

Conclusions
Activated carbon and iron filings are suitable additives for uptake of studied anions (^{99}TcO$_4^-$, ReO$_4^-$ and ^{125}I) under aerobic conditions. The yield of sorption was higher than 90% after 8 days contact of phases. The sorption of studied anions on bentonite alone is negligible under aerobic conditions.

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