



Sorption of pertechnetate anion by cation modified bentonites

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Abstract

Pertechnetate anion sorption was investigated on modified bentonites. Mn-, Cr-, Sn-bentonites were prepared by ion exchange process to sorb radioactive pertechnetate ions. In the case of Mn-, Cr-bentonite the sorb amount of metal ion was 70–90% of the cation exchange capacity of the bentonite which is expected. Interestingly in the case of Sn-bentonite this amount was 1.42 times higher than the cation exchange capacity. On Mn-bentonite the sorption was 35% at pH 5. The removal of pertechnetate ions was 100% on Cr-, Sn-bentonites and the significant sorption was achieved below 650 mV/SHE.

Keywords Pertechnetate ion · Modified bentonite · Redox reaction · Nuclear waste · Sorption

Introduction

Long-lived low- and medium-level radioactive waste and spent fuel assemblies are difficult to store because fissile products can get into the environment. Natural geological barriers do not bind anions from the fission products of ²³⁵U [1]. Among the fission products ⁹⁹Tc is a β-emitter, has no stable isotope, has a half-life of 2.13×10^5 years. ⁹⁹Tc forms by spontaneous fission of ²³⁸U in the earth's crust. It is also produced in medical diagnostic uses by the decay of ^{99m}Tc [2]. It is hard to bind, very little is known about its chemistry, but we can assume that it is similar to elements in a column VII B. (e.g., Mn, Re).

In the literature, several methods can be found for the removal of ⁹⁹Tc in most cases as pertechnetate ions such as ion exchange [3], reductive immobilization [4], adsorption [5], liquid–liquid extractions [6].

Several organic and inorganic, natural and artificial adsorbents was found to remove ⁹⁹Tc from the environment for example chitosan [7], resins and sponges [3, 8], polymers [9], metal–organic frameworks (MOFs) [10].

In this study we are looking for adsorbents which can be suitable for the construction of waste containers as

pertechnetate sorbents. They should be used as an engineering barrier and should be resistance to radioactive radiation.

There are also other adsorbents in the literature such as activated carbon [11, 12], layered double hydroxide (LDHs) [13], alumina and goethite [14], and there are the clay minerals which play an important role in the environment because by removing cations and anions either through ion exchange, adsorption and precipitation, or all these combined, they can act as natural decontaminating agents of numerous pollutants. Bentonite as geological and engineering barrier is present to isolate the radioactive waste deposited in underground disposal and the environment. The main clay mineral of bentonite is montmorillonite, which is a good sorbent because it has a large specific surface area and high cation exchange capacity. Shakira et al. [15], Vinsova, [16] Jedináková-Křížová [17]; Jaisi [18]; Milutinović-Nikolić [19], Hamárová [20] dealt with modified clays, for example Vinsova et al. [16] used mixtures of bentonite, bentonite activated carbon, iron powder, FeSO₄ and graphite to bind pertechnetate ions.

The main purpose of our work was to prepare Mn-, Cr-, Sn modified bentonites to sorb pertechnetate ions in a high degree. Our work dealt with ⁹⁹Tc, labeled with ^{99m}Tc.

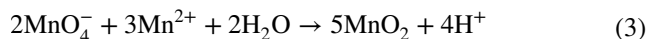
Pertechnetate anion sorption was investigated with Mn(II), Sn(II), Cr(III)-TcO₄⁻ redox reaction. It is assumed that a metal ion with a reducing effect is capable to sorb ^{99m}Tc(VII) ions in the form of TcO₂. In this form it can be sorbed.

For example Tc behaves similarly to its manganese chemistry in different reactions. Mn(II) is capable of redox

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reaction with Mn(VII) ions to form Mn(IV). During the permanganometric titration of Mn(II), a precipitate of MnO_2 is formed according to the following equations: (1), (2), (3)



If it is assumed that $^{99\text{m}}\text{TcO}_4^-$ ions react similarly to Mn(II) ions as MnO_4^- ions, then the radionuclide can theoretically be precipitated in $^{99\text{m}}\text{TcO}_2$ form, thereby it can be sorbed. Our experiences would be interpreted focusing on the pH and redox potential values that determine the chemistry forms, and on thermodynamic data.

Experimental

The modification of the cation exchanged bentonites

Modified bentonites were prepared by cation exchange procedure using Ca-bentonite (Istenmezeje, Hungary) and $\text{Mn}(\text{ClO}_4)_2$; $\text{Cr}(\text{ClO}_4)_3$; SnCl_2 solutions.

The cation exchange capacity (CEC) of Ca-bentonite determined by ammonium acetate method [21] is $4.1 \times 10^{-4} \text{ mol g}^{-1}$ for divalent ions and $2.7 \times 10^{-4} \text{ mol g}^{-1}$ for trivalent ions [22]. Chemical composition of the original Ca-bentonite were measured with EDAX. It has the following composition: 73.29% SiO_2 , 18.71% Al_2O_3 , 1.48% FeO , 2.29% CaO and 4.23% MgO . The X-ray diffraction and thermoanalytical results are: 71 m/m% montmorillonite, 12 m/m% cristobalite/opal CT, 8 m/m% illite, 4 m/m% quartz, 3 m/m% kaolinite, and 2 m/m% calcite.

$\text{Mn}(\text{ClO}_4)_2$ solution was prepared from analytically pure MnCO_3 (Reanal). 2.87536 g MnCO_3 was dissolved in $\sim 167 \text{ cm}^3$ of 0.3 mol dm^{-3} perchloric acid solution. $\text{Cr}(\text{ClO}_4)_3$ solution was prepared by the dissolution of Cr-powder (Alfa Aesar, pur. 99%) in 2 mol dm^{-3} perchloric acid solution. For SnCl_2 solution 7 g of Sn chips (Reanal, puris.) was dissolved in $10 \text{ cm}^3 \text{ cc}$. 37% HCl solution during heating to $60 \text{ }^\circ\text{C}$. The dissolution took 3 days. The concentration of $\text{Mn}(\text{ClO}_4)_2$ determined by complexometric titration; and $\text{Cr}(\text{ClO}_4)_3$; SnCl_2 solutions determined by MP-AES (Agilent Technologies 4200) were 0.09442; 6.95×10^{-2} ; $1.1 \times 10^{-1} \text{ mol dm}^{-3}$ respectively.

After preparing the modifying solutions the cation exchange procedure was carried out by suspending equivalent amount of metal-solutions and Ca-bentonite. In the case of Mn-bentonite the mixture was shaken for 5 h, and in the case of Cr- and Sn-bentonites, due to the low pH and to

avoid the significant destruction of bentonite, the mixture was shaken $3 \times 5 \text{ min}$.

After shaking, the modified bentonites were filtered through a Labex Ltd. $0.45 \text{ }\mu\text{m}$ pore size nylon bio-filter. The bentonite on the filter was returned to the beaker and the same amount and concentration of solution was added. This operation was repeated two more times. After the third change, the modified bentonites were dried in room temperature and powdered into agate mortar.

The Mn, Cr, Sn concentration of bentonite was determined by X-ray fluorescence analysis (XRF) using tungsten X-ray tube and ^{241}Am isotope source. The parts of XRF were Si(Li) detector with 20 mm^2 surface and 3.5 mm evaporated layer (Atomki, Debrecen, Hungary), Canberra DSA 1000 digital spectrum analyzer (Canberra Industries, Meriden, CT 06450, USA) and Canberra Genie 2000 3.0 spectroscopy software.

The d(001) basal spacing of the initial Ca-montmorillonite and the Mn-, Cr-, Sn-montmorillonites were determined with X-ray diffraction (XRD). The parts and settings of XRD are the following: a Philips PW1710 powder diffractometer equipped with a $\text{CuK}\alpha$ source and a graphite monochromator (operating at 30 mA, 40 kV). The scan rate was $2^\circ 2\theta/\text{min}$.

Pertechnetate ion sorption kinetic on modified bentonites

The sorption kinetic of $^{99\text{m}}\text{TcO}_4^-$ (Drytec 2.5–100 GBq radioactive isotope generator) was studied in batch experiments. 25 cm^3 physiological NaCl solution was used to eluate the isotope from the generator (Drytec 2.5–100 GBq). 100 mg modified-bentonite was added to 19 cm^3 distilled water. All samples were placed in a Bühler KS15A shaking bath at $25 \text{ }^\circ\text{C}$ for 30 min to reach the equilibrium between the liquid and the solid phase. After this time, $1 \text{ cm}^3 \text{ }^{99\text{m}}\text{TcO}_4^-$ solution was added to the samples. All samples were shaken for 5–120 min then filtered through a Labex Ltd. $0.45 \text{ }\mu\text{m}$ pore size nylon bio-filter and the radioactive intensity of the solution (c_e) and the solid phase was measured with a multi-channel gamma spectrometer equipped with (NaI)Tl scintillation detector, it had to be calibrated due to the different geometry of the solid and solution samples. pH of the solution was measured with a Clean pH200 pH meter and a Clean Cs1030 combined glass electrode.

The redox potential was measured using a platinum electrode and a calomel reference electrode containing 1 mol dm^{-3} KCl solution. The measured redox potentials were converted to potentials measured against a standard hydrogen electrode (SHE). The measurement was needed to determine the oxidation state of the $^{99\text{m}}\text{Tc}$ ion in the solution based on the potential-pH diagram.

The pertechnetate ion sorption was investigated on Mn-bentonite at different pH values (3.5; 4.5; 5) on Cr-,

Sn-bentonites without adjusting the pH. The pH values were 4.5 for Cr-bentonite and 3.1 for Sn-bentonite. The sorption was determined at room temperature.

Results and discussion

Characterization of modified bentonites

The Mn, Cr, Sn concentrations in modified bentonites were 7×10^{-4} ; 1.86×10^{-4} 5.8×10^{-4} mol g⁻¹, so 0.86 0.69 and 1.42 times of the cation exchange capacity was sorbed in bentonite, respectively.

X-ray diffractograms of the modified bentonites as well as the initial Ca-bentonite are shown in Fig. 1. The structure of the bentonites were not damaged, just the same peaks are shown. Table 1 shows that after modification with Cr and

Table 2 Results of pertechnetate ion sorption on Mn-, Cr-, Sn-modified bentonites, average result of 5–120 min; 100 mg bentonite, 20 cm³ solution

Ion	pH	Relative sorbed quantity of Tc (%)	Redox potential (mV/SHE)
Mn	3.5–3.6	16 ± 2	874 ± 17
	4.6–4.7	25 ± 1	679 ± 39
	5	35 ± 1	558 ± 59
Cr	4.5	100 ± 0.004	633 ± 21
Sn	3.1	100 ± 0.1	560 ± 15

Sn the d(001) basal spacing of montmorillonites decreased, because the ionic radii of the metal ions (Table 1) are less than that of Ca-ion. In the case of Mn-bentonite, the d(001) basal spacing of montmorillonite is the same as Ca-bentonite, because there is no big difference in ionic radii and

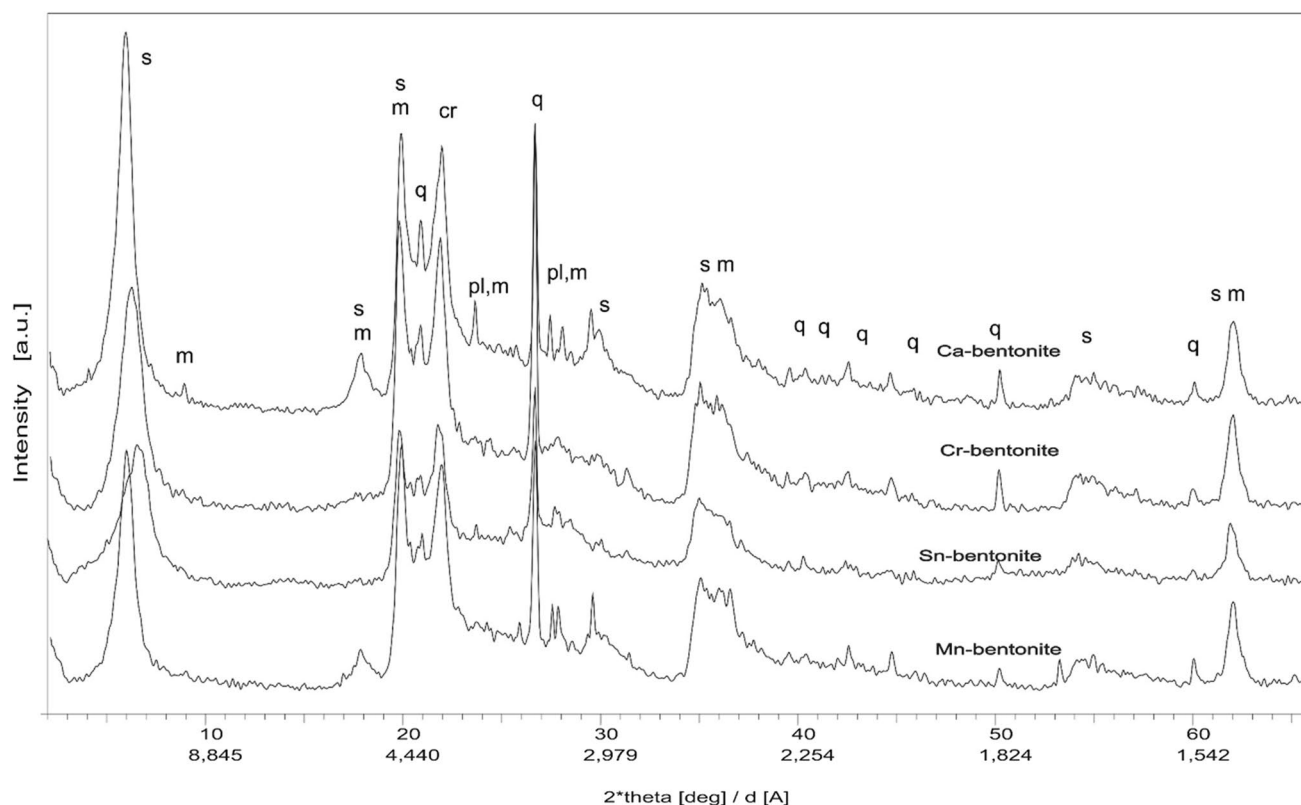


Fig. 1 XRD spectrum of Ca- and the modified; the unit of y axis is arbitrary unit (a.u.) (*m* mica, *pl* plagioclase, *s* smectite, *cr* cristobalite, *q* quartz)

Table 1 The d(001) basal spacing of Ca-, Mn-, Cr-, Sn-bentonites

	Ca-bentonite	Mn-bentonite	Cr-bentonite	Sn-bentonite
d(001) basal spacing (nm)	1.477	1.477	1.412	1.351
Ionic radii (nm)	Ca	Mn	Cr	Sn
	0.114	0.08	0.0755	0.069

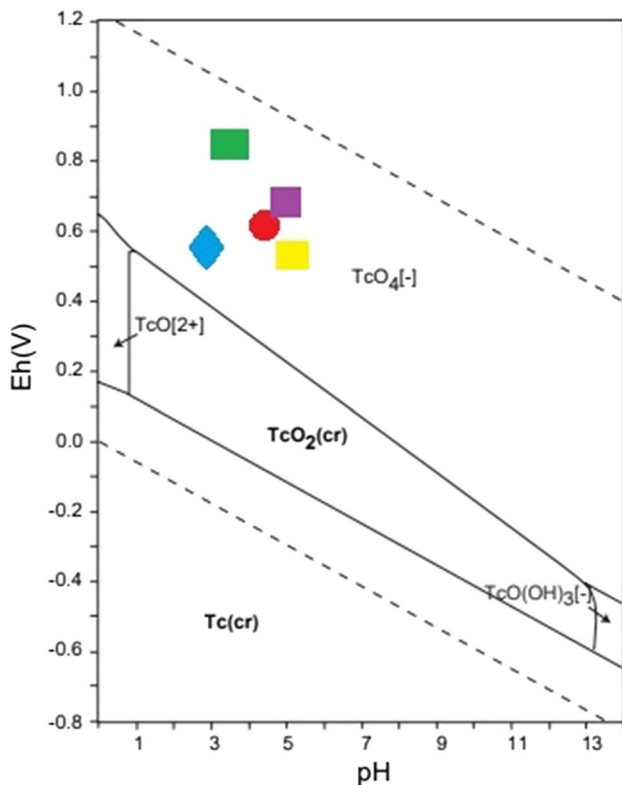


Fig. 2 The pH-Eh predominance diagrams for the sorption of technetium (Mn-bentonite: green square pH 3.5–3.6; violet square pH 4.6–4.7 yellow square pH 5; Cr-bentonite: red circle Sn-bentonite: blue diamond). (Color figure online)

Ca and Mn are bivalent ions, so they coordinate the same number of water molecules.

Results of sorption experiments

Table 2 shows the average results of 5–120 min sorption of pertechnetate ion on 100 mg modified bentonites. On Mn-bentonite, the pH 5 of the three pH ranges was the most effective, approx. 35%. Kinetics was so fast that there is an equilibrium after 5 min. Based on the results it can be concluded that the relative sorbed amount of pertechnetate ions was approx. 100% after 5 min on Cr-, Sn-bentonite.

Pourbaix diagram show the electrochemical stability for different redox states of an element as a function of pH. Figure 2 shows the Pourbaix diagram of Tc on which are summarized our experimental results. The colored shapes indicate the modified bentonites and their associated pH values. The straight lines refers to equilibrium between Tc species. In the case of Mn-bentonite with increasing sorption, the potential values are approaching the TcO_2 state. In the case of Cr-, Sn-bentonites the measured redox potential values do not fall into the region of Tc(IV) oxidation state despite the 100% sorption, but in all cases the dominant chemical form is pertechnetate. Figure 2 shows information only about the chemical species typical of technetium, but not only Tc ions are present in this solution. It is possible that a part of the modifying ions (manganese, chromium, tin) desorbed from the surface, e.g., by exchange with the hydrogen ions in the solution. Since the concentration of Tc is small (cca. 10^{-15} mol/dm³), the concentration of manganese, chromium, tin ions can significantly exceed it. Thus the redox potential does not provide information about the oxidation state of Tc, but rather the oxidation state of the modifying metal ions and this state is taken by the Tc. So we have to consider the Pourbaix diagram of the metals in each case. Figure 3 shows

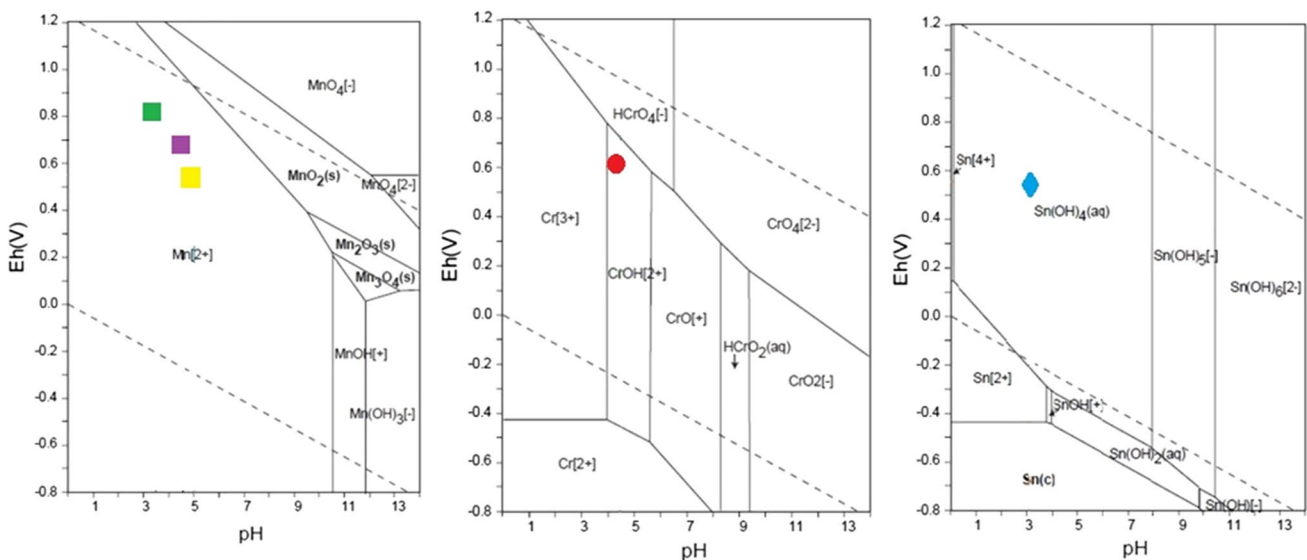


Fig. 3 The pH-Eh predominance diagrams for Mn, Cr, Sn (Mn-bentonite: green square pH 3.5–3.6; violet square pH 4.6–4.7 yellow square pH 5; Cr-bentonite: red circle Sn-bentonite: blue diamond). (Color figure online)

Table 3 Comparison of literary data of technetium removal

Adsorbent	Tc removal (%)	Species	Contact time (min)	pH	Reference
Activated carbon mixed bentonite	80	TcO ₄ ⁻	10		[16]
Activated carbon	99	TcO ₄ ⁻	Few minutes		[12]
COY zeolite	95	TcO ₂	30	2.5	[5]
	98.8		1440		
Activated carbon	~ 100	TcO ₄ ⁻	30		[11]
Sn-apatite	> 92	TcO ₄ ⁻		5	[20]
Cr-bentonite	100	TcO ₄ ⁻	5	4.5	This study
Sn-bentonite	99.94	TcO ₄ ⁻	5	3.1	This study

that in all three cases, the dominant chemical species are dissolved species, so it can be assumed that they also effect the measured redox potential values.

On the Pourbaix diagram of Sn it can be seen that Sn is in +4 oxidation state and preliminary Mössbauer-measurements indicate the +4 oxidation state. The +2 oxidation state also appears to a lesser extent. Thus, Sn ions are assumed to be present in +2 oxidation state in the interlayer space of the bentonite, and on the surface Sn ions are precipitated in +4 oxidation state, this explains the sorption over the cation exchange capacity of bentonite (1.42 times of CEC). From the pH-Eh predominance diagrams coprecipitation is assumed.

Our results correlate well with literature data (Table 3). Vinsova et al. [16] examined bentonite mixtures to remove pertechnetate ions. Bentonite-graphite and bentonite-FeSO₄ mixtures showed negligible sorption capacity, while bentonite showed less than 15%. Greater sorption was achieved with iron powder and activated carbon mixed bentonites. In both cases a sorption of 80–90% was observed. Almost 100% sorption was achieved after 30 min on activated carbon [12]. On Sn-apatite > 92% removal of technetium was observed [20]. Hercigonja et al. [5] used several types of zeolites for technetium removal. In this study firstly Tc(VII) was reduced to Tc(IV) with SnCl₂ and then adsorbed. COY (Co²⁺ was introduced into the zeolite) zeolite could adsorb 95% of TcO₂ after 30 min and 98.8% after 1440 min. The advantage of our adsorbent compared to literature is that it can sorb technetium very fast with high efficiency without reducing.

Conclusion

Mn-, Cr-, Sn cation modified bentonite were prepared from Ca-bentonite. These modified bentonites were used for pertechnetate ion removal.

From the redox potential and relative sorption values, it can be seen that the sorption on Mn-bentonite was the most effective at pH 5, approx. 35%. On Cr-, Sn-modified

bentonites the removal of Tc was 100% after 5 min. According to the results found in the literature the studied modified bentonites are suitable for faster and large-scale sorption of ^{99m}Tc ions.

Cr- and Sn-bentonites can be suitable for the construction of waste containers as pertechnetate sorbents.

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