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Anionic Sorbents for Arsenic and Technetium Species

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Abstract

Two sorbents, zirconium coated zeolite and magnesium hydroxide, were tested for their effectiveness in removing arsenic from Albuquerque municipal water. Results for the zirconium coated zeolite indicate that phosphate present in the water interfered with the sorption of arsenic. Additionally, there was a large quantity of iron and copper present in the water, corrosion products from the piping system, which may have interfered with the uptake of arsenic by the sorbent.

Magnesium hydroxide has also been proven to be a strong sorbent for arsenic as well as other metals. Carbonate, present in water, has been shown to interfere with the sorption of arsenic by reacting with the magnesium hydroxide to form magnesium carbonate. The reaction mechanism was investigated by FT-IR and shows that hydrogen bonding between an oxygen on the arsenic species and a hydrogen on the $Mg(OH)_2$ is most likely the mechanism of sorption. This was also confirmed by RAMAN spectroscopy and XRD.

Technetium exists in multiple oxidation states (IV and VII) and is easily oxidized from the relatively insoluble Tc(IV) form to the highly water soluble and mobile Tc(VII) form. The two oxidation states exhibit different sorption characteristics. Tc(VII) does not sorb to most materials whereas Tc(IV) will strongly sorb to many materials. Therefore, it was determined that it is necessary to first reduce the Tc (using $SnCl_2$) before sorption to stabilize Tc in the environment. Additionally, the effect of carbonate and phosphate on the sorption of technetium by hydroxyapatite was studied and indicated that both have a significant effect on reducing Tc sorption.

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1.0 Introduction

We reported earlier on the use of zirconium coated material and $\text{Mg}(\text{OH})_2$ for the sorption of arsenic (SAND2002-3641) and hydroxyapatite for the sorption of Tc (SAND2002-3642). In that work, batch methods were used to determine the kinetics and effectiveness of these sorbents. The zirconium coated materials and $\text{Mg}(\text{OH})_2$ exhibited high distribution coefficients, K_d values, in the hundreds of thousands. Similar high values were obtained for hydroxyapatite sorption of Tc.

In this report, we document the results for column experiments using the zirconium coated zeolite and $\text{Mg}(\text{OH})_2$ for arsenic removal from drinking water from the Albuquerque municipal water system. Additionally, the mechanisms of arsenic sorption by $\text{Mg}(\text{OH})_2$ and Tc sorption by hydroxyapatite have been investigated.

2.0 Arsenic Sorption by Zirconium Coated Zeolite

2.1 Background

New EPA regulations on the allowable concentration of arsenic in drinking water have spawned significant research in search of an economical process to reduce arsenic concentrations to the new level of 10 ppb. Using existing technologies that can lower arsenic levels to 10 ppb such as ultrafiltration can double or even triple the average household water bill. Therefore, it is essential to develop an economical treatment process that can be used for large and small water treatment facilities.

In our laboratory we completed batch experiments for two arsenic sorbents, zirconium coated zeolite and magnesium hydroxide. For zirconium, the experimental results indicated only phosphate interfered with sorption of arsenic in both the III and V oxidation states. .

2.2 Experimental

Zeolite was obtained from the St. Cloud Mining Company. Zirconium oxychloride hydrate (98%) was obtained from Aldrich and used as received. The zirconium coating was applied to the zeolite by immersing 10-100 g of zeolite in 25-50 ml 0.1 M ZrOCl_2 solution for 1-2 days. The material was then filtered and rinsed extensively with deionized water, air-dried and stored in a polyethylene bottle until used in column experiments. The cost of the treated material is approximately \$0.03/lb.

Figure 1 is a SEM image of the zirconium coated zeolite used in column experiments. An EDS analysis (Fig. 2) of the material indicated that only a small amount, 5% or less, of Zr was deposited on the surface.

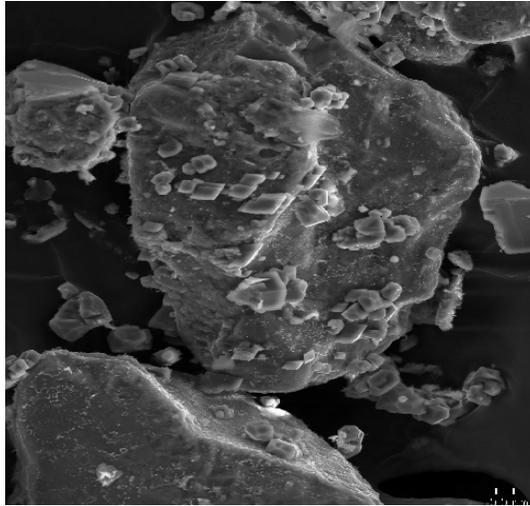


Fig 1. Zeolite particle coated with zirconium for sorption of arsenic. The material is composed of large 10µm diameter particles and much smaller (<1 µm) particles. This material was used in column experiments for removal of arsenic from drinking water.

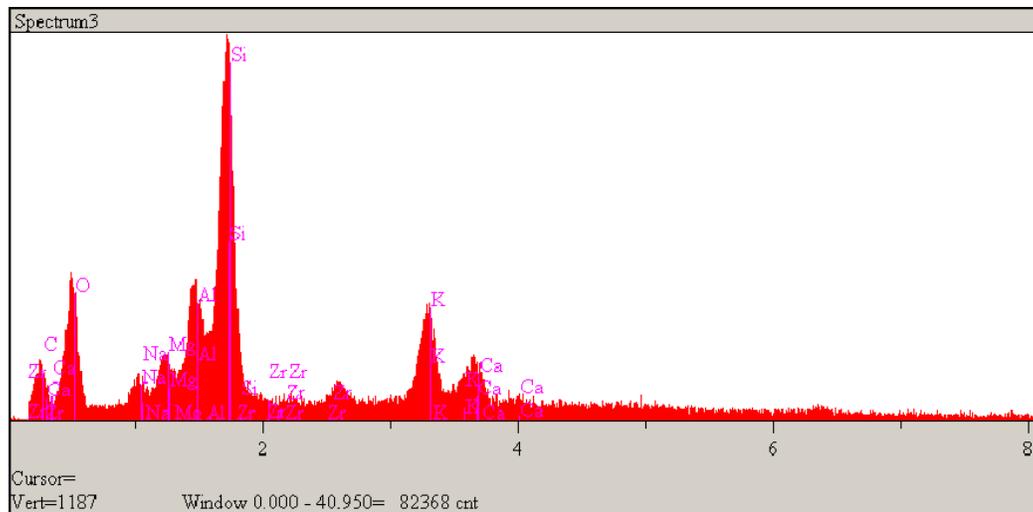


Fig 2 . EDS spectrum of zirconium coated zeolite particle. Only a small amount of Zr (< 5%) is detected in the analysis. No zirconium was detected in the untreated material.

The column apparatus used in these experiments is shown in Figure 3. The column was 2 feet high and had an internal diameter of 3 inches. A piece of filter paper and glass wool was packed into the entrance and exit of the column to contain the sorbent. Water used in the experiments was from the Albuquerque municipal water supply and contained 13 to 19 ppb arsenic as As(V). The first experiment was performed by passing water through the column at 10 mL /min. This gave a residence time of 10 min. No prefilter was used in the first experiment. In the second experiment water was first passed through a nylon fiber sediment prefilter to remove any fine solids. The second experiment was also run at 10 mL/min.

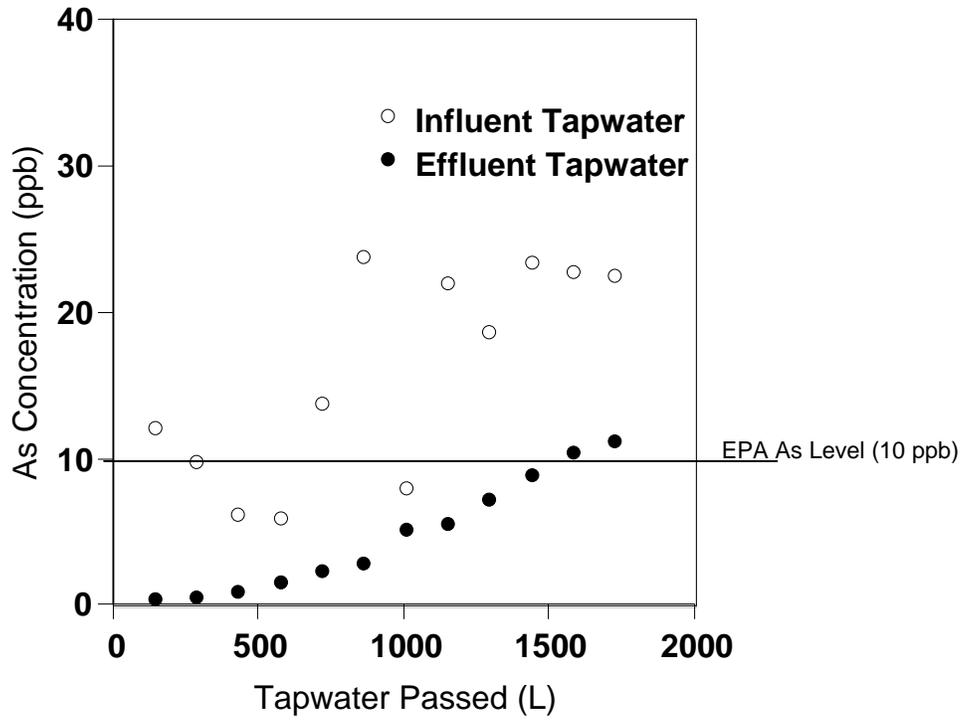


Fig 3. Experimental apparatus for column experiments. Prefilter is made of tightly wound nylon fibers. Column is 18 inches long by 3 inches diameter.

2.3 Results

The results from the first and second column experiments are given graphically in Figures 4 and 5. In the first experiment, breakthrough occurred at 50 pore volumes. The second experiment using the sediment prefilter resulted in treatment of 150 pore volumes. Examination of the sediment filter indicated the tap water contained a large amount of metal. (Fig. 6) An SEM and EDS analysis of the filtrate indicated it was composed of mainly iron with some copper present. These are corrosion products from the piping system. Additionally, a significant amount of phosphate was identified although phosphate is present in the tap water at a concentration of only 5 ppb.

In an attempt to eliminate the effects of the iron and copper on arsenic sorption, the entire experimental apparatus was moved to a new location. The prefilter is changed every week. This experiment is still in progress with the results expected in approximately 2-3 months.

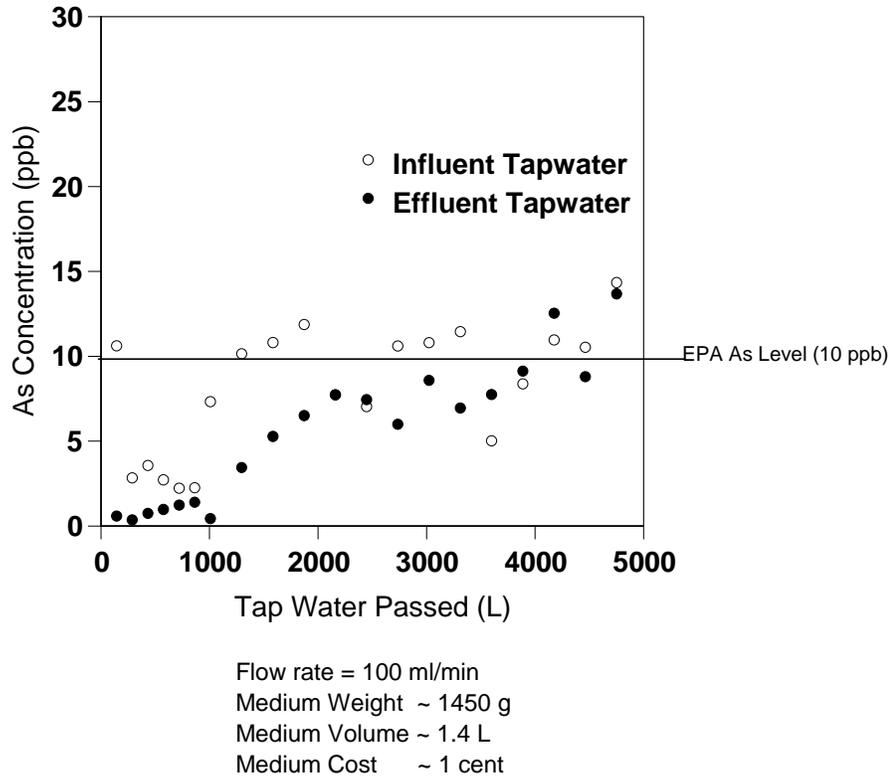


Flow rate = 100 ml/min
 Medium Weight ~ 1450 g
 Medium Volume ~ 1.4 L
 Medium Cost ~ 1 cent

* No significant change in pH value
 of Input/output Tapwater (~8.0-8.2)

Fig 4. Results from column study of arsenic removal from tap water using zirconium coated zeolite with no prefilter.

This column treated up to ~500 gallons of tap water before the As level exceeded 10 ppb.



* No significant change in pH value of Input/output Tapwater (~8.0-8.2)

Fig 5. Results from column study of arsenic removal from tap water using zirconium coated zeolite using prefiltration with a polymer sediment filter.

The As concentration in tap water of the second column study varied from that of the first. The capacity of this column with the prefilter is doubled to ~ 1000 gallon. Our goal is currently to treat up to 2000 gallons of tap water at minimum cost (a few cents).

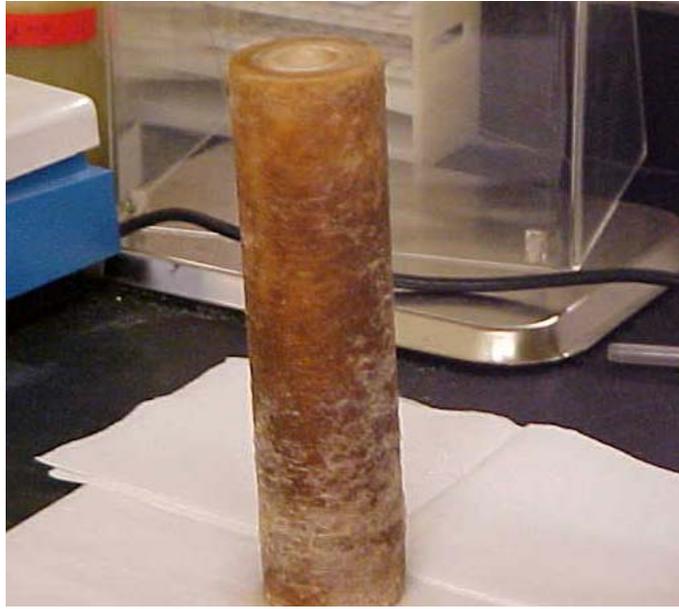


Fig 6. Sediment prefilter for zirconium coated zeolite arsenic sorption column experiment after 150L of water has passed. The filter is heavily loaded with iron and copper.

An SEM of the sediment prefilter revealed it is dominantly Fe (45 wt%), Si (16 wt%), Cu (20 wt%) and Mn(8 wt %). Minor to trace amounts (less than 4 wt %) of Al, S, Cl, Ca, and Zn are also present. Texturally, it is very fine grained and no crystallinity was evident.

3.0 Arsenic Sorption by Magnesium Hydroxide

3.1 Background

Magnesium hydroxide has been proven to be a strong sorbent for arsenic as well as other metals. Results from batch kinetic experiments indicated arsenic in both oxidation states is sorbed rapidly (1-3 min.). K_d values ranged up to 1×10^6 L/mole.

To stabilize against reaction with carbonate, $Mg(OH)_2$ was made into the form of a Sorrel's Cement by mixing with magnesium chloride and allowing to set for several days. The Sorrels' cement was much more resistant to carbonate attack, but K_d values dropped to around 20,000 to 30,000 L/mole.

Other than reduced effectiveness in the presence of carbonate, a major drawback of using $Mg(OH)_2$ as an arsenic sorbent is the increase in pH of the treated water. pH is raised to approximately 10.3. Although there is not regulation on the use of pH 10.3 water, the taste is not acceptable. Readjustment of the pH would be required if $Mg(OH)_2$ were used in a treatment process.

No compounds were identified that interfered with arsenic sorption by $\text{Mg}(\text{OH})_2$. However, magnesium hydroxide reacts with carbonate in water to form magnesium carbonate. Magnesium carbonate does not sorb arsenic. The presence of carbonate in water therefore decreases the efficiency of using $\text{Mg}(\text{OH})_2$ for arsenic removal from drinking water.

3.2 Experimental

A glass column (6 in. long x ½ in. internal diameter) was packed with 8 g of reagent grade $\text{Mg}(\text{OH})_2$. Filter paper and glass wool was used to secure the $\text{Mg}(\text{OH})_2$ in the column. A HPLC pump was used to pass tap water spiked with 100 ppb arsenic as As(V) through the column at a flow rate of 1.0 cc/min.

3.3 Results

Results from the column experiments are given in Fig 7. The 8 g of $\text{Mg}(\text{OH})_2$ treated more than 30 L of spiked tap water before the start of breakthrough. The results from batch experiment indicate that 4 g of $\text{Mg}(\text{OH})_2$ should be able to treated significantly more arsenic spiked water. The reduced effectiveness is due to the presence of high concentrations of carbonate in the water.

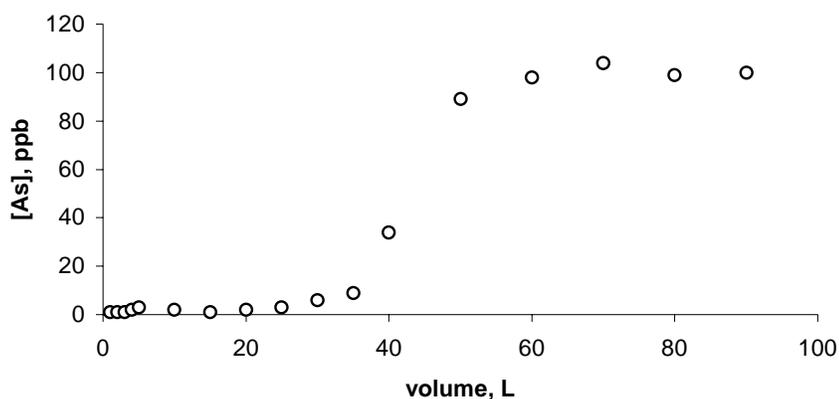


Fig 7. Column Experiments for $\text{Mg}(\text{OH})_2$ sorption of arsenic(V). The column was 6 in long x ½ in internal diameter containing 4 g of $\text{Mg}(\text{OH})_2$. Tap water spiked with 100 ppb arsenic was passed through the column at a flow rate of 1 cc/min.

3.4 Mechanistic Studies

To determine the mechanism of arsenic sorption by $\text{Mg}(\text{OH})_2$, NaAsO_3 , and $\text{Mg}(\text{OH})_2$ with sorbed arsenic were examined by FT-IR. The results are given in Figure 8. Common peaks are seen for $\text{Mg}(\text{OH})_2$ -As and NaAsO_3 at 805 cm^{-1} and 845 cm^{-1} for

Mg(OH)₂-As and 895 cm⁻¹ for NaAsO₃. There is no peak for Mg(OH)₂ at these wavelength. However, common peaks for Mg(OH)₂ and Mg(OH)-As are seen at 3700 cm⁻¹. The data indicates that hydrogen bonding between an oxygen on the arsenic species and a hydrogen on the Mg(OH)₂ is most likely the mechanism of sorption. This was confirmed by RAMAN Spectroscopy and XRD.

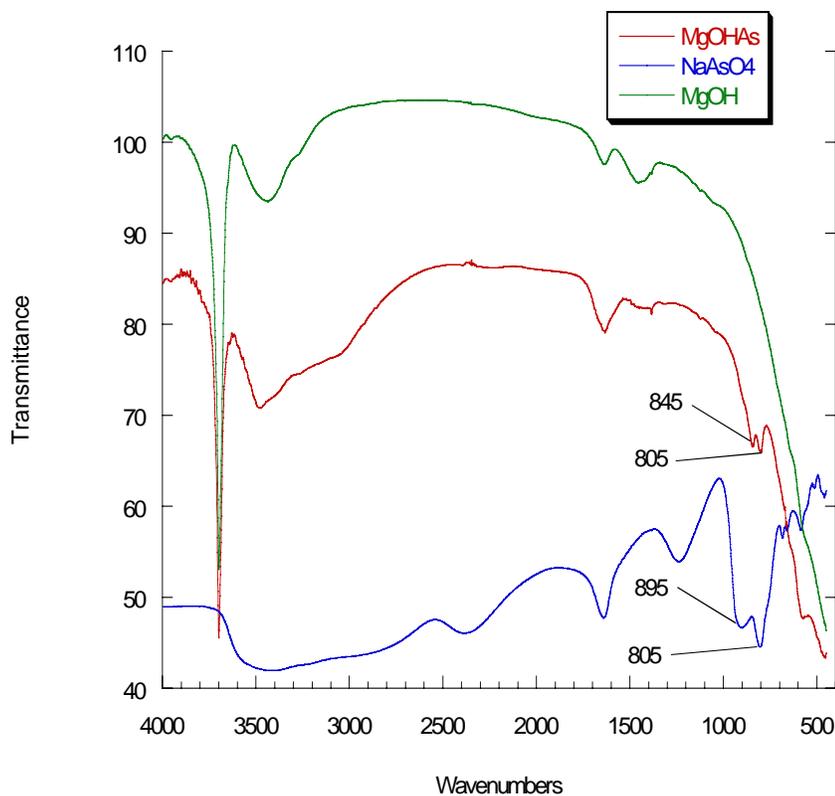


Fig 8. FT-IR of Magnesium hydroxide sorption of arsenic

4.0 Technetium Sorption by Hydroxyapatite

4.1 Background

Technetium is a problematic compound in radioactive waste disposal. Tc as pertechnetate (Tc(VII)) does not sorb appreciably to almost all geologic materials and efforts to develop a selective sorbent for Tc have not been very successful. Tc in its reduced form as Tc(IV) has been used for several decades in bone scans. In the process, Tc(IV) is chelated with an organic compound and injected into the bloodstream where it sorbs to the hydroxyapatite part of bone.

Several studies have been performed to determine the mechanism of Tc sorption to hydroxyapatite. Kanagawa *et al.* (1993) reports technetium chelated with ethylene diphosphonate preferentially sorbs to the hydroxyapatite portion of bone and suggests technetium sorbed to the surface of the hydroxyapatite and is also incorporated into the crystalline structure. Kanagawa *et al.* (1995) later reports technetium sorption by hydroxyapatite is strongly affected by pH and the presence of phosphates and calcium compounds. At low phosphate concentrations Tc sorption was unaffected. However, higher phosphate concentrations significantly reduced Tc sorption.

4.2 Chemistry of Tc(VII) and Tc(IV)

Tc exists in multiple oxidation states and is easily oxidized from the relatively insoluble Tc(IV) form to the highly water soluble and mobile Tc(VII) form (Fig 10). Although Tc(VII) does not sorb to most materials, Tc(IV) will strongly sorb to many materials. Therefore a method to immobilize Tc in the environment is by reduction and sorption to stabilize Tc in the reduced form. In our earlier work, we demonstrated that after reduction of Tc with SnCl_2 , Tc sorbs to hydroxyapatite.

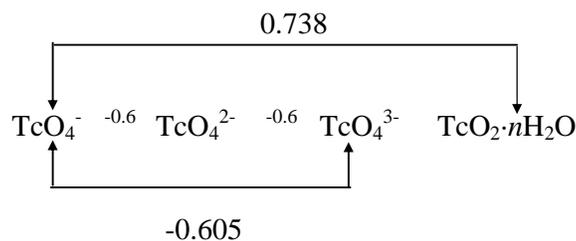


Figure 9. Redox Potentials of the Tc (VII)-Tc(IV) system(Cui and Eriksen, 1996)

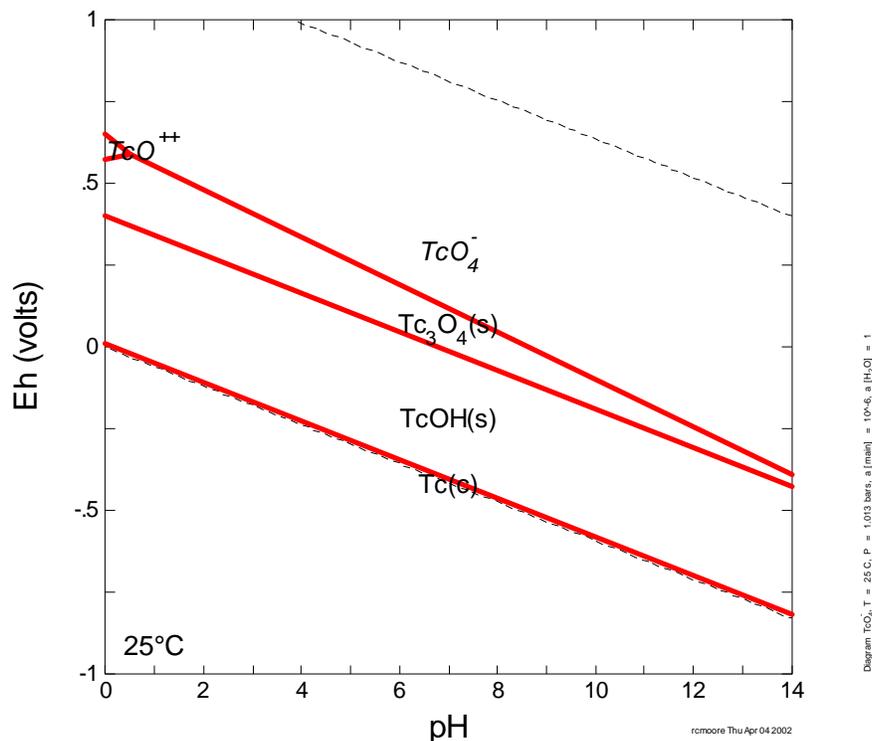


Figure 10. pH vs. Eh diagram for technetium.

4.3 Experimental

Technetium: Tc^{99} (NH_4TcO_4 in H_2O) was obtained from Isotope Products Laboratories (Valencia, CA, USA), with a specific activity of $16.97 \mu Ci/g$ and a purity of $> 99\%$. Stability experiments were performed by spiking Tc(VII) into glass containers with one containing $SnCl_2$ and the other $SnCl_2$ and synthetic hydroxyapatite. The containers were left open to the atmosphere. Tc concentrations in solution were determined by liquid scintillation counting.

Experiments were performed to determine the effect of phosphate and carbonate on Tc uptake. Varying amounts of phosphate and carbonate were added to experiments with $SnCl_2$, hydroxyapatite and Tc.

4.4 Results

The results from stability experiments indicate Tc in solution initially containing $SnCl_2$ only returned to Tc(VII) after 30 days whereas the mixture with $SnCl_2$ and hydroxyapatite remained as Tc(IV) even after 90 days (Fig 11). Experiments with added carbonate and phosphate indicated both have a significant effect on Tc sorption (Fig 12). At carbonate and phosphate concentrations of 1 M each, Tc sorption decreased by 80% for each.

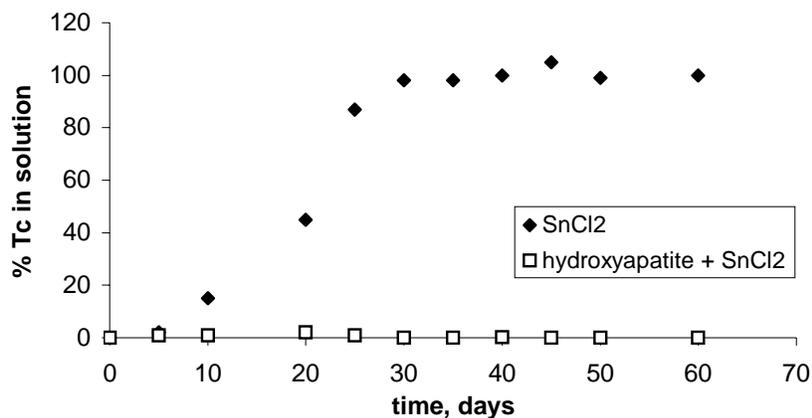


Fig 11. Effect of SnCl₂ and SnCl₂ plus hydroxyapatite on Tc concentration in solution. 0.1 gram of hydroxyapatite, 0.1 grams of SnCl₂ in 30 mL of water. Initial Tc concentration was 1 x 10⁻⁶M.

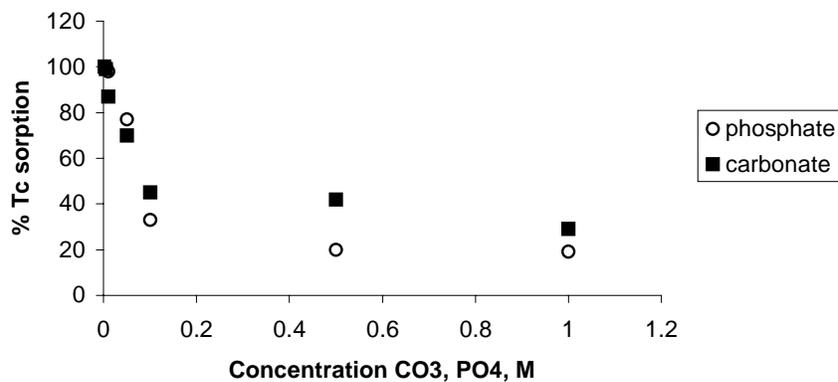


Fig 12. Effect of carbonate and phosphate concentration on Tc sorption to hydroxyapatite. Initial Tc concentration was 1 x 10⁻⁶ M with 0.1 gram of hydroxyapatite and 0.1 g of SnCl₂ in 30 mL of water.

At pH 5 and higher Tc(IV) will form complexes with carbonate and phosphate. Carbonate and phosphate complexes are also formed for other radionuclides including uranium, plutonium, and neptunium. These radionuclides all strongly sorb to hydroxyapatite and sorption is affected by the presence of carbonate and phosphate.

It has been reported that uranium sorbs to hydroxyapatite by the formation of uranyl phosphates that sorb to the hydroxyapatite surface. Unfortunately, analysis of hydroxyapatite with sorbed technetium using FT-IR and XRD did not give any valuable information because of the low concentration of Tc. If Tc behaves similar to the other radionuclides, even though their chemistry is very different, then a likely mechanism for sorption to hydroxyapatite is through formation of Tc-phosphate compounds that sorb to the hydroxyapatite surface. UV-Vis spectroscopy was also attempted to identify Tc species in solution with and without Tc present. As with the solids analysis, not enough Tc as Tc(IV) was present for an accurate measurement.

It was also discovered in this work that oxalate has a strong effect on Tc solubility. In experiments with hydroxyapatite, SnCl₂ and added sodium oxalate, Tc concentrations decrease below levels with hydroxyapatite and SnCl₂ only. Even after exposure to the atmosphere for several weeks the concentration of Tc in solution did not change. A likely explanation is that Tc(IV) may be forming an insoluble compound with oxalate.

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