Properties and Uses of Sodium Titanates and Peroxotitanates

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Sodium titanates and peroxotitanates are inorganic ion-exchangers that exhibit strong affinities for a wide range of metals. These materials serve as effective ion-exchangers in strongly alkaline, neutral, and weakly acidic solutions. One of the sodium titanates, referred to as monosodium titanate, is currently used at the Savannah River Site in a batch-contact process to separate ^{90}Sr and alpha-emitting radioisotopes from high-level nuclear waste solutions. The titanates can be incorporated into porous supporting matrices that allow deployment in a flow-through filter or column configuration. Recent studies indicate that the titanates may also be a suitable platform to either remove or deliver metals under physiological conditions.

Introduction

Over the last 30 years, a number of titanium-based substances have been developed that serve as effective ion exchangers in chemical separations. For example, monosodium titanate (MST)[1] and sodium nonatitanate (SNT)[2] are amorphous or poorly crystalline materials that are effective ion-exchange materials for the removal of strontium and actinides (e.g., Pu, Np, U) from highly alkaline nuclear waste solutions. In fact, MST is currently used at the Savannah River Site for the treatment of high-level nuclear waste solutions.[3,4] A new family of peroxotitanate materials having the general formula of $H_vNa_wTi_2O_5 \cdot (xH_2O)[yH_zO_2]$, has been prepared recently that offers increased selectivity and faster removal kinetics.[5,6] Both the sodium titanates and peroxotitanates have been shown to be effective for the removal of a wide range of metal ions from neutral and weakly acidic solutions.[7] These results suggest that these materials could prove useful in the treatment of industrial wastewaters and contaminated groundwaters,[7] in nuclear fuel reprocessing,[8] and in a number of medical applications.[9-13] This paper provides a summary of the properties and uses of the sodium and metal-exchanged titanates and peroxotitanates.

Results and Discussion

MST is a white, irregular-shaped, amorphous solid that is prepared using a sol-gel method first reported in the literature by Lynch, et al.[1] The synthetic method was modified by Hobbs, et al to produce spherically shaped particles ranging in size from about 1 – 20 microns.[3] Figure 1 provides scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of MST. The TEM image reveals an inner amorphous phase surrounded by an outer fibrous region.[13,14] Air-dried MST contains about 25% by weight of water which can be removed by heating above 110 °C.

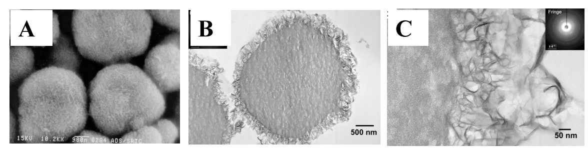


Fig. 1 SEM image of monosodium titanate. (A); TEM images of monosodium titanate (B,C).

MST exhibits excellent performance to remove dissolved strontium, plutonium, neptunium and uranium from highly alkaline salt solutions such as the high-level nuclear waste solutions stored at the Savannah River Site from fuel reprocessing operations. These salt solutions are extremely corrosive and feature free hydroxide concentrations from about 1.0 molar to 4.5 molar. These high ionic strength solutions commonly have total sodium concentrations in excess of 6.0 molar and contain oxyanions such as nitrate, nitrite, aluminate, sulfate and carbonate.

Figure 2 provides a plot of the concentrations of strontium, plutonium, neptunium and uranium versus time when a simulated waste solution is contacted with MST. In this batch contact test, the sodium concentration of the simulant was 5.6 M and was treated with 0.4 g/L MST. Strontium and the actinides are removed fairly rapidly despite the high salt concentration. Similar removal performance is seen with actual tank wastes.

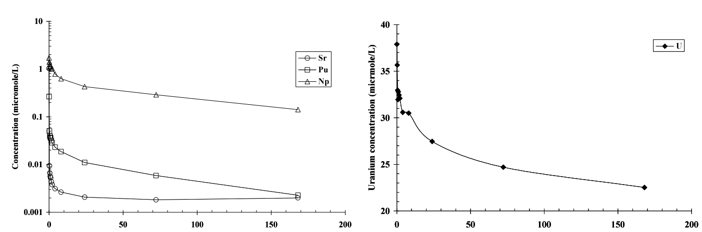


Fig. 2. Plots of sorbate concentration versus time upon contact of simulated waste solution with 0.4 g/L MST at 25 °C.

X-ray Absorption Fine Structure (XAFS) spectroscopy revealed that strontium and the actinides are bound to the titanate octahedra via inner sphere coordination through the oxygen atoms of the titanate.[16] The sodium content can be

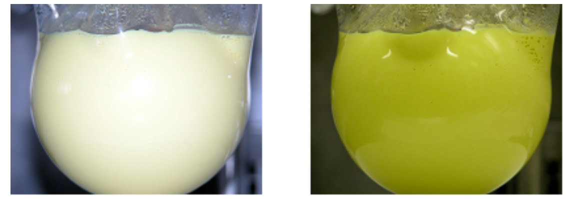
reduced in the sodium titanates by the addition of mineral acids such as nitric acid. This suggests that MST serves as an ion-exchanger for the removal of metal ions from solution.

MST is currently used in the Actinide Removal Process (ARP) at the Savannah River Site in a batch contact process in which the solid is added as an aqueous suspension to the waste solution in a well-mixed reactor. After 12 hours of mixing, the mixture is filtered to separate the MST solids, which are loaded with strontium and actinides, from the waste solution. The MST solids are washed to reduce the soluble salt content and then sent to the Defense Waste Processing Facility (DWPF) for incorporation into a borosilicate wasteform. The clarified waste solution then transfers to a second treatment step for removal of ^{137}Cs by a solvent extraction process.[17]

The fine particulate MST can be incorporated into a variety of matrices for use in continuous or semi-continuous waste treatment processes. For example, MST can be incorporated into a cellulose disk or porous membranes composed of polyethylene (PE) or polytetrafluoroethylene (PTFE).[18] The cellulose disk impregnated with MST was tested in a dead-end filter arrangement and showed good removal of strontium from aqueous solutions. The PE- and PTFE-based porous membranes were produced as sheets that could be fabricated into a spiral-wound filter unit. Aqueous solutions passed easily through the filter units and exhibited excellent removal characteristics for strontium. MST can also be incorporated into spherical beads using hydrous titanium oxide as a binder.[19,20] The beads, containing up to 50 wt% MST, have good mechanical strength. Testing showed excellent removal performance in a flow-through column configuration to remove strontium and plutonium from radioactive waste solution.

Peroxotitanates are formed by the addition of hydrogen peroxide either during the sol-gel synthesis or as a post-synthesis treatment step with a preformed sodium titanate.[5,6] The peroxotitanates exhibit a distinctive yellow color indicative of the peroxo-titanium species. Figure 3 provides photos of a reaction vessel containing a suspension of MST before and after treatment with hydrogen peroxide. The intensity of the color decreases as the pH of a suspension changes from acidic to alkaline. The particle morphology can vary widely depending on synthesis conditions. In a post-synthesis treatment step, the particle size of the peroxotitanate is very similar to that of the original sodium titanate. However, the peroxotitanate exhibits a much greater surface area than original sodium titanate. Scanning electron microscopy revealed a much more fuzzy surface for the peroxotitanates compared to the original sodium titanate.

Like MST, the peroxotitanates are effective for the removal of strontium and actinides from strongly alkaline salt solutions. Compared to MST, the peroxide-modified MST or mMST exhibited much faster removal kinetics for strontium and plutonium (see Figure 4).[21,22] This increased ion-exchange/adsorption rate likely reflected the much higher surface area of the mMST compared to MST. Interestingly, the mMST exhibits very little affinity for uranium (see Figure 5). Whereas MST readily removes uranium present as the uranyl species, UO_2^{2+}, mMST removes very little uranium from the alkaline salt solution. Since mMST shows high affinity for neptunium, which is present as neptunyl species,



A. Monosodium Titanate B. Sodium Peroxotitanate

Fig. 3 Photographs of monosodium titanate suspension (A) and sodium peroxotitanate suspension (B)

NpO_2^+, the low affinity of mMST for uranium cannot be attributed solely to the uranium being present as an uranyl species. Furthermore, uranyl is also known to form a large number of stable compounds with both bridging and terminal peroxide ligands. Studies are in progress to elucidate the structural factors responsible for the selectivities of MST and mMST.

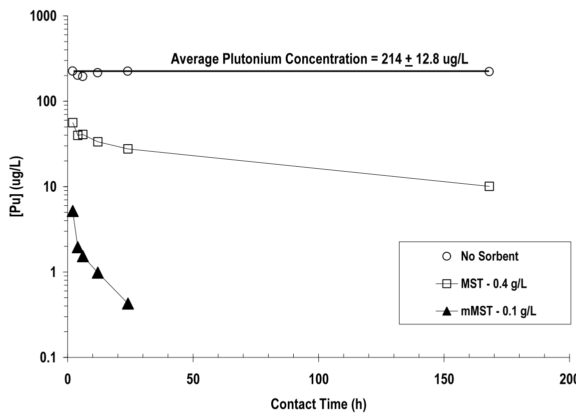


Fig. 4 Plot of plutonium concentration versus time for tests with no added sorbent, 0.4 g/L MST and 0.1 g/L mMST

Sodium titanates and peroxotitanates are also effective for the removal of metal ions from weakly acidic solutions, making them attractive for wastewater treatment. For example, MST and mMST exhibited high affinity for a number of metallic ions dissolved in a pH 3 nitric acid solution.[7] Table 1 provides a listing of the distribution values, K_d, for a number of transition and main group metals. In these tests the solutions contained multiple metal ions with initial metal concentrations of approximately 100 mg/L. Furthermore, the chemical species of the metals in these solutions include not only the hydrated metallic cations (e.g., $Al(H_2O)_6^{3+}$ and $Cr(H_2O)_6^{3+}$), but also anionic complexes such as $H_2V_{10}O_{28}^{4-}$ for vanadium and $Mo_7O_{22}(OH)_2^{4-}$ for molybdenum. The affinity of MST and mMST for anionic metal species is attributed to a positive surface charge on MST and mMST at a pH of 3 as confirmed by zeta potential measurements.

Loading isotherms indicated that MST and mMST exhibit maximum metal loadings of between 0.1 and 0.6 mmole/L in the weakly acidic solutions. Figure 6 provides the loading isotherms for solutions of Cr(III) and Hg(II), initially containing 100 mg/L of the respective metal ions. Other

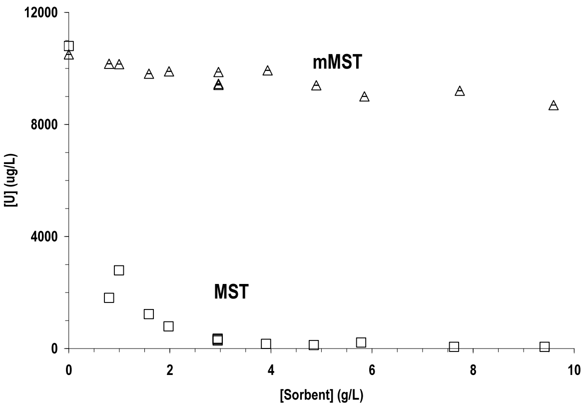


Fig. 5 Plot of uranium concentration versus time upon contact of varying amounts of MST and mMST with a simulated waste solution

Table 1. K_d Values for Selected Metals Using MST and mMST (pH 3)

	K_d (mL/g	
Metal	**MST**	**mMST**
Al	2.36E+03	2.82E+03
Ba	1.80E+03	1.73E+03
Cd	4.54E+02	1.44e+02
Cr	>3.91E+05	>3.77E+05
Fe	>1.51E+03	>1.45E+03
La	1.27E+04	1.63E+04
Mo	>6.86E+04	>.661E+04
Nb	>9.90E+04	2.92E+03
Pb	>8.39E+03	>8.08E+03
Sn	5.08E+04	>4.89E+04
V	5.61E+04	5.41E+04
Zr	1.05E+04	1.97E+04

metals such as those reported in Table 1 exhibited metal loadings similar to that shown for Cr(III) and Hg(II). The maximum metal loadings in these batch contact experiments were between 5 and 40% of the theoretical value based on the assumption that MST and mMST have 5.0 milliequivalents of exchangeable sodium cations per gram of material. In general, metal loadings are higher for the trivalent metal ions (e.g., Cr^{3+}, La^{+3}) compared to divalent metal ions (e.g., Ba^{2+}, Cd^{2+}).

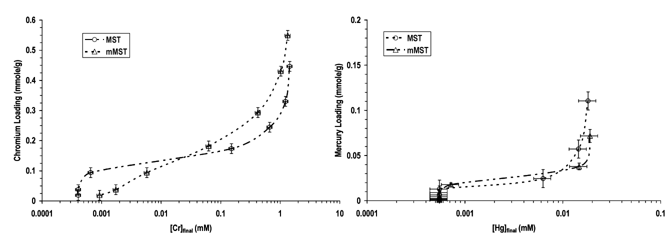


Fig. 6 Loading Isotherms for MST and mMST with Cr(III) and Hg(II) at pH 3

The high K_d values in the presence of multiple metal ions along with the ability to remove both cationic and anionic metallic species and the high metal loading values, suggest that MST and mMST are good candidates for cleanup of industrial wastewaters and contaminated wastewaters. Given the relatively high cost of sodium titanates (ca. $200/kg) and the fact that MST and mMST are not easily regenerated after metal exchange, the more attractive application for these materials would be as a final polishing stage to remove the last traces of metal impurities.

The sodium titanates and peroxotitanates exhibit good affinity for metals in near-neutral solutions as well, giving them possible applications in the medical field.[7] To date, studies have focused largely on the separation of the noble metals, mercury, and cadmium. Noble metal compounds of gold and platinum as well as mercury compounds and alloys have been used in numerous medical and dental applications. For example, gold compounds have been used to treat inflammatory diseases such as arthritis, and platinum compounds such as cisplatin are used to treat a variety of cancers. Often, these compounds are given in very high doses because of their low solubilities, which leads to adverse side effects. Cadmium was selected for study as it is a hazardous metal that is well known to be toxic when taken internally. Tests explored the affinity of the sodium titanates and peroxotitanates for metals in aqueous solutions at physiological pH. Two solution matrices were used for this testing: ultrapure water, and a solution containing a mixture of sodium and potassium chlorides and sodium and potassium phosphates. This solution, referred to as phosphate-buffered saline or PBS, has a pH of 7.3 and serves as a surrogate for mammalian physiological fluids.

Testing indicates that MST and mMST exhibit good affinity for the adsorption of noble metal, mercury and cadmium compounds from both water and PBS. Loading isotherms for these metals were similar to those presented above for pH solutions of nitric acid. Figures 7 and 8 provide loading isotherms for Au(III) and Hg(II), respectively, onto MST in both water and PBS solution. Higher metal loadings were observed for Au(III) in water versus the PBS solution. The initial concentrations for Au(III) were similar for both solutions. The lower gold loading from the PBS solution is attributed to much higher concentration of chloride ion, which complexes with Au(III). In contrast to gold, mercury exhibits much higher metal loadings from the PBS solution compared to water.

Since the sodium titanates and peroxotitanates exhibit affinity for a variety of therapeutic metals in both water and PBS, testing explored the cytotoxicity of the sodium titanates.[10] For these tests, human monocyte or mouse fibroblast cells were exposed to MST and mMST suspensions for 24 – 72 hours. After the exposure, cellular mitochrondrial activity was estimated by measuring the succinate dehydrogenase (SDH) activity and cytokine secretion. The initial studies indicated that both materials have only minor effects on monocyte and fibroblast cells. Interestingly, sodium peroxotitanate altered mitochrondrial activity of both cell types less than the sodium titanate despite the presence of a peroxo species. Thus, these materials may be suitable for removing toxic levels of biometals.

Further studies explored the possibility of using metal-exchanged titanates and peroxotitanates to deliver therapeutic metals.[11-13] The initial testing evaluated the cytotoxicity of metal-loaded peroxotitanates in which the metal was Gd(III), Hg(II), Pd(II), Pt(IV) or Pt(II). Cisplatin was the source

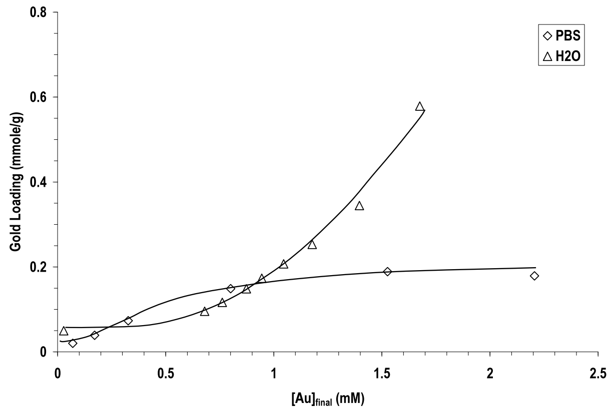


Fig. 7 Loading Isotherms for MST with Au(III) in Water and PBS Solutions

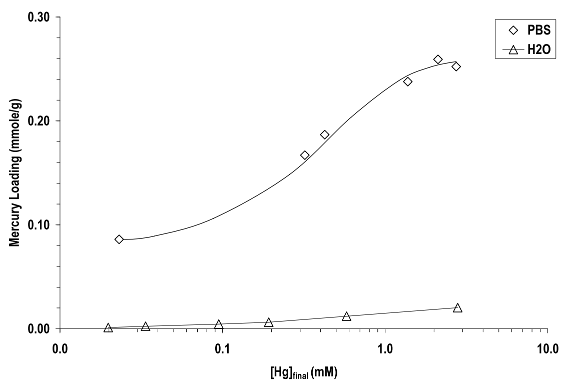


Fig. 8 Loading Isotherms for MST with Hg(II) in Water and PBS Solutions

compound used to prepare the Pt(II)-exchanged peroxotitanate. Human monocyte and mouse fibroblast cancer cells were treated with the metal-exchange peroxotitanates. In all cases, the metal-exchanged peroxotitanates suppressed the mitochondrial activity of the fibroblast cells. The concentration of the metal-peroxotitanate required to suppress cellular mitochondrial activity was below that of metals alone. This suggests that simple extracellular release of the metals from the metal-peroxotitanate materials is not the primary mechanism for suppression. None of the metal-peroxotitanate materials suppressed mitochondrial activity in human monocyte cells. However, more recent testing with metal-peroxotitanates including Au(I), Au(III), Pd(II), Pt(IV) and Pt(II)-loaded peroxotitanates shows that these materials do deliver metals to monocyte cells, as evidenced by cytokine secretion. These studies with cancer cell lines are continuing and have been expanded to look at the ability of these materials to suppress growth of bacteria cells.

Conclusions

Sodium titanates and peroxotitanates are effective materials for the removal of a wide variety of metals from aqueous solutions. These materials are effective in strongly alkaline, neutral and weakly acidic solutions. Thus, these materials are attractive sorbents for the treatment of metal-contaminated waste streams and groundwaters. The metal-loaded titanates and peroxotitanates also appear to be an effective platform for either the removal or delivery of metals under physiological conditions. Consequently, these materials may find use in treating patients with toxic levels of metals, as therapeutic agents for treating cancer, and as bactericides, for wound treatment and in dental materials.

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