Ion Exchange Performance of Titanosilicates, Germanates and Carbon Nanotubes

Fuel Cycle Research & Development

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SUMMARY

This report presents a summary of testing the affinity of titanosilicates (TSP), germanium-substituted titanosilicates (Ge-TSP) and multiwall carbon nanotubes (MWCNT) for lanthanide ions in dilute nitric acid solution. The K-TSP ion exchanger exhibited the highest affinity for lanthanides in dilute nitric acid solutions. The Ge-TSP ion exchanger shows promise as a material with high affinity, but additional tests are needed to confirm the preliminary results. The MWCNT exhibited much lower affinities than the K-TSP in dilute nitric acid solutions. However, the MWCNT are much more chemically stable to concentrated nitric acid solutions and, therefore, may candidates for ion exchange in more concentrated nitric acid solutions.

This technical report serves as the deliverable documenting completion of the FY13 research milestone, M4FT-13SR0303061 –measure actinide and lanthanide distribution values in nitric acid solutions with sodium and potassium titanosilicate materials.

ACRONYMS

CST	crystalline silicotitanate
Ge-TSP	germanium-substituted titanosilicate
ICP-MS	inductively coupled plasma mass spectrometry
FCR&D	Fuel Cycle Research and Development
K_d	distribution value
MWCNT	multiwall carbon nanotube
SRNL	Savannah River National Laboratory
TSP	titanosilicate having the pharmacosiderite structure

INTRODUCTION

The development of simpler and more robust minor actinide separations is key to efficient nuclear fuel cycles. Burn-up of nuclear fuels for power production generates lanthanides and higher atomic number actinides. These elements must be separated from the uranium fuel as they are deleterious if present in the regenerated nuclear fuel. An inorganic-based ion exchange process that can provide efficient separation of minor actinide and lanthanides is attractive due to the relatively simple flowsheet and equipment design. Ion exchange materials can be formulated to operate over a wide range of environmental conditions including acidic, neutral and alkaline conditions. Thus, this project seeks to identify ion exchange materials and solution conditions that result in efficient separations of americium from lanthanides and americium from curium.

EXPERIMENTAL

Synthesis of $HK_3Ti_4O_4(SiO_4)_3{\cdot}4H_2O$ (K-TSP). Fumed silica (1.5 g), titanium isopropoxide (3.57 g) and ultrapure water (20 g) were mixed in a beaker overnight forming a white gel. The solid was collected by centrifugation and washed with ddi water two times. While stirring, 5.06 M KOH (7.81 mL) was added to the solid. The mixture was then loaded into a 23 mL autoclave where it was sealed and heated to 200 °C in an oven for 2 days. After cooling, the solid was filtered, washed several times with pure ethanol, and pH adjusted to 7-8. The final product was transferred to a box furnace and dried at 55 °C.

Synthesis of $Na_2Ti_2O_3SiO_4{\cdot}H_2O$ (CST). Titanium isopropoxide (2.28 g) and tetraethylorthosilicate (1.665 g) were mixed in a beaker. While stirring, 6.32 M NaOH solution (13 mL) was added. After mixing, the solution was loaded into a 23 mL autoclave where it was sealed and heated to 170 °C in an oven for 8 days. After cooling, the solid was filtered, washed using a 90% ethanol solution several times, and pH adjusted to 7-8. The final product was transferred to a box furnace and dried at 55 °C.

$HCs_3(TiO)_{3.5}(GeO)_{0.5}(GeO_4)_{2.5}(SiO4)_{0.5}{\cdot}4H_2O$ (Ge-TSP-1). Fumed silica (0.1875 g), titanium isopropoxide (0.9155 g) and ultrapure water (5 g) were mixed in a beaker overnight forming a white gel. The solid was collected by centrifuging and washed with ultrapure water two times. In a separate beaker, germanium oxide (0.3365 g) and 11.77 g of CsOH (50 wt%) were combined. Then, poured into the white gel. After mixing, the solution was loaded into a 23 mL autoclave, sealed and heated to 200 °C in an oven for 2 days. After cooling, the solid was filtered, washed several times with pure ethanol, and pH adjusted to 7-8. The final product was transferred to a box furnace and dried at 55 °C.

$HCs_3(TiO)_4(GeO_4)_3{\cdot}4H_2O$ (Ge-TSP-2). Fumed silica (0.885 g), germanium oxide (0.314 g) and ultrapure water (3.3 g) were mixed in a beaker overnight forming a white gel. The solid was collected by centrifuging and washed with ultrapure water two times. In a separate beaker, germanium oxide (0.942 g) and 19.15 g of CsOH (50 wt%) were combined. Then, poured into the white gel. After mixing, the solution was loaded into a 23 mL autoclave, sealed, and heated to 200 °C in an oven for 2 days. After cooling, the solid was filtered, washed several times with pure ethanol, and pH adjusted to 7-8. The final product was transferred to a box furnace and dried at 55 °C.

Nitric Acid Treatment of Carbon Nanotubes. Previously reported CNT results that were performed in FY12 were done on as-received materials. For current experiments, the CNTs with diluted in nitric acid to a pH 3 and pH 6, respectively to minimize any pH changes upon addition to the lanthanide stock solution. A more rigorous chemical modification approach was taken by suspending the CNTs in 8M HNO_3 overnight with agitation. This treatment is reported to introduce nitrate groups onto the surface of the CNT particles. After treatment overnight, the suspensions were centrifuged and the concentrated nitric acid solution separated from the solids. The solids were briefly rinsed with ultrapure water and separate portions diluted to pH 3 and 6 with dilute sodium hydroxide solution. The suspensions were once again centrifuged and the supernatant removed. The remaining solids were air dried in an oven at 90°C overnight.

Preparation of Lanthanide Stock Solution

A lanthanide stock solution was prepared from dissolving the nitrate salts of La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, and Er in ultrapure water to provide a stock solution containing 21.0 mM total lanthanides. The composition of the lanthanide stock solution is provided in Table 1.

Table 1. Composition and concentration of the lanthanide stock solution used for ion exchange testing.

Lanthanide Salt	MW	[Ln] (µg/L)	[Ln] (mM)
$La(NO_3)_3{\cdot}6H_2O$	138.90547	3.90E+05	2.81
$Ce(NO_3)_3{\cdot}6H_2O$	140.116	6.72E+05	4.80
$Pr(NO_3)_3{\cdot}6H_2O$	140.90765	3.30E+05	2.34
$Nd(NO_3)_3{\cdot}6H_2O$	144.242	1.16E+06	8.06
$Sm(NO_3)_3{\cdot}6H_2O$	150.36	2.55E+05	1.69
$Eu(NO_3)_3{\cdot}5H_2O$	151.964	3.82E+04	0.251
$Gd(NO_3)_3{\cdot}6H_2O$	157.25	7.97E+04	0.507
$Dy(NO_3)_3{\cdot}5H_2O$	162.5	2.97E+04	0.187
$Er(NO3)_3{\cdot}5H_2O$	167.259	2.83E+04	0.174
$Tb(NO_3)_3{\cdot}5H_2O$	158.9	2.91E+04	0.174
Total Lanthanides		3.01E+06	21.0

Results and Discussion

Ion Exchange Testing of Titanosilicates and Germanium-Substituted Titanosilicates

Three titanosilicates having the same crystalline structure as the mineral, pharmacosiderite, were prepared hydrothermally using previously reported methods.[1-3] The idealized chemical formulas for the three materials are $Na_2Ti_2O_3SiO_4{\cdot}H_2O$ (Na-TSP-1), $HK_3Ti_4O_4(SiO_4)_3{\cdot}4H_2O$ (K-TSP), and $Na_3HTi_4O_4(SiO_4)_3{\cdot}4H_2O$ (Na-TSP-2). Powder X-ray diffraction patterns collected for each material were consistent with those in the literature.

The fine powders were tested for lanthanide affinity by contacting 20 mL of a dilute nitric acid (pH 3) containing a total lanthanide concentration of 20 mM comprised of ten lanthanide ions (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Er) with 1.0 grams of the TSP sample. The specific concentrations of each lanthanide ion were prepared based on uranium fission yields. After contacting for 24 hours at ambient laboratory temperature (ca. 23 °C), the mixtures were filtered through a 0.1-micron filter. Each of the filtrates was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) to determine the remaining concentrations of each of the lanthanide ions. Distribution values (K_d) were determined based on the filtrate analyses.

Figure 1 provides a plot of the K_d values for each material. The sample identified as Na-TSP-1 exhibited the highest K_d values ranging from about 200,000 to well over 1,000,000 mL/g. The K-TSP sample exhibited very similar K_d values across the entire series of lanthanide ions. The Na-TSP-2 sample exhibited the lowest K_d values of about 100 mL/g across the lanthanide series, which is about 3 – 4 orders of magnitude lower than that observed for the other Na-TSP sample. The high K_d values for the Na-TSP-1 and K-TSP samples result in part due to an increase in solution pH during the test. The lanthanide stock solution is adjusted to a pH 3 prior to the addition of the ion exchanger. After the addition of the ion exchanger and mixing for 24-hours, the pH of the test mixtures increased to above pH 6 due to the exchange of H^+ for Na^+ and K^+. The K_d values for the Na-TSP-1 and K-TSP samples are similar to that measured with sodium titanates at pH 6. Thus, preadjustment of the ion exchanger to the desired pH is necessary to determine performance at a particular pH condition.

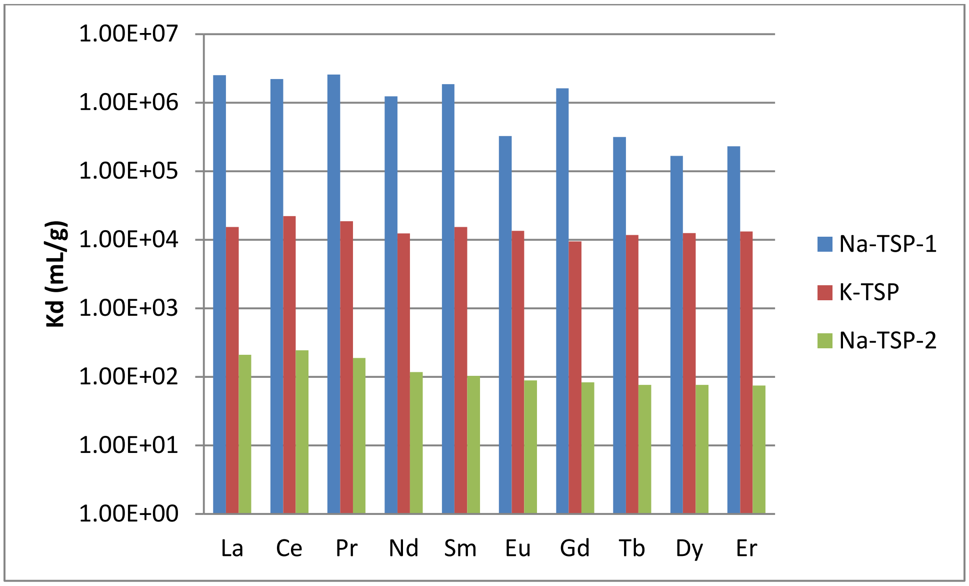

Figure 1. K_d values for Ln^{3+} upon contact with Na-TSP-1, K-TSP, and Na-TSP-2.

Additional tests explored the performance of the K-TSP, a germanium-substituted TSP (Ge-TSP), a titanosilicate having a different tunnel structure than that of the TSP materials, referred to as crystalline silicotitanate or CST. Tables 2 – 4 show the K_d values for K-TSP, CST, and Ge-TSP, respectively. The available quantity of the Ge-TSP limited the testing of this material to a single 24-hour contact at pH 3.

In these tests, the ion exchange performance was measured using a ^{154}Eu radiotracer spiked into the lanthanide stock solution. The ^{154}Eu activity was then measured before and after contact with the respective ion exchanger using a Cobra II Auto-Gamma Counter. A control sample was also measured to determine if sorption of the radiotracer occurred on the walls or filter. In all cases, no sorption of the ^{154}Eu radiotracer was observed.

The K-TSP material exhibited the highest affinity for lanthanides of the three materials. In general, the K_d values increase with increasing pH for the K-TSP and CST samples. Due to limited quantity, Ge-TSP was tested at only pH 3 for 24 h with the K_d value of 16.26. However, this value is close to the value of K-TSP (14.6), at the same pH and contact time. Consequently, additional tests with the Ge-TSP material are planned after additional quantities of this material have been synthesized. From Table 3, the maximum uptake of ^{154}Eu occurs between 8 and 24 hours of contact and at a pH of 5. Previous reported results with sodium titanate materials indicated a similar trend with pH with the exception that the K_d values for lanthanides and actinides were somewhat higher at pH 6 than pH 5. Nevertheless, the K_d values for the K-TSP sample at both pH 5 and pH 6 indicate good affinity for lanthanides and would be expected to exhibit similar values for actinides in the +3 oxidation state as well.

Table 3. K_d values for the uptake ^{154}Eu by K-TSP at pH 3 – 6 and contact times from 0.5 – 24 hours.

	K_d (ml/g)			
Contact Time (h)	pH 3	pH 4	pH 5	pH 6
0.5	13.3	54.1	41.2	33.1
1	15.4	76.2	104	64.1
2	15.5	105	458	197
4	14.1	158	5,820	1,270
8	15.4	209	19,200	4,340
24	14.6	272	5,200	3,330

Table 4. K_d values for the uptake ^{154}Eu by CST at pH 3 – 6 and contact times from 4 – 24 hours.

	K_d (ml/g)			
Contact Time (h)	pH 3	pH 4	pH 5	pH 6
4	3.34	4.03	4.03	5.2
8	0	0.19	2.62	6.47
24	0	2.81	5.54	10.8

Table 5. K_d value for the uptake ^{154}Eu by CST at pH 3 and contact times of 24 hours.

	K_d (mL/g)
Contact Time (h)	pH 3
24	16.3

Ion Exchange Testing of Multiwall Carbon Nanotubes

Experiments have also been conducted to determine the affinity of four commercially-available MWCNT to remove lanthanides in dilute nitric acid (pH 3 and 6). The MWCNT were obtained from NanoLab Inc. (Waltham, MA). See Table 6 for a list of product identification and reported materials characteristics.

Table 6. Multiwall carbon nanotube samples

Product	Characteristics	Sample ID
MWCNT – PD30L5-20	Hollow structure, 30 nm diameter, 5-20 microns in length	1-PD20
NH_2 Functionalized MWCNT – BPD30L20	Bamboo structure, 30 nm in diameter, 20 microns in length	2-BP20
NH_2 Functionalized MWCNT – BPD30L5-20	Bamboo structure, 30 nm in diameter, 5-20 microns in length	3-BD520
MWCNT – 122YJ, CT	Very high purity graphitized MWCNT	4-122Y

For these tests, we used the same lanthanide stock solution as described above with the TSP samples. The phase ratio in the experiments with the MWCNT was 50 mL/g. Each test featured a 24-hour contact time. Figures 2 and 3 provide the measured K_d values for each lanthanide at pH 3 and 6, respectively. The K_d values for the MWCNT samples measured between 15 and 28 mL/g at pH 3 and between 10 and 48 mL/g at pH 6. These values are considerably lower than that reported above for the TSP samples.

The K_d values are consistent and follow the same pH trend as recently reported for MWCNT by Pyrzynska and Stafiej for the removal of Cu^{2+}, Zn^{2+} and Pb^{2+} ions over the pH range 2 – 9.[4] The somewhat higher K_d values in the paper by Pyrzynska and Stafiej likely reflects the much lower metal ion concentrations (0.5 – 1.5 μM) in their tests compared to the lanthanide concentrations (200 – 8,300 μM) in these tests. At pH 3, there is no significant difference between the four MWCNT samples. However, at pH 6 the K_d values show a wider variation with the functionalized samples (2-BP20, 3-PD520 & 4-122Y) exhibiting higher K_d values than that of the untreated sample (1-PD20).

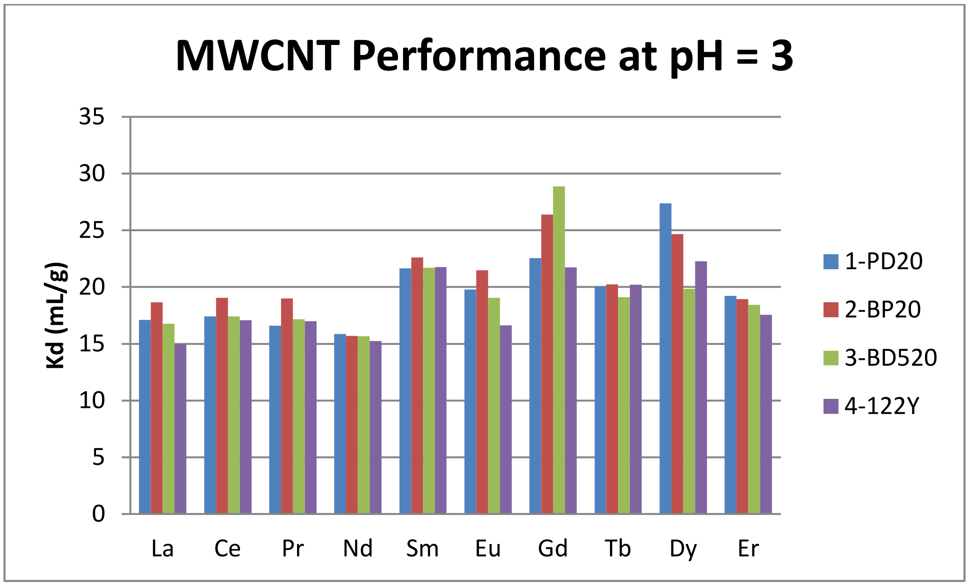

Figure 2. K_d values for Ln^{3+} upon contact with MWCNT at pH 3.

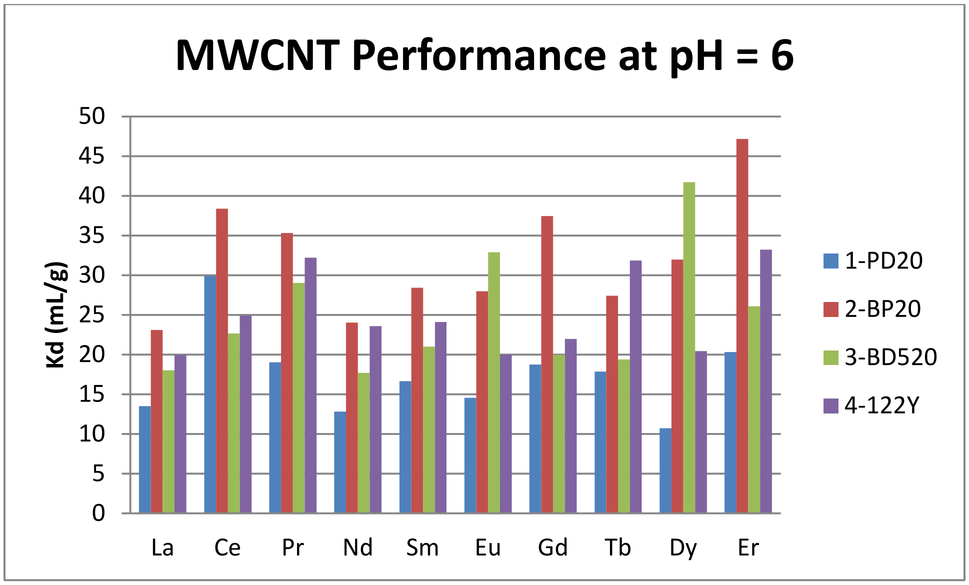

Figure 3. K_d values for Ln^{3+} upon contact with MWCNT at pH 6.

Tests were also carried out to determine if the nitrated MWCNT exhibited increased ion exchange performance with respect to the uptake of lanthanides. This test set used the ^{154}Eu radiotracer method reported above with the KTSP, CST and Ge-TSP samples. The K_d values in this test for the MWCNT Sample ID 1-PD20 were much lower than those in the previous set determined by ICP-MS. The cause of the much lower K_d values is not known. Nevertheless, the low or absence ($K_d = 0$) of ^{154}Eu removal for both the as-received and nitrated MWCNT suggests that the nitration treatment is not effective for increasing the affinity of the MWCNT for lanthanide ions at pH 3 or pH 6. Tests with the other three MWCNT samples are in progress. Given the chemical stability of the MWCNT materials to concentrated nitric acid solutions, tests are planned to determine if removal of lanthanides occurs in nitric acid solutions ranging from 0.1 – 6 M. If these tests show reasonable affinity for lanthanides, tests will be carried out to determine the affinity of these materials to remove americium at the higher nitric acid concentrations.

Table 7. K_d values for the as-received MWCNT and nitrated-MWCNT.

	K_d (mL/g)	K_d (mL/g)	K_d (mL/g)	K_d (mL/g)
Contact Time (h)	As-received pH 3	Nitrated pH 3	As-received pH 6	Nitrated pH 6
4	0	0.79	0	0
8	4.06	2.6	0.92	0
24	2.41	0	0	2

Conclusions

In dilute nitric acid solutions (pH 3 – 6), the K-TSP ion exchanger exhibited the highest affinity for lanthanides. The Ge-TSP ion exchanger shows promise as a material with high affinity, but additional tests are needed to confirm the preliminary results. The MWCNT exhibited much lower affinities than the K-TSP in dilute nitric acid solutions. However, the MWCNT are much more chemically stable to concentrated nitric acid solutions and, therefore, may candidates for ion exchange in more concentrated nitric acid solutions.

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