Advances in Materials Science for Environmental and Energy Technologies

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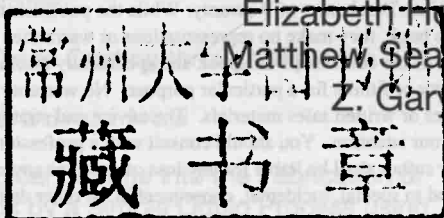## Ceramic Transactions, Volume 236

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Preface

The Materials Science and Technology 2011 Conference and Exhibition (MS&T'11) was held October 16–20, 2011, in Columbus, Ohio. A major theme of the conference was Environmental and Energy Issues. Papers from four of the symposia held under that theme are included in this volume. These symposia include Energy Conversion/Fuel Cells; Energy Storage: Materials, Systems and Applications; Green Technologies for Materials Manufacturing and Processing III; and Materials for Nuclear Waste Disposal and Environmental Cleanup. These symposia included a variety of presentations with sessions focused on Fuel Cells & Electrochemistry, Energy Storage, Green Manufacturing and Materials Processing; Waste Minimization; and Immobilization of Nuclear Wastes

The success of these symposia and the publication of the proceedings could not have been possible without the support of The American Ceramic Society and the other organizers of the program. The program organizers for the above symposia is appreciated. Their assistance, along with that of the session chairs, was invaluable in ensuring the creation of this volume.

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MATERIALS FOR NUCLEAR WASTE DISPOSAL AND ENVIRONMENTAL CLEANUP

ENERGY CONVERSION/FUEL CELLS

*Paper presented at the MS&T 2010 meeting in the Materials Solutions for the Nuclear Renaissance symposium.

ENERGY STORAGE: MATERIALS, SYSTEMS AND APPLICATIONS

Green Technologies for Materials Manufacturing and Processing

Green Technologies for Materials Manufacturing and Processing

MESOPOROUS MATERIALS FOR SORPTION OF ACTINIDES

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ABSTRACT

The efficient absorption and separation of actinides is of critical importance to numerous aspects of the nuclear industry. For example, uranium extraction from ores and reprocessing of used fuel rods can be significantly simplified and generate less waste by the use of solid actinide extractants. Also, the environmental impact form uranium mining, milling, and extraction activities, the use of spent uranium penetrators, and the legacy of nuclear weapon production can be ameliorated by the use of a highly-efficient adsorbant. Such an adsorbant can also be used to remove uranium from drinking water or ocean water leading to a potentially large increase in uranium reserves. We have developed a mesoporous silica that has significantly enhanced wall-thicknesses and pore sizes that provide improved thermal and hydrothermal stabilities and absorption kinetics and capacities. Grafting of ethylenediamine groups onto the surface using N-[3-(trimethoxysilyl)propyl]ethylenediamine produces extractants that can be used to remove actinides from water.

INTRODUCTION

Uranium is a common contaminant of ground water and can arise from natural and anthropogenic sources. Uranium occurs naturally in the earth's crust and in surface and ground water. When bedrock consisting mainly of uranium-rich granitoids and granites comes in contact with soft, slightly alkaline bicarbonate waters under oxidizing conditions, uranium will solubilize over a wide pH range. These conditions occur widely throughout the world. For example, in Finland exceptionally high uranium concentrations up to 12,000 ppb are found in wells drilled in bedrock [1]. Concentrations of uranium up to 700 ppb have been found in private wells in Canada [2] while a survey in the United States of drinking water from 978 sites found a mean concentration of 2.55 ppb [3]. However, some sites in the United States have serious contamination with uranium. For example, in the Simpsonville-Greenville area of South Carolina, high amounts of uranium (30 to 9900 ppb) were found in 31 drinking water wells [4]. The contamination with uranium is believed to be the result of veins of pegmatite that occur in the area. Besides entering drinking water from naturally occurring deposits, uranium can also contaminate the water supply as the result of human activity, such as uranium mining, mill tailings, and even agriculture [5, 6]. Phosphate fertilizers often contain uranium at an average concentration of 150 ppm and therefore are an important contributor of uranium to groundwater [7]. The Fry Canyon site in Utah is a good example of the dangers of uranium mine tailings. The uranium concentrations measured in groundwater at this site were as high as 16,300 ppb with a median concentration of 840 ppb before remedial actions were taken [8]. Depleted uranium

ammunition used in several military conflicts has also been demonstrated as a source of drinking water contamination [9].

Animal testing and studies of occupationally exposed people have shown that the major health effect of uranium is chemical kidney toxicity, rather than radiation hazards [10]. Both functional and histological damage to the proximal tubulus of the kidney have been demonstrated [11]. Little is known about the effects of long-term environmental uranium exposure in humans but there is an association of uranium exposure with increased urinary glucose, alkaline phosphatase, and ß-microglobulin excretion [12], as well as increased urinary albumin levels [13]. As a result of such studies, the World Health Organization has proposed a guideline value of 2 ppb for uranium in drinking water while the US EPA has specified a limit of 30 ppb.

Current municipal treatment practices are not effective in removing uranium. However, experimentation indicates, that uranium removal can be accomplished by a variety of processes such as modification of pH or chemical treatment (often with alum) or a combination of the two [14]. Several sorbants have been shown to be useful for removal of uranium from water. Activated carbon, iron powder, magnetite, anion exchange resin and cation exchange resin were shown to be capable of adsorbing more than 90% of the uranium and radium from drinking water. However, two common household treatment devices were found not to be totally effective for uranium removal [4].

Besides treatment of well water, there is also a strong need for prevention of the spread of uranium contamination from concentrated sources such as uranium mine tailings. Commonly used aboveground water treatment processes are not cost-effective and do not provide an adequate solution to this problem. However, permeable reactive barriers have been demonstrated to be financially viable and elegant alternatives to active pump and treat remediation systems. Such barriers composed of metallic iron, ferric oxyhydroxide, and bone char phosphate have been designed and proven effective for uranium [8]. Iron metal performed the best and consistently lowered the input uranium concentration by more than 99.9% after the contaminated groundwater had traveled 1.5 ft into the permeable reactive barrier.

In this investigation a functionalized mesoporous silica that had pendant ethylenediamine groups was explored as an adsorbant for the separation and removal of uranium from aqueous solution. Amino-functionalized mesoporous silicas show notable adsorption capacities for heavy metals and transition metals from solution [15]. This investigation also took advantage of a novel mesoporous silica with very large pores, thick walls, and thermal and hydrolytic stability that is superior to conventional mesoporous silicas [16].

EXPERIMENTAL

All reagents were commercial products (ACS Reagent grade or higher) and were used without further purification. Water was purified by reverse osmosis and was deionized before use. OSU-6-W mesoporous silica was synthesized via the procedure previously reported by Al-Othman and Apblett [16].

X-ray powder diffraction (XRD) patterns were recorded on a Bruker AXS D-8 Advance X-ray powder diffractometer using copper K_α radiation. The diffraction patterns were recorded for a 2θ range of 17-70° with a step size of 0.02° and a counting time of 18 seconds per step. Crystalline phases were identified using a search/match program and the PDF-2 database of the International Centre for Diffraction Data [17]. Colorimetry was performed on a Spectronic 200 digital spectrophotometer using 1 cm cylindrical cuvettes. The uranium concentrations in the

treated solutions were analyzed at $\lambda = 415$ nm after 5 mL solutions were treated with concentrated nitric acid (1.0 mL) to ensure no speciation of metal ions would interfere with the measurement. For infrared spectroscopic measurements, roughly 10 mg of the sample was mixed with approximately 100 mg FTIR-grade potassium bromide and the blend was finely ground. Spectra in the range of 4000 to 400 cm^{-1} were collected by diffuse reflectance of the ground powder with a Nicolet Magna-IR 750 spectrometer. Typically, 128 scans were recorded and averaged for each sample (4.0 cm^{-1} resolution) and the background was automatically subtracted. Dynamic light scattering (DLS) measurements were performed using aqueous suspensions and a Malvern HPPS 3001 instrument

Preparation of Ethylene Diamine-Derivitized Mesporous Silica

The OSU-6-W mesoporous silica was activated by refluxing 10.0 g of the mesoporous silica in 100 ml of dry toluene for 4 hours under dry atmosphere, followed by washing with 50 ml dry toluene, and drying at 80 °C under vacuum. Next, 6.0 g of the dried material was mixed in 100 ml of dry toluene with twenty milliliters of triethylamine and stirred for around one hour at room temperature and was then filtered off with a fine filter funnel and washed with dry toluene (3 X 50 ml). Subsequently, a mixture of 3.0 g (~ 50 mmol) of the activated mesoporous silica and a solution of 25 mmol (~ 5.5 ml) of N-[3-(trimethoxysilyl)propyl]ethylenediamine (TMSPEDA) in 100 ml of dry toluene was heated at relux for 48 hrs under a dry atmosphere. The mixture was then cooled to room temperature and the resulting light brown mixture was filtered with a fine filter funnel. The solid was washed three times with toluene (3 X 50 ml) and then ethanol to rinse away any leftover TMSPEDA. During washing the light brown solid turned white. The white solid was then dried at 80 °C under vacuum for 24 hrs in a Chem Dry apparatus. After drying, the solid product was stirred with 50 ml of distilled water for five hours. The mixture was filtered to recover a white solid that was then washed with dry toluene and dried at 80°C under vacuum for 24 hours. The silica was reacted at reflux with a fresh solution of 25 mmol (~5.5 ml) of TMSPEDA in 100 ml of dry toluene using the same procedure as the first treatment. After cooling, the resulting solid was isolated by filtration with a fine filter funnel, washed plentifully with toluene (3 X 50 ml) and ethanol then dried at 80°C under vacuum for 24 hours. The final product, a white solid, was obtained in a yield of 4.96 g.

Uptake of Uranium and Thorium by the Ethylenediamine-Derivitzed Mesoporous Silica

The adsorption experiments were conducted as follows; five different amounts (25-125 mg) of the functionalized mesoporous silica, were shaken for 4 hours with 10 ml of 100 ppm solutions of Th^{4+} and UO$_2^{2+}$ using 20-ml glass vials for each metal ion separately. Measurement of the metal ion concentration was carried out by allowing the insoluble complex to settle down and filtering an appropriate volume of the supernatant using a 0.45μm syringe filter. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was then used to measure the concentration of the metals.

RESULTS AND DISCUSSION
The ordered mesoporous silicas, OSU-6-W modified with ethylenediamine functional groups were prepared by a post-synthesis method from the reaction of the ordered mesoporous silica, OSU-6-W, with TMSPEDA according to our previously published procedure [dien paper] Diamine-derivitized mesoporous silicas prepared by this method was obtained in good yield and had excellent surface coverage. The mesoporous silica starting material OSU-6-W, and the

sample functionalized with TMSPEDA were characterized by XRD. The resulting diffraction patterns in the range of 1.0-10.0° are shown in Figure 1. The XRD patterns of the derivitized samples show strong (100) peaks and smaller (110) and (200) peak intensities, suggesting that the modification process does not strongly affect the framework integrity of the ordered mesoporous OSU-6-W. It can also be noted that the (100) peak shifted to a higher angle upon derivitization indicating an effective decrease of the pore diameter. This can be understood in terms of the volume excluded as the silylation of the OSU-6-W surface walls takes place. According to the average pore diameter of the material from the surface area measurements (see below), this indicates an average thickening of the walls of about 25.9 Å, an increase that statistically would correspond to at least one extra layer of Si-O-Si homogeneously spread on the original wall (~21.0 Å). It also can be noticed that the d_{100} peak has become broader with the addition of the functional groups, indicating a slight alteration of the ordering of the mesoporous structure.
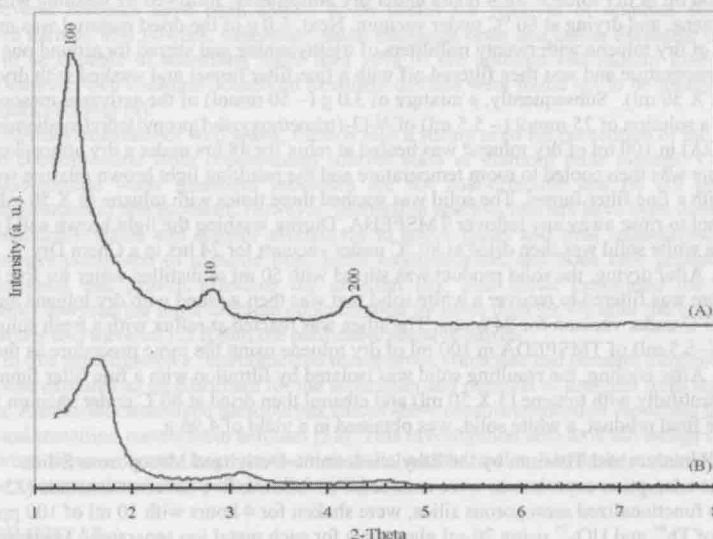
Figure 1. XRD patterns for (A) OSU-6-W mesoporous silica an (B) the treated product. The spectra are shifted vertically for the sake of clarity

Nitrogen adsorption-desorption isotherms were performed at 77 K for the mesoporous silcas. The initial mesoporous silica exhibited a type IV isotherm that showed a sharp, reversible step at ~0.3-0.4 P/P_0, typical of the N_2 filling of uniform mesopores. Analysis of the data gave an average pore diameter of about 51 Å, a pore volume of 1.24 cm³/g and a surface area of 1283 m²/g. After introduction of the functional groups, the nitrogen adsorption-desorption experiments yielded a surface area of 691 m²/g and a total pore volume of 0.58 cm³/g for the derivitized mesoporous silica. The adsorption isotherm curve obtained for the derivitized mesoporous silica showed that the total adsorbed amount of nitrogen (taken at $P/P_0=0.99$) had

diminished, as had the specific surface area. The nitrogen uptake corresponding to the filling of the mesopores was shifted to lower relative pressures indicating a reduction of the pore diameter (from 51.1 to 33.8 Å). An opening of *ca.* 33.8 Å is sufficiently large enough to allow all metal ions and most small organic molecules to be incorporated into the pore channels. The surface area and the total pore volume dropped significantly compared to the un-functionalized sample, OSU-6-W (BET surface area 1283 m^2/g; total pore volume 1.24 cm^3/g). The decrease of the mesoporous volume of the material after silanization is the direct consequence of the silanization process filling the mesopores. However, this quite large decrease probably might also be due to some pore blocking due to partial surface polymerization at the mouths of some mesopores, possibly with silsequioxane polymers. Notably, the pore size distribution (Figure 2) contains three peaks indicating increased heterogeneity of the pore sizes as compared to the more-ordered pores of the mesoporous silica material. Most of the decrease of the specific surface area can be accounted for the uptake of organic species into the pore structure. The textural properties of the mesoporous silica after derivitization are compared to those of the starting materials are provided in Table I.

Table I Textural Properties Determined from Nitrogen Adsorption-Desorption Experiments at 77 K and Powder XRD Measurements.

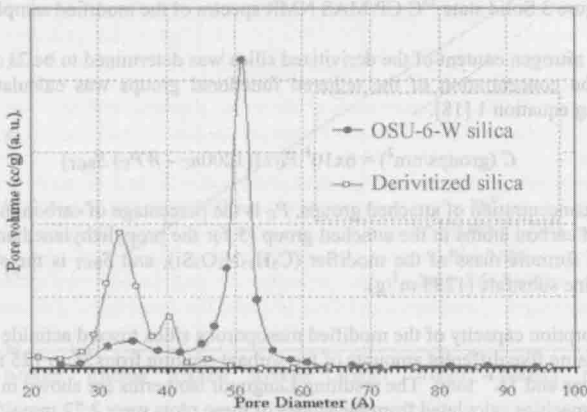| Sample	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size (Å)	d_{100} (Å)	Wall Thickness(Å)
OSU-6-W silica	1283	1.24	51.1	2.4	20.9
Derivitized silica	691	0.58	33.8	1.7	25.9

Figure 2. The pore size distribution of OSU-6-W mesoporous silica before and after derivitization.

The presence of covalently linked organic moieties bearing diamine groups in the as-synthesized OSU-6-W mesoporous silicas were also confirmed by ^{13}C CP/MAS solid state NMR

spectroscopy [dien paper]. Figure 3 shows the solid state ^{13}C CP/MAS NMR spectra for diamino-functionalized mesoporous silica, The spectrum contained peaks at ^{TM} of 11.4, 23.8, 41.1, 51.6 ppm attributable to the carbon atoms in ($\equiv$Si-CH_2-CH_2-), ($\equiv$Si-CH_2-CH_2-), ($\equiv$Si-CH_2-CH_2-CH_2-NH-) and (-NH-CH_2-CH_2-NH_2), and (-CH_2-NH_2), respectively. The lack of peaks attributable to methoxy groups is indicative of complete hydrolysis and condensation of the silane reagent onto the silica surface.
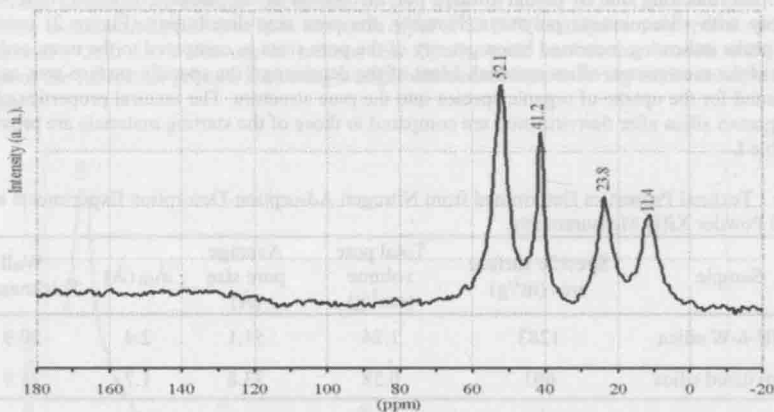

Figure 3 Solid state ^{13}C CP/MAS NMR spectra of the modified samples

The carbon and nitrogen content of the derivitized silica was determined to be 21.56 and 8.59 %, respectively. The concentration of the tethered functional groups was calculated to be 4.63 groups/nm^2 using equation 1 [18].

$$C \ (\text{groups/nm}^2) = 6 \times 10^5 \ P_C / [(1200 n_C - W P_C) \ S_{BET}] \tag{1}$$

Where C is the concentration of attached groups, P_C is the percentage of carbon in the sample, n_C is the number of carbon atoms in the attached group (5 for the propylethylenediamine group), W is the corrected formula mass of the modifier ($C_5H_{13}N_2O_3Si$), and S_{BET} is the specific surface area of the pristine substrate (1283 m^2/g).

The adsorption capacity of the modified mesoporous silica toward actinide metal ions was examined using five different amounts of the sorbant ranging from 25 to 125 mg and 100 ppm of UO_2^{2+} ions and Th^{4+} ions. The resulting Langmuir isotherms are shown in Figures 4 and 5. The uptake capacities calculated from the slopes of these plots were 2.22 mmol/g for UO_2^{2+} (528 mg/g) and 2.66 mmol/g for Th^{4+} (616 mg/g). The extremely high capacities correspond to the uptake of 53% by weight of uranyl ions and 62% by weight of thorium ions. Since the density of ethylenediamine groups is 5.32 mmol/g, the uptake can be attributed to the formation of complexes between the metal ions and two of the ethylenediamine ligands.
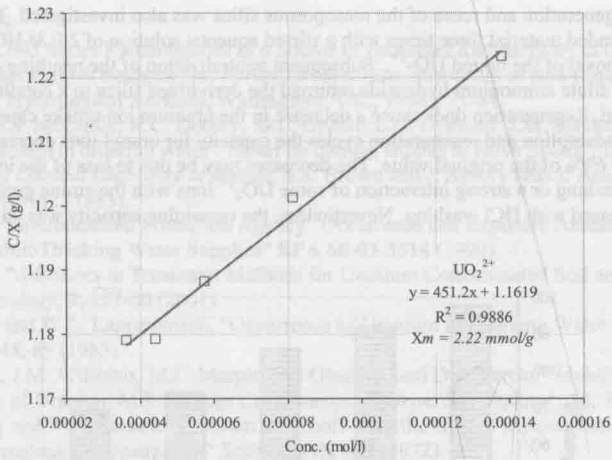
Figure 4. The Langmuir adsorption isotherm for uptake of UO_2^{2+} ions.
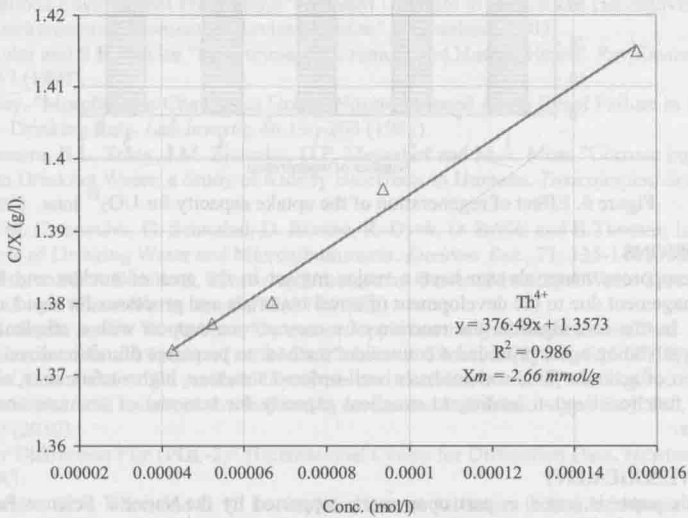
In the figure:
UO_2^{2+}
$y = 451.2x + 1.1619$
$R^2 = 0.9886$
$Xm = 2.22 \; mmol/g$

Figure 5. The Langmuir adsorption isotherm for uptake of Th^{4+} ions

In the figure:
Th^{4+}
$y = 376.49x + 1.3573$
$R^2 = 0.986$
$Xm = 2.66 \; mmol/g$

The regeneration and reuse of the mesoporous silica was also investigated. Treatment of the uranium-loaded material three times with a stirred aqueous solution of 2.0 M HCl for 1 hour resulted in removal of the bound UO_2^{2+}. Subsequent neutralization of the resulting protonated amines with a dilute ammonium hydroxide returned the derivitized silica to a condition where it could be reused. Regeneration does cause a decrease in the uranium ion uptake capacity (Figure 6). After four adsorption and regeneration cycles the capacity for uranyl ions decreased to approximately 69% of the original value. The decreases may be due to loss of the immobilized groups with washing or a strong interaction of some UO_2^{2+} ions with the amine groups so that it can not be released with HCl washing. Nevertheless, the remaining capacity was still remarkably high.
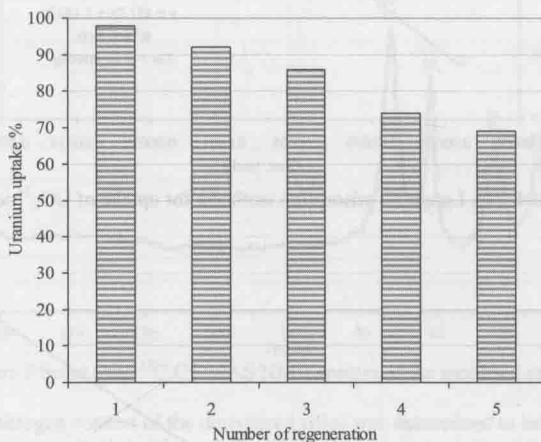

Figure 6. Effect of regeneration of the uptake capacity for UO_2^{2+} ions.

CONCLUSIONS

Mesoporous materials can have a major impact in the area of nuclear and hazardous waste management due to the development of novel materials and processes for rapid adsorption of metals. In this investigation, the reaction of a mesoporous support with a ethylene-diamine containing silylating agent provided a convenient method to prepare a dfunctionalized materaial for sorption of actinide. This sorbant has a well-ordered structure, high surface area, and a high degree of functionalization leading to excellent capacity for removal of uranium and thorium from water.

ACKNOWLEDGEMENT