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TABLE OF CONTENTS

EXECUTIVE SUMMARY

This project developed an innovative single material, minimum volume approach for the selective sorption of metal ion radionuclides from aqueous waste solutions and creation of a final nuclear waste form that is suitable for long term storage or geological burial. This work addressed the "New Technologies for Management of Nuclear Waste" field of research and development of the Nuclear Energy Research Initiative.

The basis of our approach was a chemically functionalized porous silica ion exchange medium known as Diphosil. Diphosil strongly sorbs highly charged metal ions, such as lanthanides and most actinides, from aqueous solution. However, Diphosil itself is a poor high level waste form candidate due to its organic content. Our approach eliminates this deficiency by heating metal ion-loaded Diphosil to remove its organic content and thermally densify it to vitreous silica at temperatures below those often used to make borosilicate-based nuclear waste glasses.

Our work in this project provided evidence that thermal densification chemically fixes the initially sorbed heavy metal ions (such as lanthanides or actinides) as heavy metal phosphate nanophases that are embedded in vitreous silica. In addition, we identified and tested an innovative method for assuring criticality control with no loss of fissile isotope loading of Diphosil. This method uses non-specifically sorbed gadolinium ions and readily incorporates as much as three times as many gadolinium ions as the number of initially sorbed heavy metal ions. Using laser-induced fluorescence

techniques, we determined some of the microscopic consequences of alpha decay-induced radiation damage in thermally densified Diphosil and probed for metal ions leached from thermally densified heavy metal ion loaded Diphosil. Finally, we established an international collaboration with workers at three nuclear research centers in the Republic of Korea for the purpose of advancing assessment of the use of Diphosil in the treatment of emerging waste streams of importance in the operation of nuclear power reactors.

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INTRODUCTION

This project developed a single material approach to reducing nuclear waste volume based on a chemically functionalized porous silica that is termed Diphosil. Diphosil was created by Chiarizia and coworkers as an ion exchange medium that selectively and nearly irreversibly sorbs highly charged metal ions, such as actinides, from appreciably acidic aqueous solutions[1] and a version of it is now commercially available. The chelating power of Diphosil is due to diphosphonic acid groups that are anchored to its silica surface via organic spacer groups. Approximately 90% of the weight of dry Diphosil is silica (SiO_2). Vitreous silica is one of most radiation resistant glasses known [2].

DIPHOSIL

Diphosil is an acronym that stands for "Diphonix™ on silica" [1] although, strictly speaking, it is not Diphonix on silica because Diphonix ion exchange resin incorporates both sulfonic and diphosphonic acid groups whereas Diphosil relies solely on diphosphonic acid chelating groups (see Fig 1).

Diphosil was designed to extract long-lived actinide and other highly charged metal ions from acidic aqueous solutions while providing radiation resistance superior to ion exchange materials based on organic polymer supports. Scale-up to industrial production of a version of Diphosil by Eichrom Technologies Inc. (Darien, IL) was funded in part by the U. S. Department of Energy. Eichrom first demonstrated the ability of produce its version of Diphosil, termed "Diphonix® Resin on silica" at the industrial scale in December, 1997 [3]. Our work built on these past efforts, extended them into new application areas as to the composition of treated solutions, and, in a paradigm shift, exploited Diphosil as the basis for nanoencapsulating and chemically fixing the metal ions that it selectively sorbs from aqueous solutions. Eichrom's "Diphonix® Resin on silica" is the Diphosil material that we used in our studies.
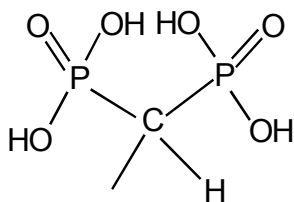

Figure 1. Schematic diagram of a diphosphonic acid group. A metal ion chelated to a diphosphonic acid group displaces a proton from one or more acidic phosphoryl oxygen atoms.

Diphosil was created in a research collaboration between Argonne National Laboratory and the University of Tennessee[1]. Its ability to strongly sorbed actinide and

other highly charged metal ions, such as Fe^{3+}, arises from diphosphonic acid chelating groups that have been chemically attached to the surface of highly porous silica gel. These pores typically are 15 nm in diameter. Each pore, therefore, likely can contain a maximum of 500 to 1000 sorbed metal ions. Distribution ratios, which are a measure of sorption strength, have been reported for the interaction of Diphosil with a broad range of actinide ions (Th^{4+}, UO_2^{2+}, Am^{3+}, Pu^{4+}), fission products species (TcO_4^-, Eu^{3+}) and common, nonradioactive metal ions (Na^+, Ca^{2+}, Zn^{2+}, Co^{2+}, Al^{3+}, and Fe^{3+}) that are often present in high level waste (HLW) [1]. The influence of acid (HNO_3 or HCl) concentration from 0.01 mole/liter to 10 mole/liter as well as competition between sorption of actinide ions and other common nonradioactive waste constituents, such as Fe^{3+} and Al^{3+}, has been reported [1]. No work at pH values above 2 or with mineral acids, such as phosphoric, that can strongly complex metal ions has been reported. Diphosil, as originally developed [1], contains 0.68 millimole of phosphorus per gram of resin on a dry weight of resin basis. The maximum metal ion loading achievable using Diphosil has not been reported in the scientific literature.

As envisioned by its developers, Diphosil is primarily applicable to nitric or hydrochloric acid solutions for the purpose of reducing the hazard classification of such solutions from HLW to low level waste (LLW) by removing highly charged ions of long-lived actinide isotopes [1]. Singly charged ions, such as Na^+, are not sorbed into Diphosil under acidic conditions. Some doubly charged ions, such as Ca^{2+}, Co^{2+}, and Zn^{2+}, are significantly sorbed. Most triply charged ions, such as Fe^{3+}, are strongly and nearly irreversibly sorbed from acid solutions. If desired, sorption of Fe can be suppressed

effectively by conversion of Fe^{3+} to Fe^{2+} via addition of environmentally benign ascorbic acid [1]. In terms of interference with respect to sorption of Am^{3+} from common, nonradioactive waste metal ions, Al^{3+} was identified as the likely limiting factor. An upper limit of 0.01 mole/liter of Al^{3+} has been recommended [1]. Methanediphosphonic acid (MDPA) whose chemical formula is $CH_2(PO(OH)_2)_2$, is a model compound for the chelating groups in Diphosil. A recent study on MDPA [4] concluded that the predominant complex between Eu^{3+} and MDPA consists of a Eu^{3+} ion coordinated to two surrounding MDPA molecules (four phosphorus atoms per Eu^{3+} ion).

ORGANIZING PRINCIPLE FOR OUR INVESTIGATIONS

Underlying this project was our hypothesis that heating metal ion-loaded Diphosil in air would oxidize its organic content to water vapor and carbon dioxide and its phosphonic acid groups to phosphoric acid that would react with the sorbed metal ions to produce metal phosphates. Based on literature reports of the properties of porous silica, we further hypothesized that additional heating would either volatilize any excess phosphoric acid[5] or cause it to react with the silica to form silicophosphates[6]. Finally, at still higher temperature, we saw the possibility that pore collapse[7] would occur thereby microencapsulating and chemically fixing the sorbed metal ions in phosphate-rich metal phases in vitreous silica. Vitreous silica is one of the most radiation resistant glasses known [2].

The work that we have carried on this project has confirmed our hypotheses as to the events that might occur when metal ion-loaded Diphosil is heated in air. The process of converting porous silica to fully dense silica is referred to as thermal densification in the literature because it occurs at temperatures far below the melting point of bulk silica and, in consequence, does not involve a phase change such as melting. We have adopted the term "thermal densification" to refer to the entire set of processes that occur when metal ion-loaded Diphosil is heated in air to the point of pore collapse.

RESEARCH PROGRESS

Details concerning the laser-based luminescence apparatus that we have used in this project have been published [8]. For most of the luminescence studies reported here, 355 nm pulses from a Q-switched Nd:YAG laser (Continuum Surelite I-10) were used for excitation as described in our published work on thermal densification of Diphosil [9]. Small angle neutron scattering studies were carried out at the Intense Pulsed Neutron Source at Argonne National Laboratory. Small angle X-ray scattering studies were carried out at the Basic Energy Sciences Synchrotron Research Center at the Advanced Photon Source at Argonne National Laboratory. NMR spectra were recorded in the Chemistry Division's NMR research facility.

The primary findings of this project are listed below, organized by the project tasks.

Task A: Solution composition effect on metal ion sorption

Work on this task investigated the influence of solution composition variables on sorption of heavy metal ions into Diphosil. Our work showed that Diphosil can sorb metal ions from aqueous solutions that contain significant concentrations of ethylenediaminetetracetic acid (EDTA) at mildly acidic pH values. At near-neutral pH sorption occurs at lower EDTA concentration. Aqueous solutions of EDTA frequently are used in decontaminating surfaces due

to its powerful chelating action for many metal ions. These studies used the laser-induced fluorescence methods that we developed during this project.

Task B: Maximum metal ion loading

Work on this task determined the maximum heavy metal ion loading that can be achieved using Diphosil. Previous work by others determined distribution ratios for a number of heavy metal ions sorbed into Diphosil, but only at trace concentrations of those ions. We used optical spectroscopy to measure metal ion concentration during the sorption process. For example, in the case of trivalent neodymium ions (Nd^{3+}) sorbed from dilute nitric acid, we monitored a characteristic near-infrared optical absorption band of Nd^{3+} [9] and determined that the maximum uptake of Nd^{3+} ions by Diphosil under these conditions was one Nd^{3+} ion per four phosphonic acid groups. These studies involved Diphosil fully loaded with each of the following metal ions Fe^{3+}, Cr^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+}, Ho^{3+}, Er^{3+}, and UO_2^{2+}.

Task C: Influence of +1 and +2 metal ions

This task determined the influence of selected singly and doubly charged metal ions on the ability of Diphosil to sorb other more high charged metal ions, such as uranyl in which the formal charge on uranium is 6+. The influence of such +1 or +2 ions on sorption of trivalent lanthanides and other highly charged metal ions was found to be minimal because those highly charge ions are nearly

irreversibly sorbed by Diphosil. In some cases, these studies involved both anion and cation competition. For example, we studied the influence of sodium ions on the ability of Diphosil to sorb trivalent lanthanide ions. In another case, we investigated the influence of a mixture of sodium ions and ethylene-diaminetetraacetic acid (EDTA) and found evidence that the trivalent metal ions preferentially sorbed into Diphosil rather than remain in solution as complexes with EDTA if the solution pH was mildly acidic or the EDTA concentration was low.

Task D: Densification optimization

We carried out on-line, real time infrared analysis of the gases evolved during thermal densification of Diphosil in purified air as a function of heating rate and metal ion loading [9]. These studies identified the optimum heating rate to ensure complete destruction of the organic content of Diphosil. Such destruction was complete at 700 °C, however, other evidence, such as that from metal ion luminescence, indicated that heating to higher temperature was necessary to achieve complete densification and encapsulation of the sorbed metal ions.

Because a preliminary test showed that small angle neutron scattering (SANS) likely would be able to determine phase size as a function of thermal densification temperature, we submitted a request for run time on the Small Angle

Neutron Diffractometer (SAND) instrument at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. SAND is equipped to carry out small angle neutron scattering (SANS) studies. Our requests were granted and SANS runs were carried out on a series of lanthanide and actinide ion-doped Diphosil samples that had been heated at 1 °C/minute in air to a particular temperature, held at that temperature for one hour, and then quickly cooled to ambient temperature.   The temperatures at which the sample were held for one hour were 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C, and, in some cases, 1200 °C. For comparison purposes, as-received Diphosil and Davisil® samples were heated using the same temperature cycles and their SANS properties also were investigated. Davisil® is a registered trademark of W. R. Grace Company. It is a highly porous silica that is the substrate used in synthesis of Diphosil.

SANS measures relative neutron scattering length density. Because the neutron scattering factors for the elements and isotopes in our samples differed by only a few percent from each other, this means that SANS primarily determined the presence of phases of different density than the bulk material if those phases were in the size range of approximately 0.5 nm to 50 nm. The determinable phase size was set by the range of neutron energies available at the SAND and the configuration of that instrument. Traditionally, SANS data are presented as log-log plots of I(Q) versus Q where I(Q) is the observed intensity of elastically scattered neutrons as function of Q and Q is a parameter that is termed the

momentum transfer. Numerically, $Q = 4\pi\sin\theta/\lambda$ where 2θ is the scattering angle and λ is the wavelength of the incident neutron flux.

Examples of the observed SANS data are shown in Figs 2 - 4 for Davisil®, Diphosil, and Nd-doped Diphosil, respectively.   In Fig 2, there is little change in the observed I(Q) vs. Q data for Davisil heated to 700 °C, 800 °C, and 900 °C. Davisil heated to 1000 °C shows slightly increased I(Q) over the range of Q = 0.03 to 0.06 Å^{-1} which is indicative of sintering and aggregation that are the first stages of pore collapse. Davisil heated to 1100 °C in air shows a power law decrease in I(Q) versus Q that is typical of fully dense, amorphous silica and is therefore indicative of full pore collapse. In contrast, Diphosil heated to 900 °C shows evidence of the first stages of pore collapse with such collapse being nearly complete for Diphosil heated to 1000 °C.

The primary difference between Davisil and Diphosil is presence of phosphoric acid in the pores of Diphosil as a consequence of the destruction of the organic content of Diphosil and oxidation of its diphosphonic acid groups to phosphoric acid. Evidently, phosphoric acid acts as "mineralizer" and enhances the rate of pore collapse of silica in the 900 °C to 1000 °C temperature range. In contrast, I(Q) versus Q data for fully Nd-loaded Diphosil (see Fig 4) is indicative of pore collapse leading to nanophase formation for material heated to 1000 °C and further reduction in the size of those nanophases on heating to 1100 °C. This suggests that at least some of the phosphoric acid resulting from destruction of the organic content of Diphosil has reacted with Nd^{3+} and is no longer
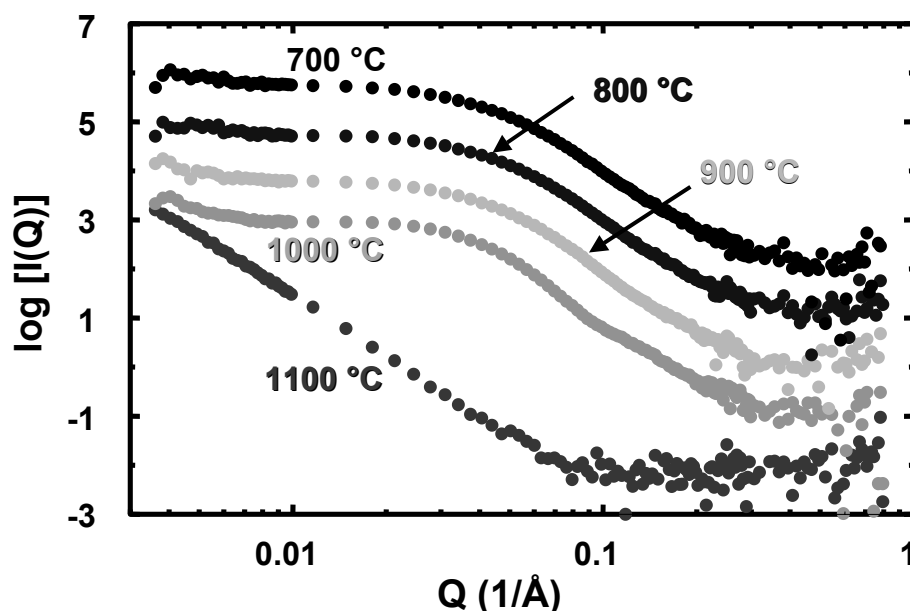
Fig. 2. Small angle neutron scattering data recorded at ambient temperature for fully Davisil® that had been heated in air to the temperature shown. To facilitate comparison, the I(Q) data were multiplied by the following scale factors: 10^0, 10^1, 10^2, 10^3, and 10^4 for the materials heated to 1100 °C, 1000 °C, 900 °C, 800 °C, and 700 °C, respectively.
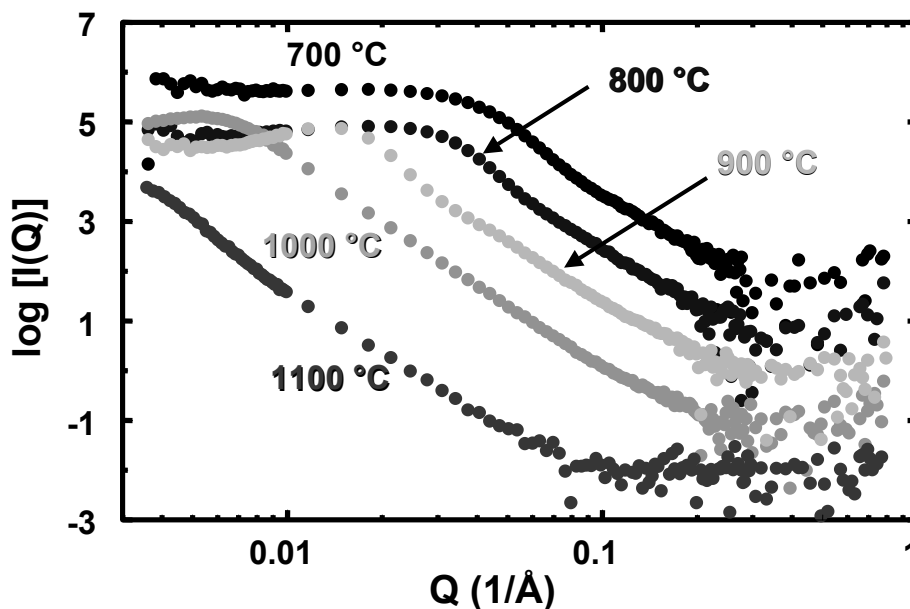

Fig. 3. Small angle neutron scattering data recorded at ambient temperature for fully Diphosil that had been heated in air to the temperature shown. To facilitate comparison, the I(Q) data were multiplied by the following scale factors: 10^0, 10^1, 10^2, 10^3, and 10^4 for the materials heated to 1100 °C, 1000 °C, 900 °C, 800 °C, and 700 °C, respectively.
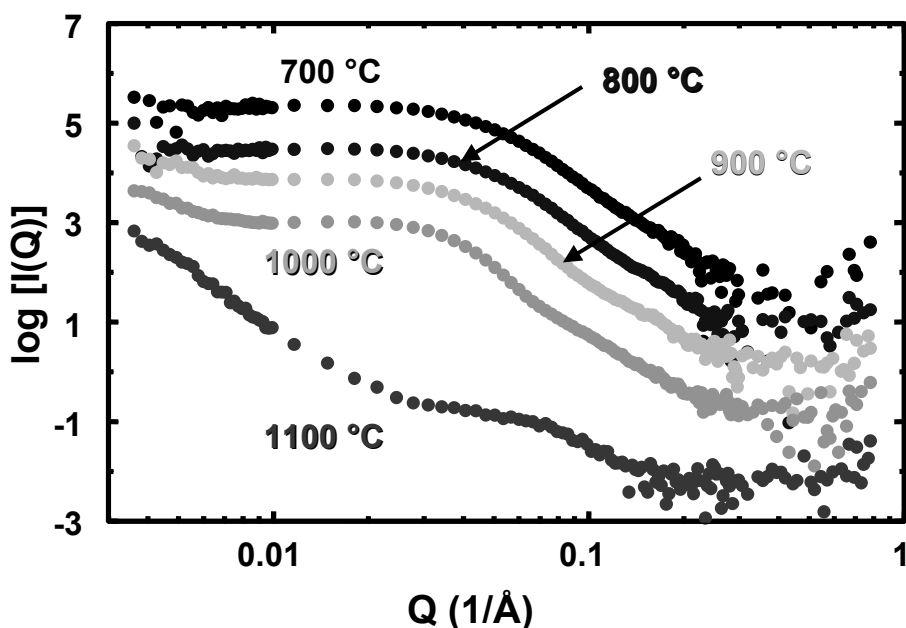
Fig. 4. Small angle neutron scattering data recorded at ambient temperature for fully Nd-loaded Diphosil that had been heated in air to the temperature shown. To facilitate comparison, the I(Q) data were multiplied by the following scale factors: 10^0, 10^1, 10^2, 10^3, and 10^4 for the materials heated to 1100 °C, 1000 °C, 900 °C, 800 °C, and 700 °C, respectively.
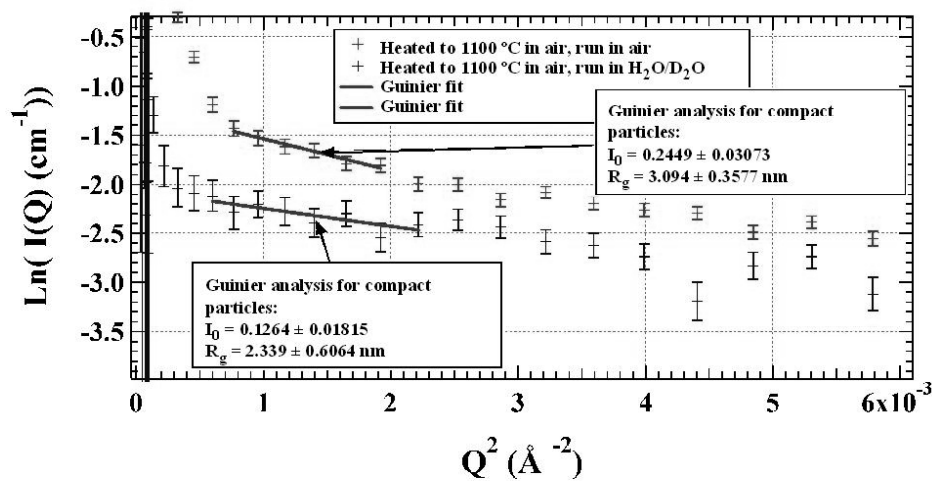

Fig. 5. Guinier analysis of SANS data for fully Nd-loaded Diphosil that had been heated in air to 1100 °C and then run in air (upper curve and symbols) or 58% D_2O + 42% H_2O to contrast match silica (lower curve and symbols). If the detected nanophases are spherical, then their diameter is (6.0 ± 1.5) nm based on the R_g = (2.34 ± 0.61) nm value determined using immersion in 58% D_2O + 42% H_2O.

available to acts as mineralizer. It also suggests the Nd phosphate phase that forms has little if any solubility in vitreous silica.

Neutron scattering factors are signed quantities and the signs of the scattering factors hydrogen and deuterium atoms are different. A mixture of 58% (by volume) D_2O and 42% H_2O has been found to give the same neutron scattering intensity as does amorphous silica (SiO_2). Immersing a primarily silica material, such as metal ion-doped, thermally densified Diphosil, in a mixture of 58% D_2O + 42% H_2O and then recording SANS data on that slurry largely eliminates scattering from the silica content of the sample. This effect is termed "contrast matching". We used this technique to improve our ability to determine the properties of nanophases embedded in the thermally densified Diphosil.

Analysis of those data using the Guinier method was carried out. The results of that analysis are presented in Fig 5. Guinier analysis for compact particles results in fit values for their radius of gyration, R_g. Assuming that the nanophases that form when fully Nd-loaded Diphosil is heated to 1100 °C in air are spherical, their diameter is (6 ± 1.5) nm. Our SANS studies were carried out in collaboration with P. Thiyagarajan who is an IPNS instrument scientist and L. Fan who was doing postdoctoral research with Dr. Thiyagarajan.

Based on our success in using SANS to determine the size of the nanophases that form when metal ion-loaded Diphosil is heated, we then carried out SANS studies on Diphosil that had been fully loaded with lanthanum (La), terbium (Tb), ytterbium (Yb), lutetium (Lu), thorium (Th) or uranium (U). All the of lanthanide ions (La, Nd, Tb, Yb, and Lu) were loaded as trivalent ions in dilute nitric acid. Thorium was loaded as Th^{4+} and uranium as uranyl (UO_2^{2+}) in nitric acid.

Unexpectedly, given the chemical similarity of the lanthanide series of elements, the heavier lanthanide (Tb, Yb, Lu) doped Diphosil samples did not exhibit as rapid pore collapse as a function of the temperature to which the material had been heated as was the case for La- or Nd-loaded Diphosil. This observation raised the possibility that observed nanophases were, in part or in whole, bubbles (trapped air) because SANS identifies phases that are either heavier or lighter than the bulk of the material. \

The P-31 MAS-NMR spectra and conventional X-ray powder diffraction studies described below and our past metal ion luminescence studies on Diphosil loaded with lighter lanthanide or uranyl showed that the originally sorbed metal ions were present in phosphate phases and remained in close proximity to each other following thermal densification. These observations, however, do not preclude the presence of trapped air bubbles of nanometer dimension. In addition, SANS is not applicable to gadolinium-doped Diphosil due to the very large

neutron absorption cross-section of gadolinium. However, it is the very large neutron absorption cross-section that makes gadolinium the element of choice for criticality control. For these reasons, we decided to attempt anomalous small angle X-ray scattering (ASAXS) studies on lanthanide-doped Diphosil studies.

We requested and were granted a day of run time on a small angle X-ray scattering instrument on the 12ID-C beam line at the Advanced Photon Source (APS) at Argonne National Laboratory to determine the applicability of ASAXS to our materials. The APS is a third generation X-ray synchrotron light source and its insertion device beam lines, such as 12ID-C, provide both exceptional brilliance and rapid tunability in the energy range where the L_3 X-ray absorption edges of the mid- to-heavy lanthanide elements occur. This allowed us to vary the energy of incident X-rays over a series of values that ranged from 200 eV below the L_3 edge of a given lanthanide element to near coincidence with that edge.

In ASAXS, if a sample contains the resonant element, then the observed elastically scattered X-ray intensity, I(Q), will decrease as the X-ray energy comes into coincidence with the absorption edge of that element. For SAXS and ASAXS, I(Q) is the observed intensity of elastically scattered X-rays as function of Q and Q is a parameter termed the momentum transfer. For SAXS and ASAXS, $Q = 4\pi\sin\theta/\lambda$ where 2θ is the scattering angle and λ is the wavelength of the incident X-ray flux. If, in addition, the resonant element is present in

compact nanophases whose size range is appropriate, then reduction in I(Q) as the incident X-ray energy comes into coincidence with the absorption edge will occur most prominently over the range of Q values that correspond to the size of those nanophases. At larger or smaller Q, a lesser reduction in I(Q) will be observed.

We observed a systematic decrease in I(Q) as the incident X-ray energy approached resonance with the L_3 edge of the contained lanthanide only from those samples that had been heated to sufficiently high temperature as to induce at least the initial stages of pore collapse based on SANS measurements. Fig 6 shows an example of our SAXS data for Tb-loaded Diphosil that had been heated to 1100 °C. These data show a large ASAXS effect given that the material only contained 2.2 weight% terbium. Samples that had not been heated to 1000 °C or above (i.e., that had not been heated to the onset of pore collapse or above) showed no ASAXS effect that was larger than limit imposed by the 3% to 4% irreproducibility of the observed I(Q) values because, prior to pore collapse, the ASAXS effect is spread out over a much larger range of Q values. The success that we achieved in these studies resulted in our being granted additional run time at APS.

Our SAXS studies were carried out on a single layer of as-heated Diphosil particles on adhesive-backed Kapton tape. Because as-heated Diphosil particles are irregularly shaped and the X-ray beam size (0.3 mm diameter) was comparable to the particle size, the recorded I(Q) values can not be normalized to
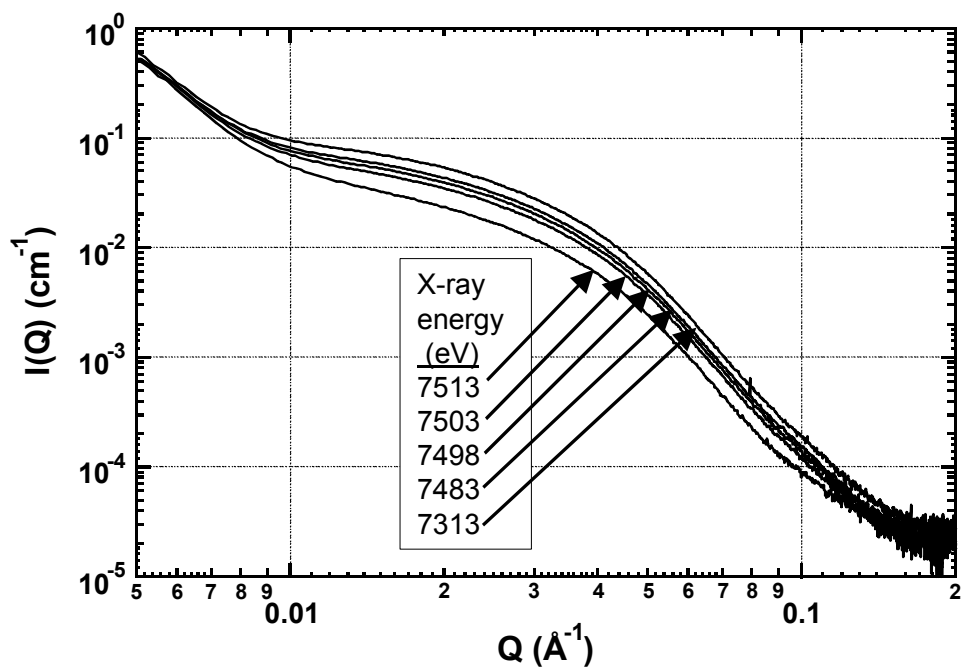
Fig. 6. Small angle X-ray scattering data for fully Tb-loaded Diphosil had been heated to 1100 °C in air as a function of the incident X-ray energy. The observed increase of I(Q) with decreasing incident X-ray energy starting at the Tb L_3 edge at 7513 eV and continuing down to 200 eV below that edge is the hallmark of anomalous small angle X-ray scattering and is compelling evidence that the observed nanophase contains Tb ions.

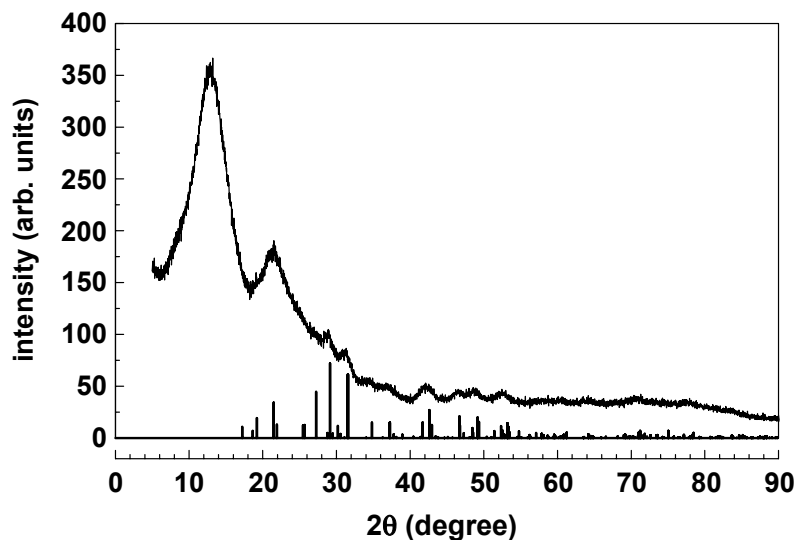Fig. 7. X-ray powder diffraction pattern, recorded using Cu k_α radiation, of fully Nd-loaded Diphosil that had been heated to 1100 °C (upper curve) and the pattern expected from crystalline $NdPO_4$ of the monazite structure type (lower curve).

the "per unit sample thickness" basis that is needed for Guinier analysis of ASAXS effect data. We can, however, carry out Guinier analysis of the SAXS data that were recorded off-resonance with the absorption edge. Such analysis indicates that the radius of gyration. R_g, for nanophases in Tb-loaded Diphosil heated to 1100 °C is 6.1 nm (which, if those nanophases are spherical, corresponds to 16 nm diameter). To within the mutual uncertainty of our neutron and X-ray measurements, we found the same R_g values for this material using SANS and SAXS. The large observed ASAXS effect is compelling evidence that these observed nanophases contain terbium. SAXS and ASAXS work at APS was carried out in collaboration with S. Skanthakumar of the Chemistry Division's Actinide Facility, S. Seifert, who is the instrument scientist in charge of the SAXS instrument on 12ID-C and P. Thiyagarajan, and L. Fan of the Intense Pulsed Neutron Source.

SAXS primarily is influenced by electron density (a heavy element, such as Nd, being a much better scatterer of X-rays than are Si or O which make up the bulk of our materials). SANS, in contrast, is primarily influenced by differences in neutron scattering length density. In the case of our materials, there is little difference in neutron scattering length density for the constituent light elements; the heavy element atoms presents only a moderate difference in neutron scattering length density when averaged over distances typical of the neutron wavelengths used. In consequence, SANS work on the studied material primarily senses variations in physical density as a function of length scale.

To provide additional insight into the phases that form during thermal densification, we have investigated some our metal ion-loaded Diphosil samples using conventional X-ray powder diffraction. An example of such conventional X-ray powder diffraction patterns is shown in Fig 7 for the case of fully Nd-loaded Diphosil that had been heated to 1100 °C in air. Based on our SANS studies, heating this material to 1100 °C results in complete pore collapse (see Figs 4 and 5). The upper curve in Fig 7 is the observed diffraction pattern, using Cu k$_\alpha$ X-ray radiation, from fully Nd-loaded Diphosil that had been heated to 1100 °C and then cooled to ambient temperature. The diffraction pattern shows a series of weak, broad peaks that are most noticeable beginning at 2θ = 28 degrees and continuing to larger 2θ values (2θ is the scattering angle). Diphosil with no sorbed metal ions that had been heated to 1100 °C showed only the extremely broad scattering peaks (at small values of 2θ) that are typical of an amorphous material. In Fig 7, the pattern expected from crystalline NdPO$_4$ in its monazite structural form is shown in "stick" form. The close similarity of this pattern with that observed from Nd-loaded Diphosil is evidence of the presence of NdPO$_4$ in its monazite form in Nd-loaded Diphosil that had been heated to 1100 °C in air.

Additional direct evidence at to the chemical form of lanthanide ions in thermally densified Diphosil was obtained by P-31 magic angle spinning nuclear magnetic resonance (MAS-NMR) on an as-heated sample of La-loaded Diphosil. Fig 8 shows the observed P-31 MAS-NMR spectrum of La-loaded Diphosil that

had been heated to 1100 °C. The chemical shifts are with respect to 85% orthophosphoric acid solution that was used as a reference. Based on a recent study of the P-31 MAS-NMR spectra of silicophosphate phases [10], the peak at -36 ppm is due to phosphorus in a silicophosphate phase whereas the peak at
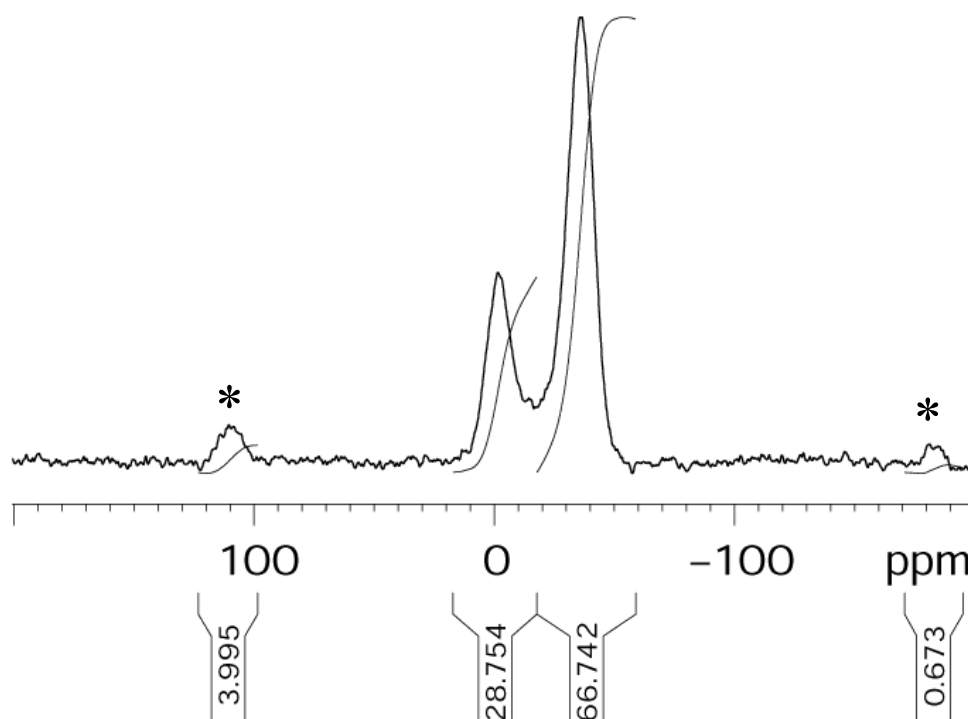

Fig. 8. P-31 magic angle spinning nuclear magnetic resonance (MAS-NMR) spectrum of fully La-loaded Diphosil that had been heated to 1100 °C in air (-200 ppm to +200 ppm curve). The data were recorded using a magnetic field of 2.30 tesla. The two peaks denoted by an asterisk are spinning side bands. Peak areas in % are indicated. The chemical shift data above are with respect to 85% orthophosphoric acid. Based on peak position, the peak near 0 ppm is due to phosphorus atoms in a lanthanum orthophosphate (LaPO$_4$) phase and the peak at -36 ppm is due to phosphorus atoms in silicophosphate phases. Taking into accounting a small silicophosphate peak between 0 ppm and -15 ppm that is obscured by the LaPO$_4$ peak, the above spectrum indicates that 26% of the phosphorus atoms in this material are in a LaPO$_4$ phase and 74% are in silicophophate phases.

-4 ppm agrees with the chemical shift expected for phosphorus in $LaPO_4$ in its monazite form [11]. The ratio of the area of the $LaPO_4$ peak to that of the silicophosphate peak agrees with that expected from our past studies on the maximum uptake of trivalent Nd ions by Diphosil [9] and the manufacturer's data for the amount of phosphorus in Diphosil. MAS-NMR was also carried out on Sm- and Gd-loaded Diphosil that had been heated to 1100 °C. Due to the paramagnetism of the Sm^{3+} and Gd^{3+} and consequent line broadening, no P-31 resonances due to Sm- or Gd-containing phases were observed. MAS-NMR spectra were recorded by John Muntean in the Chemistry Division's NMR research facility.

Task E: Nonradiative decay

Work on this task determined and modeled the factors that influence nonradiative decay of excited electronic states of metal ions sorbed into Diphosil both before and following thermal densification [9]. These studies exploited the f-f transitions that are characteristic of trivalent lanthanide and actinide ions[12] as well as the lowest-lying excited electronic state of uranyl ion which often has been used to identify uranyl species (see for example [13]. Our work focused on the long-lived luminescing 4f electron state of Eu^{3+} and luminescence from the lowest lying excited charge transfer state of uranyl ion. Extremely nonexponential luminescence decays were observed from Diphosil fully loaded with a luminescing heavy metal ion. In contrast, nearly pure radiative decay of

the $^5D_0$ state of Eu^{3+} was observed when Diphosil was fully loaded using a solution that contained a $La^{3+}:Eu^{3+}$ metal ion ratio of 500:1 and then underwent thermal densification at 1000 °C. It is clear that ion-ion energy transfer dominates the nonradiative decay of heavy metal ion-loaded Diphosil when the heavy ion is a luminescing metal ion. The observed ion-ion energy transfer is consistent with Forster-Dexter energy transfer theory in which the transfer rate scales as $1/R^6$ where R is the ion-ion separation distance[14]. The resulting comparatively the short range nature of the observed ion-ion energy transfer suggested an unusual and very productive method for investigation of radiation damage that is described under Task F (see below) of this project. Our laser-based optical studies provided detailed and precise information about the local environment of metal ions sorbed into Diphosil prior to and following thermal densification.

Task F: Leach rate and radiation damage

We prepared a nitric solution that contained La^{3+}, $^{245}Cm^{3+}$, $^{249}Bk^{3+}$, and $^{253}Es^{3+}$ ions in the atom ratios 0.9892:0.0036:0.0036:0.0036 respectively (i.e., 0.36% of each transplutonium ion) and loaded Diphosil with that solution. This Diphosil material was dried and then heated to 1100 °C at 1 °C per minute in air after which is was rapidly cooled to ambient temperature. The resulting solid particles were transferred to a fused silica tube that was evacuated, back filled with a small amount of helium gas, and flame-sealed. The tube was transferred

into an optical access cryostat and time- and wavelength-resolved luminescence studies carried out. The Cm, Bk, and Es isotopes that we used were produced by the Heavy Elements Chemistry program of the Office of Science and this sample was prepared as part of collaboration between our NERI project and an Office of Science program that is interested in the optical properties of heavy element-containing nanophases. Because ^{253}Es is a 20.5 day half life alpha emitter, radiation damage rapidly accumulated in our sample. This manifested itself in two ways: 1) an increase in luminescence emission line widths and 2) decreased luminescence lifetimes and intensities for most of the observed luminescence bands. The decay daughter of ^{253}Es is ^{249}Bk which is a 320 day primarily beta emitter. The beta decay daughter of ^{249}Bk is ^{249}Cf which is a 350 year alpha emitter that decays to ^{245}Cm. Our observations of in-growth and decay of luminescing metal ion species in this material are consistent with the following:

1) Neither alpha decay nor beta decay altered the valence of the heavy metal ions. For example, ^{253}Es^{3+} decayed to ^{249}Bk^{3+} that decayed to ^{249}Cf^{3+}

2) Following alpha decay, the recoiling decay daughter heavy metal ion, on average, was ejected from the LaPO$_4$ nanophase into the surrounding vitreous silica.

3) Energy transfer from excited f-electron states of ions, notably Cm^{3+}, within $LaPO_4$ nanophases to other heavy elements ions in the same nanophase was rapid particularly to Cf^{3+}.

4) Energy transfer to or from decay daughter heavy metal ions ejected from the nanophases was not rapid. This is evidence that the ejected ions were relatively isolated from each other and from other heavy metal ions in the Diphosil.

To obtain insight into the recoil of decay daughter heavy metal ions following alpha decay, calculations using TRIM 2000 were carried out. TRIM is an acronym for "Transport of Ions in Matter" and TRIM 2000 is a computer program that simulates ion implantation. The heaviest atom available in the TRIM 2000 database is ^{238}U. TRIM 2000 assumes that an ion in vacuum strikes a planar surface and embeds itself in that surface. It does allow the surface to a layered stack. For our case, we assumed a 3 nm thick layer of $LaPO_4$, then a 1.7 nm thick silicophosphate layer, and finally an effectively infinitely thick layer of silica.

To simulate ^{253}Es alpha decay, we assumed that 106 keV U ions were incident on this layered stack and determined that the calculated range of such ions is 42.5 nm with an average of 1554 atoms displaced per incident ion. The number of atoms displaced per nm of depth peaked at 35 nm depth. To simulate

damage from the alpha particles that result from ^{253}Es decay, TRIM 2000 calculations for 6.633 MeV alpha particles were carried out. The calculated range of such alpha particles is 32900 nm (32.9 microns) and an average of 270 atoms are displaced per incident alpha particle. Based on these TRIM 2000 calculations, the number of displacements per atom achieved by decay of Es-253 sorbed into Diphosil was 0.02. This is equivalent to ~3000 year storage of Diphosil fully loaded with the actinides (U through Cm) present in 33,000 MWD spent LWR nuclear fuel after 10 years of storage.

A wide variety of observations have shown that heating heavy metal ion loaded Diphosil to 1000 °C results in pore collapse of the outer pores of a given particle of Diphosil but does not result in collapse of all of the interior pores. For example, the ability of dried metal ion-loaded Diphosil to sorb liquid water into its pores by capillary attraction is readily determined by visual observation. Material that been heated no higher than 900 °C absorbs sufficient liquid upon immersion in water to generate gas bubbles on the surface of the immersed particles as the gas within the pores is displaced by water drawn into the pores by capillary attraction. Material heated to 1000 °C or higher fails to sorb liquid water and does not generate visible gas bubbles upon immersion in water.

Both our SANS and SAXS data are consistent with these visual observations in that materials heated no higher than 900 °C remained highly scattering to neutrons or X-rays at high Q values whereas heating to 1100 °C or

1200 °C resulted in materials in which little scattering due the silica substrate occurred at high Q. Further evidence for "closed porosity" in material heated to 1000 °C was found in studies in which Eu^{3+} loaded Diphosil, previously heated to 1000 °C, was immersed in 1 mole/liter nitric acid.   Using laser-induced fluorescence techniques sensitive to the presence of less than 1 micromole/liter of Eu^{3+}, no Eu^{3+} luminescence was observed in the nitric acid phase after more than one year immersion at ambient temperature nor was there any observable change in the luminescence from Eu^{3+} ions within the immersed particles.

Task G: Criticality control

It is clear that incorporation of gadolinium into fissile isotope-loaded Diphosil represents the best approach to criticality control because of the very large neutron absorption cross-section of gadolinium of natural isotopic abundance.

We carried out a small angle neutron scattering (SANS) study of Diphosil loaded primarily with non-specifically sorbed trivalent lanthanum (La^{3+}) ions to test a method that promises to enable criticality control with no loss of fissile isotope loading of Diphosil. We prepared Diphosil loaded primarily with non-specifically sorbed La^{3+} ions by contacting a weighed amount of Diphosil with a solution that contained La^{3+} in excess of that which the Diphosil could irreversibly sorb. The La-loaded Diphosil was then rinsed with water to remove

non-sorbed La^{3+} ions and dried at 105 °C in air. At this point, the La:P atom ratio of this material was 0.25. A portion of this material was set aside and the rest of the material then was wet with a concentrated La^{3+} solution that contained sufficient La to give an La to P (La:P) atom ratio of 1 (taking into account the La^{3+} already irreversibly sorbed into Diphosil). This material and the reserved material were dried at 105 °C and then heated to 1100 °C at 1 °C/minute in air and rapidly cooled to ambient temperature. SANS data for these materials showed that the nanophases in La:P = 1 material were larger as to R_g by a factor of approximately 1.6 in comparison with the La:P = 0.25 material which is the expected result if all of the La^{3+} ions in the La:P = 1 material had been incorporated into $LaPO_4$ nanophases.

These observations are evidence that a metal ion-containing aqueous solution is drawn by capillary attraction into already metal ion-loaded Diphosil and that the metal ions in that solution, although non-specifically sorbed, are retained in the pores during drying and destruction of the organic content of Diphosil. It also suggests that those metal ions reacted with the phosphoric acid that results from the destruction of the organic content of Diphosil in preference to that acid reacting with the silica content of Diphosil to form silicophosphate phases. If this behavior also were to occur with non-specifically sorbed trivalent gadolinium (Gd^{3+}) ions, then criticality control could be achieved with no loss in fissile isotope loading by non-specifically sorbing Gd^{3+} into fissile isotope-loaded Diphosil prior to thermal densification.

Unfortunately, the large neutron absorption cross-section of gadolinium of natural isotopic abundance precludes carrying out SANS studies for characterizion of Gd-doped Diphosil with and without the presence of other heavy metal ions. However, our work at the APS, described under Task D above, showed that Gd-loaded Diphosil can be characterized by SAXS and ASAXS. We heated fully Tb-loaded Diphosil to 700 °C to fully oxidize its organic content, leaving its pores coated with Tb phosphate and silicophosphate phases. We then sorbed a solution that contained Gd^{3+} ions in dilute nitric acid into the previously heated, Tb-loaded Diphosil in an amount to given a Gd:Tb atom ratio of 3:1. Aliquots of the resulting material, that we termed "Tb+3Gd loaded Diphosil" were then heated to dry the material at which point the temperature was increased at a rate of 1 °C per minute to a final temperature of 700 °C, 900 °C, 1000 °C, 1100 °C, or 1200 °C. In each case the final temperature was maintained for one hour before the power to the furnace was turned off which resulted in a rapid initial decrease in temperature and eventual return to ambient temperature. Conventional X-ray diffraction on these materials showed that the material heated to 1100 °C contained lanthanide orthophosphate whereas the material heated to 1200 °C showed in addition the presence of cristobalite which is a crystalline form of silica.

Gadolinium oxide phases might have been expected if the gadolinium nitrate in the pores of the dried material thermally decomposed as would be the

case if gadolinium nitrate were heated to such high temperatures. ASAXS studies near the Gd and Tb L_3 X-ray absorption edges showed a significant anomalous scattering effect that was nearly identical at both the Gd and Tb edges. This is evidence that the Gd and Tb ions in the lanthanide orthophosphate nanophases are distributed nearly uniformly throughout the nanophases. As was the case for our SANS studies on La-loaded Diphosil, larger R_g values were observed from the "Tb+3Gd loaded Diphosil" samples than was the case for Diphosil fully loaded with Tb or Gd ions and then rinsed with water to remove metal ions not chemically bound to the pore surface of Diphosil by its diphosphonic acid groups.

Because the thermal processing temperatures that we used are far below the reported melting points of silica or lanthanide orthophosphate, our observations also are evidence that the observed lanthanide phosphate nanophases are formed by directed (forced) assembly as the porous the silica substrate of Diphosil underwent pore collapse during heating. It is clear that gadolinium ions in dilute acid solution, non-specifically sorbed into porous heavy metal loaded Diphosil, are incorporated into the metal phosphate nanophases that result from heating the material to the point of thermal densification. Gadolinium loading for the purpose of critically control can readily be achieved at the level of three times the number of Gd ions as compared to the number of heavy metal ions that were chemically bound to diphosphonic acid groups on the surface of Diphosil.

Task H: Emerging waste stream application

A formal, signed Technical Cooperation Agreement (TCA) between Argonne National Laboratory and the Nuclear Environment Technology Institute (NETEC) of the Korean Hydroelectric and Nuclear Power Company (KHNP) was executed on July 20, 2001 although the process of generating the agreement and securing all necessary DOE and Argonne National Laboratory approvals for it began the previous winter. The purpose of the TCA is to foster collaboration between NETEC and our NERI project to advance use of nuclear energy for peaceful purposes.

To realize this collaboration, six Korean research workers for three different Korean nuclear research institutes visited Argonne National Laboratory on August 28-30, 2001 and, subsequently, five Korean research workers from the same three Korean nuclear research institutes visited Argonne National Laboratory on August 28, 2002 for a series of meetings and discussions that included mutual sharing of research results. The Korean workers and their travel expenses were funded by Korean sources. The Korean research is largely engineering oriented. It seeks to define parameters, such as adsorption isotherms and metal ion uptake kinetics, that are important for assessment of the relative merits of various radionuclide removal methods as well as to aid in the design of processing equipment to exploit the unusual properties of Diphosil and related ion exchange resins. Work in Korea has included bench scale tests of Diphosil with

nuclear reactor-related waste solutions, notably solutions that contained cobalt ions. Those studies were in generally good agreement with the metal ion uptake characteristics of Diphosil as originally determined by Chiarizia and coworkers[1].

We identified another emerging waste stream application for our single material approach to reducing nuclear waste volume, namely the treatment of spent chloride salts that are generated during electrometallurgical or pyrochemical processing of spent nuclear reactor fuel. The present reference waste treatment process for such spent salts generates a glass-bonded sodalite waste form that contains all of the chloride ions that were present in the spent salt. In the current Yucca Mountain repository concept, if chloride ions leached from such a waste form, accelerated corrosion of the primary waste container could result because that container will be stainless steel.

We see the potential for treating spent pyrochemical processing salts (dissolved in a minimal amount of water and slightly acidified) with Diphosil to remove long-lived alpha emitting isotopes. The resulting treated salt solution with its chloride ions would then be suitable for disposal in grout as low level waste that is suitable for relatively low cost near-surface burial. The resulting heavy metal-loaded Diphosil, after thermal densification, would be free of chloride ions and suitable for disposal as high level waste in a geologic repository such as Yucca Mountain. Our process, by selectively sorbing heavy metal ions

from concentrated salt solutions, should reduce the volume of high level waste generated during disposal of a given quantity of spent salts in comparison with the present glass-bonded sodalite process. Our proof-of-concept test of this process consisted of contacting Diphosil with a trivalent lanthanide ion-containing slightly acidified brine (NaCl) solution. Laser-induced fluorescence studies on the characteristic luminescence of the sorbed lanthanide ions showed that their coordination environment was essentially identical that for the same lanthanide ion sorbed from dilute nitric acid solution and remained so upon washing the chromatography column with deionized water to remove the brine solution.

PROJECT ACCOMPLISHMENTS COMPARED TO EXPECTED RESULTS

We achieved all of our major project goals with one exception. That exception resulted from notification that we received in September 2002 that problem had been discovered in beam line data processing software for SAXS and ASAXS data that been collected with a particular X-ray detector at 12ID-C at APS over the previous two years. Our data had been collected with that detector. The problem was a subtle bias in the beam line data treatment algorithms the net result of which was truncation to zero of some otherwise valid, but very low X-ray intensity values. This had the result of altering baseline correction values and thereby skewing nonlinear least squares fits of the observed data to models as to the shape and size distribution of the observed heavy metal phosphate nanophases. This bias was not detected earlier due to the absence of nanophase materials that are recognized standards for ASAXS studies and the fact that the presence of such a bias only occurred for Q values at which I(Q) resulted from detector pixel elements that, on average, had recorded less than one X-ray photon.

The necessity of reprocessing the raw detector data for the over three thousand determinations of I(Q) versus Q in our SAXS and ASAXS data sets resulted in our missing the original date of our project's third year milestone by three months. The data most strongly impacted such reprocessing was for light lanthanides (most notably Nd^{3+} which is an analog of Am^{3+}) because that part of the lanthanide series of elements gave rise to the smallest nanophases.

CONCLUSIONS

Diphosil possesses the unusually ability to selectively and strongly sorb high valent metal ions, such actinides, from aqueous solution [1]. Our work has shown that heating heavy metal ion-loaded Diphosil, in a process termed thermal densification, both nanoencapsulates and chemically fixes such sorbed heavy metal ions in phosphate phases that are embedded in vitreous silica. This is proof that the basis of our approach to reducing nuclear waste volume is sound. Vitreous silica is one of the most radiation resistant glasses known [2]. Our work has shown that a broad range of aqueous waste solutions, ranging from those that contain strong metal ion chelators, such as ethylenediaminetetraacetic acid (EDTA) or concentrated phosphoric acid, to minimally complexing acid solutions and salt brines, are amenable to processing using our single material method for reducing nuclear waste volume.

ACKNOWLEDGEMENTS

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