

Final progress report of DOE-AFCI project entitled “Conjugates of Actinide Chelator-Magnetic Nanoparticles for Used Fuel Separation Technology”

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INTRODUCTION

The actinide separation method using magnetic nanoparticles (MNPs) functionalized with actinide specific chelators utilizes the separation capability of ligand and the ease of magnetic separation. This separation method eliminated the need of large quantity organic solutions used in the liquid-liquid extraction process. The MNPs could also be recycle for repeated separation, thus this separation method greatly reduces the generation of secondary waste compared to traditional liquid extraction technology. The high diffusivity of MNPs and the large surface area also facilitate high efficiency of actinide sorption by the ligands. This method could help solving the nuclear waste remediation problem.

Research work has been conducted under this project to investigate the use of ligand-functionalized MNPs for actinide separations. Ligands that have strong affinity with actinide ions in solution are selected and bound to the surface of MNPs. Sorption experiments with radionuclides including actinides are conducted to evaluate the efficiency of separation.

By functionalizing MNPs with actinide chelators, we have generated conjugates of MNP-Ls that can specifically bind actinides. Such functionalized nanoparticles retain the affinity and specificity of the chelators for actinides while remaining susceptible to magnetic field manipulation. We accomplished three major objectives:

Objective 1: Develop reliable methods for conjugation of actinide chelating ligands to MNPs and evaluate functional properties of MNP-Ls.

Objective 2: Characterize the MNPs and functionalized MNP-L conjugates.

Objective 3: Evaluate the conjugate effectiveness in separating actinides and develop concept for an electromagnetic process/device using functionalized MNP-Ls for actinide separations.

The design, processing, characterization and actinide separation are explained in detail in the following section. The students supported by this project and publications are given at the end of this report.

ACCOMPLISHMENTS:

Objective 1:

We have synthesized a highly swelling, high capacity magnetic conjugates using a two-step coating procedure. The first coating renders the MNPs resistant to iron leaching in 0.1 M HNO₃. The second coating with physically imbedded PA results in a high density of primary amine

groups that were used for coupling actinide chelating molecules, DTPA and DMOGA. The silica/PA coated MNPs have 10x the number of reactive amine groups as compared to surface functionalization of MNPs with APTES. In order to determine the efficiency of MNP-DMOGA and MNP-SG-SG/PA-DTPA in binding actinides, the distribution coefficient (K_d) was measured for $^{233}\text{U(VI)}$, $^{237}\text{Np(V)}$, $^{243}\text{Am(III)}$, and $^{239}\text{Pu(IV)}$ in batch sorption experiments. As a negative control acetylated Nanofer MNP-SG-SG/PA was used. There was no significant sorption of actinides to either of the control samples. The kinetics of the sorption with Nanofer MNP-SG-SG/PA-DTPA was very slow compared to the controls and DMOGA [15-16]. Equilibrium was not reached for 22 hrs. Intramolecular crosslinking between DTPA and PA could form a tighter network, which would slow diffusion, resulting in the long equilibration time during sorption. For Nanofer DTPA-PA+SG/SG-MNP the calculated K_d was highest for $^{239}\text{Pu(IV)}$ in pH 1 NaNO_3 solution and $^{243}\text{Am(III)}$ in pH 3 NaNO_3 . The distribution coefficient for $^{243}\text{Am(III)}$ in pH 1 NaNO_3 solution started high but decreased over time. This decrease is likely related to instability of the complex or sample degradation. The calculated K_d value for $^{239}\text{Pu(IV)}$ sorption at pH 1 was 1758, while the K_d value for $^{243}\text{Am(III)}$ pH 3 sorption was 10620 after 22 hours. Maximum sorption with DMOGA-PA+SG/SG-MNP occurred within 10 minutes and was greatest for $^{239}\text{Pu(IV)}$ pH 1 with a K_d of 14367. This value gradually decreased over time. For $^{243}\text{Am(III)}$ pH 1 the calculated K_d was 4302 at pH 3 the K_d value was 5028 but increased to 7012 over ~5 hours. The K_d for $^{237}\text{Np(V)}$ pH 1 was 280 and for $^{233}\text{U(VI)}$ pH 3 the K_d was 210. For all other actinide species/pH values tested the K_d values were less than 100. The K_d values using MNP with acetylated PA+SG/SG-MNP were also less than 100 for all actinide species [15].

To improve the amine density on the surface of the particles the polyelectrolyte PA was chosen because each mole of PA contains approximately 180 moles of primary amines. In addition, the physical properties of PA are compatible with the silica gel. PA associates with silica surfaces because of the net negative charge of silica above pH 3 (The point of zero charge for silica is <3) while PA has a net positive charge over a wide range of pH values and remains predominately ionized until the pH exceeds its pK_a ($pK_a = 8.8$). Further evidence of the compatibility of PA with silica is described in the literature where PA is used to mimic silica biomineralization *in vitro*. PA initiates silicic acid polymerization *in vitro* at neutral pH, and becomes completely imbedded in the newly formed silica precipitate. The PA accelerates condensation of silicic acid by bringing numerous monomers in close proximity due to ionic or hydrogen bonding. Our approach for partially imbedding PA into the MNPs second silica coating resulted in stable preparations with high amine densities available for reaction ($>0.5 \text{ mmol g}^{-1}$); The imbedded PA also contributed to a swelling effect that increased the volume of material obtained by many fold. By optimizing conditions of the second coating, we determined that titration of the reaction to pH 9.2 resulted in a coating with the highest stability and hydration capacity, despite the fact that silica precipitation initiates at a near neutral pH. Studies of PA adsorption to surfaces and layer-by-layer assembly have found that films of PA formed at pH values >8.5 are substantially thicker than films formed at pH 5. This is thought to be due to positively charged PA becoming less ionized above the pK_a of PA, while the negatively charged surface becomes more ionized, thus requiring more PA to be absorbed in order to neutralize the surface charge. At low pH, the protonated PA would ionically bind deprotonated hydroxyls of surface silanol molecules of the coated MNPs. As the pH increases to pH 9.2, the charge density of PA decreases and the silica gel could also begin to solubilize. In alkaline pH the decrease in charge density could relax the silica gel and allow the uncharged portion of the PA molecule to separate from the silica surface and protrude into solution while the ionized portion of the molecule remains associated with the

surface and becomes imbedded in the newly formed silica gel. Also, at alkaline pH the silica gel will begin to and the relaxation of the silica gel could allow the Based upon the theoretical length of PA, the volume of the silica coated Nanofer particles would be predicted to increase no more than 10-fold after imbedding PA. The observed volume increase was 60 to 70-fold after settling in solution for 24 hours. Zwitterionic properties of the silica/PA co-polymer and hydrogen bonding with organized water could be a significant factor in the observed swelling. Dynamic light scattering measurements confirmed the observed volume increase. The hydrodynamic diameter of MNP-SG-SG/PA increased 75-fold relative to uncoated Nanofer MNPs [15].

Objective 2:

The important criteria of MNP selection for nuclear waste application includes large surface area, which directly affect the loading capacity, physical integrity under acid conditions and high specific magnetic moment to achieve a fast magnetic separation. Four kinds of MNPs have been studied in this project. The characteristics properties of these MNPs are compared in Table 1.

MNPs	M _s (emu/g)	M _r	H _c (Oe)	D(nm)	A
Ademtech FeO _x	35		<10	200	15*
Sigma Aldrich Fe ₂ O ₃	67	15	179	<50*	50-245*
NanoFer25	116	14	304	<50*	>25*
Lab made	87	2	25	12	580
Preferable	Large	Small	Small	small	Large

*Table 1 Comparison of the MNPs used for the conjugation process. H_c is the coercivity, M_r is the remanent magnetization and M_s is the saturation magnetization. All the magnetic data are obtained at room temperature. D is the size of MNPs. A is the surface area of the MNPs. * Data obtained from the products' specification.*

Among those, the UI lab synthesized MNPs shows superparamagnetic behaviors with high specific magnetization and small size with very large surface area. They are all desirable for achieving the efficient nuclear waste separation. Besides, its properties are also flexible to be controlled to achieve a better sorption results. Thus, it is the most promising candidate for nuclear waste application.

We characterized the MNPs with TEM. In the commercial Iron oxide MNPs from Sigma Aldrich, the particle size has a large distribution range from a couple of to several tens of nanometer. For the core-shell MNPs fabricated in UI, the particle size distribution is uniform in about 12 nm. Electron diffraction patterns illustrate that the commercial Iron oxide MNPs mainly consist of polycrystalline Fe₂O₃, whereas the MNPs clearly show the Fe-Fe₃O₄ core/shell structures. The specific magnetization of NanoFer25 MNPs is 1.7 times higher compared to the Fe₂O₃ MNPs. The high magnetization is due to its Fe-FeO core shell structure, which is desirable for a fast magnetic separation after actinide sorption. But the two MNPs show typical ferromagnetic behaviors, which means they remain magnetic when there is no external magnetic field applied, this is not desirable because the magnetic dipole forces between MNPs will generate significant aggregation, consequently greatly reduces the surface area of the MNPs. To prevent this kind of agglomeration, surfactant coating is necessary to keep these kinds of MNPs from quick aggregation and sedimentation. However, in case of process optimization, the NanoFer25 is suitable for the optimization experiment due to the similar core shell structure of NanoFer25 and its low degree of agglomeration in water. For the 3rd run sorption test, NanoFer 25 has been used to achieve high ligand loading capacity with a stable conjugate in acidic

conditions similar to the nuclear waste stream. Among the MNPs, NanoFer25 Fe-FeO core-shell MNPs has the highest specific magnetization, which may increase the magnetic separation speed in the sorption test. Thus, in the 3rd run sorption test, we chose the NanoFer25 Fe-FeO core-shell MNPs as the carrier for conjugation optimization and actinide separation. Silica coating procedure was optimized by varying the amount of water, catalyst (ammonium hydroxide), and silane precursor, tetraethoxysilane (TEOS), in the reaction. The particles were evaluated for acid resistance by incubation in 1M HCl and following the release of soluble iron over time using a colorimetric iron assay [2-3]. Results summarized in **Figure 1**: show that a 10% stock solution of TEOS used to coat MNPs is sufficient for a silica coating that is acid resistant for at least for 25 days of incubation in 1 M HCl. Similarly silica coated MNPs were resistant to 0.1M HNO₃ treatment. As presented in Fig. 2, the saturation magnetization (M_s) of the MNPs drops by increasing TEOS concentration. At 10% of TEOS, the M_s remains as large as 44.1emu/g, which is high enough for magnetic separation [3].

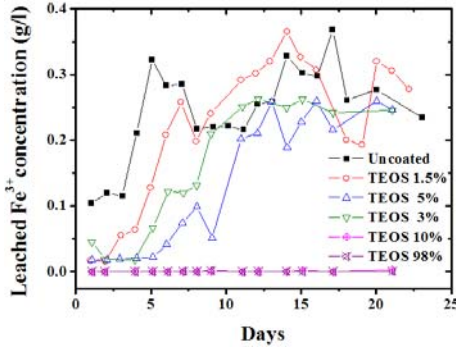


Figure 1: Measurement of iron solubilized in 1M HCl solution from MNPs coated using different concentrations of TEOS precursor.

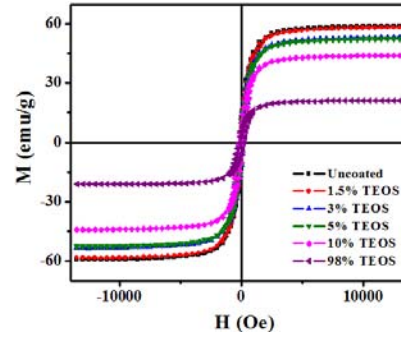


Figure 2: Hysteresis loops of silica-coated MNPs (Fe_2O_3) produced with increased TEOS concentration.

Objective 3:

Magnetic separation device is designed to study the colloidal properties of magnetic nanoparticles (MNPs) in solution [16]. This device will be utilized after extraction process to separate complex conjugate of MNPs with actinides from the rest of the used nuclear waste solution. The MNPs can be separated by passing the colloidal solution through the column held under the magnetic field gradient generated by an electromagnet. The parameters such as flow rate, field gradient, concentration, pH of solution, and type of MNPs has been used to study the possible effect on separation time and removal efficiency of particles with actinides from solution. Theoretical work has been performed to calculate the force required to pull the MNPs from solution. It has been seen that the force is linearly proportional to the field gradient (Figure 3) which in turn exponentially decay with distance. Preliminary measurement was carried out in a small glass vial with suspended solution of un-functionalized and functionalized MNPs by silica (Si-MNPs), polyamine (PAA-MNPs), and DTPA chelators (DTPA-MNPs) which is used for the extraction of actinides from the nuclear waste. The vial is held by two permanent magnets (0.5 T) on each side as shown in the inset of Fig. 4. Different lengths of vials are used to change the magnetic field gradient ΔB . The concentration and strength of magnetic field is kept constant and the time was recorded using stop watch to see the clear solution after the particles get trapped in the magnetic field. Fig. 4 shows the exponential behavior of separation time of MNPs

from solution as a function of ΔB . The unfunctionalized MNPs take much smaller separation time compared to functionalized MNPs. The thickness of non-magnetic coating on the surface of functionalized MNPs results in the drop of magnetization, as it is calculated with respect to mass of the particles. As a result, the separation time increases from un-functionalized particles to functionalized particles. All curves are fitted with first order exponential decay.

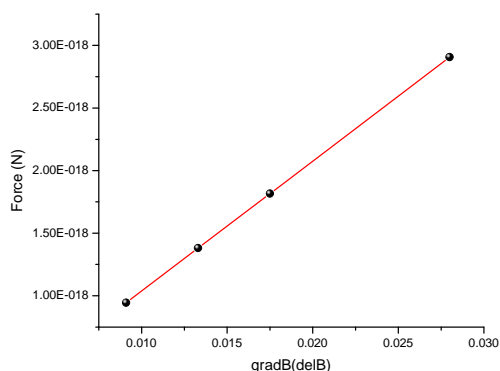


Figure 3: Magnetic force as a function of field gradient

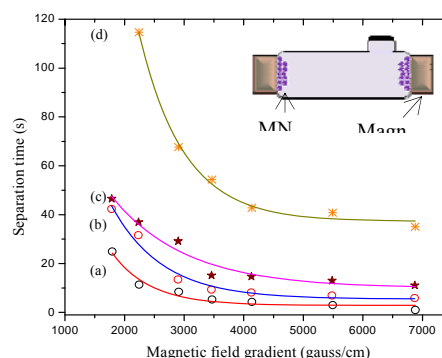


Fig. 4: Separation time of MNPs as a function of magnetic field gradient where (a) Uncoated MNPs, (b) Si-MNPs, (c) PAA-MNPs, and (d) DTPA-MNPs.

EDUCATION:

Postdoctoral Fellow and Visiting Scholar: Dr. Guoxin Tian, Dr. Hongmei Han and Dr. Joseph Kaczor,

Graduate Students:

- Andrew Johnson; Ph.D; graduated 2011
- Maninder Kaur, Ph.D, will graduate in May 2012
- Huijin Zhang, MS, will graduate in De. 2011

Undergraduate Students:

- Alex Bowyer (Fall 2009, Spring 2010)
- Tayler Schimel (Fall 2009 to now, Undergraduate Research fellowship award)
- Paul Bailey (Spring 2011 to now)
- Todd Schoelleberg (Spring 2011 to now)

AWARDS

2010 U.S. Department of Energy Innovations in Fuel Cycle Research Honorable Mention Award for the paper-“Silica Coated Magnetic Nanoparticles for Separation of Nuclear Acidic Waste.”- published in J Appl. Phys, 107, 09B520, 2010. Awarded a prize of \$1500.00 in the category of Universities with Less Than \$500M in 2008 R&D Expenditures. The award also included a travel reimbursement of up to \$1500.00 for travel. Andrew K. Johnson presented the paper of “Magnetically Assisted Chemical Separation of Actinides by Silica/Polyamine Coated Nanoparticles Functionalized with N,N-dimethyl-3-oxa-glutaramic acid”, at the Fuel Cycle Research & Development Meeting, Oct. 26-28, Gaithersburg, MD.

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3. M. Kaur T. Singh, H. Han, A. Johnson, A. Paszczynski and Y. Qiang, "Application of core shell iron-iron oxide magnetic nanoparticles in nuclear waste separation technology ", American Physical Society Northwest Section meeting, University of British Colombia, Vancouver, B. C., Canada, May 14-16, 2009,
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6. H. Han, J. Kaczor, M. Kaur, A. Johnson, A. Paszczynski and Y. Qiang, "Silica Coated Magnetic Nanoparticles for Separation of Nuclear Acidic Waste", 11th Joint MMM-Intermag Conference, Washington, DC, USA, Jan. 18-22, 2010.
7. You Qiang, Maninder Kaur, Andrew Johnson, Jozef Kaczor, Hongmei Han, and Andrzej Paszczynski, "Conjugates of Magnetic Nanoparticle-Actinide Chelator for Used Fuel Separation", MRS-Spring Meeting 2010.
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10. You Qiang, J.A. Sundararajan, M. Kaur, Q. Yao, C.M. Wang, and D.R. Baer, "Novel Nanotechnology for Nuclear Fuel Recycling", The International Symposium of Advanced Functional Materials 2010, July 7-8, 2010, Shenyang, China,
11. You Qiang, "Selective Conjugates of Magnetic Nanoparticle-Chelator for Nuclear Waste Separation and Environmental Remediation", Environmental Science Department, Fudan University, China, July 9-13, 2010.
12. Andrew K. Johnson, Jozek Kaczor, Hongmei Han, Maninder Kaur, Guoxin Tian, Linfeng Rao, You Qiang and Andrzej J. Paszczynski "Synthesis of a Magnetic Hydrogel for Use as a High Capacity Carrier of Organic and Biological Molecules", Idaho Space Grant Consortium Meeting, Aug. 18-19, Nampa, ID.
13. Andrew K. Johnson, Jozek Kaczor, Hongmei Han, Maninder Kaur, Guoxin Tian, Linfeng Rao, You Qiang and Andrzej J. Paszczynski, "Magnetically Assisted Chemical Separation of Actinides by Silica/Polyamine Coated Nanoparticles Functionalized with N,N-dimethyl-3-oxa-glutaramic acid", Fuel Cycle Research & Development Meeting, Oct. 26-28, Gaithersburg, MD.

14. Andrew K. Johnson, Jozef Kaczor, Hongmei Han, Maninder Kaur, Guoxin Tian, Linfeng Rao, You Qiang and Andrzej J. Paszczynski, "Silica/Polyamine Hydrogel Coated Magnetic Nanoparticles: Highly Swelling, High Capacity Carriers of Organic and Biological Molecules", Paper submitted to ACS Nano.
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