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# Conjugates of Magnetic Nanoparticle—Actinide Specific Chelator for Radioactive Waste Separation

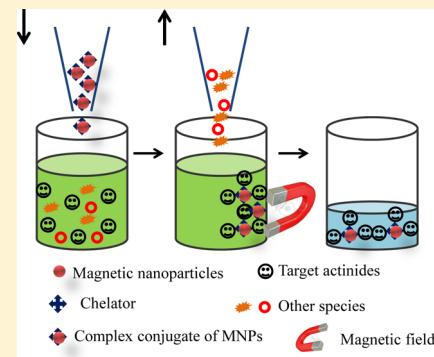
Maninder Kaur,<sup>†</sup> Huijin Zhang,<sup>‡</sup> Leigh Martin,<sup>§</sup> Terry Todd,<sup>§</sup> and You Qiang<sup>\*,†,‡</sup>

<sup>†</sup>Department of Physics, University of Idaho, Moscow, Idaho 83844, United States

<sup>‡</sup>Environmental Science, University of Idaho, Moscow, Idaho 83844, United States

<sup>§</sup>Idaho National Laboratory, Idaho Falls, Idaho 83415, United States

**ABSTRACT:** A novel nanotechnology for the separation of radioactive waste that uses magnetic nanoparticles (MNPs) conjugated with actinide specific chelators (MNP-Che) is reviewed with a focus on design and process development. The MNP-Che separation process is an effective way of separating heat generating minor actinides (Np, Am, Cm) from spent nuclear fuel solution to reduce the radiological hazard. It utilizes coated MNPs to selectively adsorb the contaminants onto their surfaces, after which the loaded particles are collected using a magnetic field. The MNP-Che conjugates can be recycled by stripping contaminates into a separate, smaller volume of solution, and then become the final waste form for disposal after reusing number of times. Due to the highly selective chelators, this remediation method could be both simple and versatile while allowing the valuable actinides to be recovered and recycled. Key issues standing in the way of large-scale application are stability of the conjugates and their dispersion in solution to maintain their unique properties, especially large surface area, of MNPs. With substantial research progress made on MNPs and their surface functionalization, as well as development of environmentally benign chelators, this method could become very flexible and cost-effective for recycling used fuel. Finally, the development of this nanotechnology is summarized and its future direction is discussed.



## I. INTRODUCTION

One of the major requirements for sustaining human progress is an adequate source of energy. Currently, the largest sources of energy are coal, oil, and natural gas. They will last for a while longer, but each will probably become scarce and/or harmful in tens to hundreds of years.<sup>1</sup> To meet future energy needs without injecting more carbon dioxide into the environment, nuclear energy is one of the best and cleanest sources of energy.<sup>2,3</sup> A few pounds of “nuclear fuel” replaces thousands of tons of diesel or coal, and provides electrical power without the air pollution associated with burning coal, petroleum, and vegetation. There is however, one major concern, and that is how disposal of the spent nuclear fuel is carried out.

“Spent” or “used” nuclear fuel is fuel that has been irradiated in a nuclear reactor (usually at a nuclear power generation plant). It is no longer useful for sustaining the nuclear reaction in an ordinary thermal reactor. Although their mass contribution in spent fuel is relatively small, transuranic elements such as plutonium and neptunium, and minor actinides (americium, and curium), are the primary contributors to long-term radiotoxicity and heat generation in spent fuel.<sup>4</sup>

The shortage of storage capacity and management of nuclear wastes is a worldwide problem.<sup>5</sup> Currently, France, Britain, and Russia reprocess their spent nuclear fuel, both for their own facilities and for other nations paying to have it recycled for them. No one has large scale storage plants in service, while

spent fuel destined for those facilities is currently stored on-site.<sup>6</sup> One option to resolve the buildup is direct disposal into a deep geologic repository to isolate spent fuel for the hundreds of thousands of years that it may remain hazardous. Another option is to reprocess it and separate out the uranium and plutonium for use as new fuel.

Any waste processing, whether for disposal or remediation, must have a minimal impact on the environment. The ongoing problem at Japan’s Fukushima Daiichi power plant—caused by the March 11, 2011 earthquake and tsunami—have been significantly exacerbated by the presence of spent fuel housed in the reactor buildings. They demonstrate the urgency of finding a way to deal with such waste, especially as the amount of spent nuclear fuel housed at existing nuclear plants continue to grow. One important action that might help counter the erosion of public support for a renewal of nuclear power, a portion of which stems from the Fukushima crisis, is to implement clear spent fuel policies now.

Countries around the world that are looking to nuclear power for their energy needs must consider how spent fuel will be handled as they construct new reactors and examine existing ones. As more nuclear power plants become operative and

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**Table I. Comparison of Different Radioactive Waste Treatment Methods**

| method  | extraction mechanism               | advantage  | drawbacks  |
|---|------------------------------------|--|--|
| <sup>10</sup> solvent extraction                      | liquid–liquid ion exchange         | 1. practical technique in large<br>2. medium scale operations when solute concentrations are high  | 1. large amount of organic waste<br>2. not for low concentration   |
| <sup>11</sup> ion exchange resin                      | ion exchange resin                 | 1. very low running costs and very little energy is required<br>2. the regenerant chemicals are cheap and if well maintained resin beds can last for many years before replacement is needed | 1. fouling of resin<br>2. presence of organic matter<br>3. commercially available resins are nonselective 4. It is not a continuous process  |
| <sup>17</sup> precipitation                           | metal surface adsorption           | 1. good at alkaline<br>2. cost effective<br>3. instruments are easily available<br>4. high degree of accuracy  | 1. not selective<br>2. low metal recovery<br>3. time consuming if done manually  |
| <sup>18</sup> magnetic separation                     | magnetic susceptibility difference | 1. can separate almost all actinides   | 1. will not remove nonmagnetic materials or grinding swarf   |
| <sup>19</sup> volatility processes                    | fluoride volatility process        | 2. there are no media to replace or dispose of   | 2. it requires low flow rate, which increases floor area required  |
| <sup>20</sup> molten fuel and coolant salt processing | reprocessing with reagents         | 1. non aqueous technique<br>2. used to remove the cladding on spent fuel elements  | 1. use of halides & $\beta$ -diketones<br>2. the radiolytic decomposition  |
| <sup>33,35,121</sup> MACS                             | chelator extraction                | 1. inherent resistance to the radiation damage<br>2. the decay heat is useful for maintaining the pyrochemical fluid at process temperature  | 1. high temperature process<br>2. low output<br>3. difficult processing of slag<br>the chelating agents wind up in the water and environmental regulations prohibit their discharge. |
| <sup>134</sup> MNP-Che                                | chelator extraction                | 1. magnetic separation<br>2. low concentration<br>3. consumption of organic solvents almost eliminated   | the method is underdevelopment   |
|   |                                    | 1. better kinetics for the adsorption<br>2. efficient separation of particles<br>3. simple, versatile and compact<br>4. minimize secondary waste   |  |

"spent fuel pools", which shield and cool the used fuel on site, approach their capacity by 2015,<sup>7</sup> the treatment of nuclear waste materials is recognized as a matter of great urgency. According to a report in April 2013 from the Government Accountability Office, nearly 70,000 metric tons of spent nuclear fuel resides at the country's 75 commercial nuclear power plants waiting to be disposed of by the government. This spent fuel inventory is expected to more than double by 2055.<sup>8</sup> With long-term storage of used nuclear fuel, there is potential for soil and groundwater contamination due to the performance of interim and long-term geologic storage containers.<sup>9</sup>

The next generation of nuclear power requires minimal generation of waste and maximum proliferation resistance (the adoption of reactor and fuel cycle technologies that are difficult to weaponize). Finding cost-effective and environmentally benign technologies for spent fuel reprocessing, with the goal of treating the radioactive liquid tank waste into a safe, stable form for ultimate disposal or recycling, is critical in our efforts to meet growing energy requirements, protect the environment and human health, and allow our economy to flourish.

Nuclear waste streams have traditionally been treated by solvent extraction<sup>10</sup> and ion exchange.<sup>11</sup> The PUREX (Plutonium Uranium Extraction) process, invented by Anderson and Asprey in 1940s, has become a standard nuclear reprocessing method to recover plutonium and uranium for reuse in mixed oxide (MOX) fuel.<sup>12,13</sup> Besides these two processes, many other methods have been developed including electrophotolysis,<sup>14–16</sup> precipitation,<sup>17</sup> magnetic separation,<sup>18</sup> volatilization,<sup>19</sup> molten fuel and coolant salt processing.<sup>20</sup> Some of these methods are in practical use, but research into alternative approaches that potentially simplify the remediation process is warranted. We will first compare these major radionuclide waste treatment methods and then describe, in detail, one appealing new method that uses chelating agents grafted onto magnetic nanoparticles (MNPs), conjugates of MNP-Chelator (MNP-Che), in a solid–liquid extraction process. Table I summarizes the extraction mechanisms, advantages, and drawbacks of each of these major nuclear waste treatment methods.

(1) Solvent extraction processes, such as PUREX, are used for extracting ion species from a liquid phase. Uranium and plutonium are removed from spent fuel by dissolution in acid, after which liquid–liquid extraction between aqueous and organic liquid phase takes place. They have been successfully applied in practice, but there are limitations. PUREX can only separate U and Pu. Moreover, it usually does not provide the selectivity necessary to create valuable product streams suitable for recycling or reusability.

(2) Ion exchange has been widely studied for the recovery of metal ions from diluted streams. Commercially available ion-exchange resins perform well, but they generally exhibit poor selectivity between different metal ions. A high selectivity can be observed in some cases, but the kinetics are slow due to the hydrophobic character of the polymeric backbone.<sup>21</sup>

(3) Electrolysis uses electric field to separate charged species from one another in electrolyte solution due to differences in their mobility.<sup>22–25</sup> The driving potential of this process is provided electrically and can be controlled very precisely to produce a cathode product that is extremely pure. However, this technique has difficulties when scaled up, since heat dissipation is required to prevent convection currents from perturbing the migration pattern. It is also not cost-effective for treating low concentration waste.

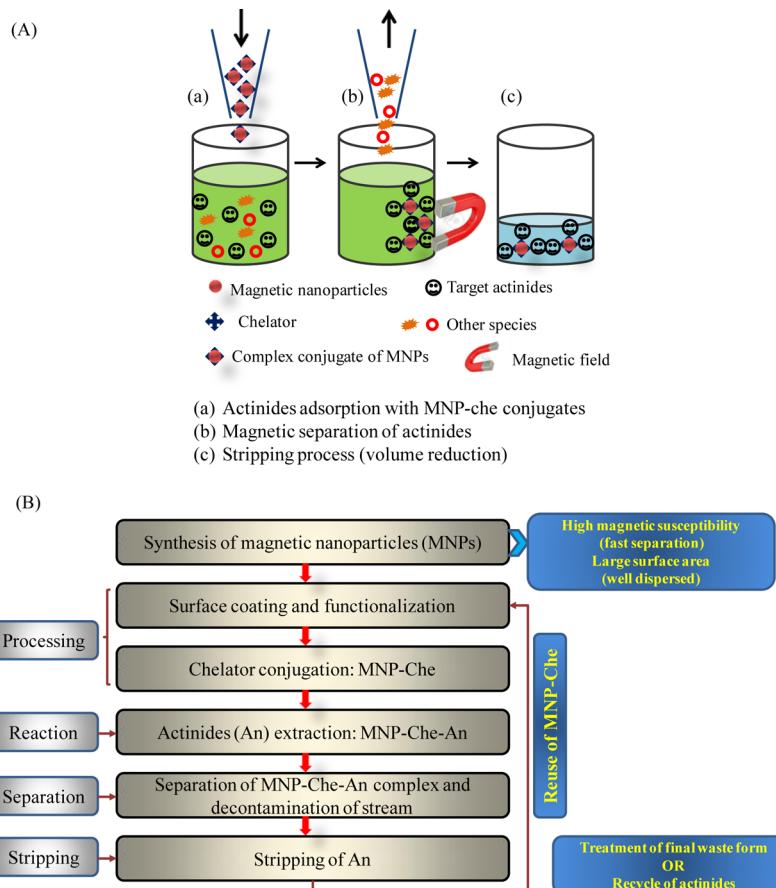
(4) Recently, biological methods have been used to investigate the removal of actinides and heavy metals due to their cost effectiveness at moderate metal concentrations. Precipitation can be achieved by sorption onto hydrous oxide surfaces. Many strains have been isolated that precipitate out metals on the outer membrane of the cell.<sup>26–29</sup> This process may not be applicable in more complex waste streams or environments due to the relatively low binding affinities of cellular components for metals compared to chelators, such as humic or organic acids.

(5) Magnetically assisted chemical separation (MACS)<sup>30</sup> processes utilize magnetic carrier microparticles (rare earth or ferromagnetic materials embedded in a polymer material) coated with selective chemical extractants (Carbamoylmethylphosphine oxides (CMPO), tributyl phosphate (TBP), amines etc) that have an affinity for the target elements. Though this process shows promise as an efficient and compact separation technology, dissolution of the bare magnetic particles in acid could be a limitation of the recyclable batch process.<sup>31</sup> The possibility of designing particles with large surface area should be investigated for employment in large scale separations.

(6) Volatilization isolates uranium from bulk impurities or fission products. This process has some limitations. The volatilization of molten fuel and coolant salt requires high temperature. In addition, some fluorides of other transuranic elements are not volatile and/or are unstable, while a number of elements that can be volatilized, such as molybdenum, technetium, and iodine, separate from the spent fuel along with the uranium. These present formidable engineering problems to be solved before the process can be applicable.<sup>32</sup>

The concept of using the MNP-Che complex to separate radionuclides while in the contaminated liquid stream is similar to the so-called MACS process first demonstrated in Argonne National Laboratory.<sup>31,33–35</sup> The applicable nuclear waste stream for this treatment method is aqueous, and it may either come from the strong acidic high level waste produced by the PUREX process, low level waste from other processes, or underground contaminations. The MACS process combines the selective and efficient separation afforded by chemical sorption with magnetic recovery of the radionuclide. The key advantages of this MNP-Che radioactive waste remediation are the high mobility related with nanomaterials<sup>36–39</sup> and the recent development of environmentally benign chelators.<sup>40,41</sup> MNP-Che separation has many advantages over MACS process such as (1) MNPs' extremely small size and high surface area to volume ratio provide better kinetics for the adsorption of metal ions from aqueous solutions; (2) the high magnetic susceptibility of MNPs aids in efficient separation of particles from waste solution; (3) it is a simple, versatile, and compact process which is cost-effective in terms of the materials and equipment used; (4) the production of secondary waste is low, which minimizes disposal costs and storage area.

In order to separate the radioactive waste from the aqueous stream, the MNP-Che conjugations are first added to the waste stream, which can either be in a tank or in situ. To maintain the conjugates' suspension, the treatment stream can be mixed by mechanical stirring or other methods. The actinides are then extracted onto the MNP-Che conjugates, usually taking about an hour to reach saturation.<sup>42</sup> The particles, now loaded with actinides, are magnetically collected and separated by a magnetic field gradient. The waste solution is decontaminated and can be released. The actinide-loaded particles can then be stripped with a small amount of liquid (relative to the original



**Figure 1.** (A) Illustration of MACS process for the radioactive waste streams treatment using MNP-Che conjugates; (B) Flowchart of nuclear waste separation using complex conjugates of MNPs-chelator.

waste stream) and magnetically separated from the resulting solution, allowing their reuse in the next waste treatment. Finally, the concentrated actinide contaminants are ready to be treated for permanent waste disposal or for a fuel recycle process. An illustration of this process is shown in Figure 1A.

The steps to make the MNP-Che for this waste treatment are shown in the flowchart in Figure 1B. First, the MNPs with specific properties suitable for the separation are synthesized. The MNPs are coated in order to prevent their leaching under acidic nuclear waste streams. Finally, the most critical conjugation process takes place between the actinide specific chelators and MNPs, which produces MNPs-Che conjugates that are ready for the remediation process. With highly selective chelators, this method can be developed into a versatile and simple separation technology that facilitates the recovery and recycling of heat generating minor actinides contained within these streams. No significant reduction in radiological hazard of the waste can be obtained without recycling the minor actinides (*Np*, *Am*, *Cm*).<sup>4</sup> A fully closed fuel cycle where all actinides are recycled through fast reactors or accelerator driven systems could potentially reduce repository storage space, radiotoxicity of the waste, and heat loading in the final waste form. To achieve this goal however, the difficult separation of the minor actinides *Am* and *Cm* from the trivalent lanthanides has to be performed.<sup>43</sup>

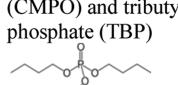
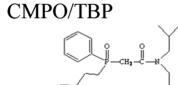
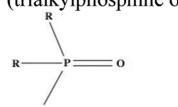
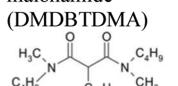
Almost two decades have passed since the original research using chelator-loaded magnetic particles to treat the radioactive waste stream was performed.<sup>33,35,44</sup> Much progress has since been made in radioactive waste remediation using MNP-Che

conjugates. This review focuses on the design and process development of the MNP-Che's radioactive waste treatment method. First, applicable MNPs suitable for this process are reviewed; comparing different MNPs and their synthesis processes. Second, the chelators that are used to extract radioactive wastes are compared, and their extraction mechanisms are briefly summarized. Subsequently, the conjugation process between MNP and chelator is described. The experimental and pilot test results of separation using MNP-Che are reviewed with respect to their corresponding chemical reaction parameters and waste stream conditions. Furthermore, the magnetic separation and recycling of particles are described. Finally, research progress is summarized and the future direction of radioactive waste remediation technology using MNP-Che conjugates is outlined.

## II. MAGNETIC NANOPARTICLES

The first crucial step in successful waste treatment using MNP-Che conjugates is to select a MNP to be conjugated with the chelator. In this section, we briefly review the synthesis and characteristics of different MNPs that are currently used and can be used in the future for this separation technology. Table II reviews some of the particles and related chelators used to separate actinides, along with the corresponding experimental conditions and removal efficiencies. The high mobility of MNPs with large specific surface areas and their controllable separation by magnetic field makes it possible to use MNP-Che conjugates to extract radioactive waste. This method becomes more attractive with higher competency compared to other

Table II. Magnetically Assisted Chemical Separation processes

| Magnetically Assisted Chemical Separation processes  |   |  |   |  |
|--|---|--|---|--|
| Magnetic carrier   | Chelators   | Contaminants   | K <sub>d</sub> (ml/g)   | Strip feed/Experimental conditions                                     |
| <sup>35</sup> Magnetite being incorporated with charcoal in a cross-linked N, N-methylene bis-acrylamide. 0.1 to 25 µm with variety shapes.<br>(Cortex-Biochem)                    | octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and tributyl phosphate (TBP)<br> | uranium  | 3000 to 30,000  | nitride acid   |
| <sup>121</sup> Ferromagnetic-charcoal-polymer microparticles, 1-25 µm<br>(Cortex-Biochem)  | CMPO/TBP<br>   | <sup>241</sup> Am  | 3000 to 5000  | nitride acid   |
| 34 Charcoal poly bis-acrylamide coated magnetite particles, 1-25 µm (Cortex-Biochem)   | CMPO/TBP, diethylhexyl phosphoric acid (D <sub>2</sub> EHPA), trioctyl phosphine oxide (TOPO)   | <sup>238</sup> Pu, <sup>233</sup> U and <sup>241</sup> Am  | 2E4 <sup>238</sup> Pu,<br>1E4 <sup>233</sup> U,<br>2E4 <sup>241</sup> Am<br>(1.2M MPO/TBP);<br>5E4 <sup>233</sup> U<br>(0.1M TOPO/0.5M D <sub>2</sub> EHPA) | Nitric acid  |
| <sup>166</sup> Magnetite being incorporated with charcoal in a cross-linked N, N-methylene bis-acrylamide, particle distribution averaging ~ 20 µm in diameter<br>(Cortex-Biochem) | trioctyl phosphine oxide (TOPO) Cyanex 921 in dodecane and diethylhexyl phosphoric acid (D <sub>2</sub> EHPA)   | U(VI)  | ~6.4E4 or less for D <sub>2</sub> EHPA; ~3.9E4 or less for D <sub>2</sub> EHPA and TOPO   | nitride acid   |
| <sup>159</sup> Carboxylic acid modified iron oxide (Micromode)   | pre-organised CMPO-calix[4] arenes as ligands   | <sup>152</sup> Eu, <sup>241</sup> Am, and <sup>139</sup> Ce  | ~3500 ml/g  | Covalent attachment of ligands to the particle surface                 |
| <sup>156</sup> Silanized magnetite particles   | CMPO and TBP (0.75:1 m ol)  | Eu <sup>3+</sup>   | 30 or less  | nitride acid, reaction time 20 minutes, physical sorption of chelators |
| <sup>142</sup> Iron oxide (Micromode)  | CMPO, Picolinamide, DMDGA   | Eu and Am  | CMPO: ~40 or less Eu, ~84 Am;<br>Picolinamide: ~1.4E4 or less for Eu, 1.8E4 or less for Am;<br>DMDGA: 170 Eu, 54 Am   | Excessive H <sub>2</sub> O as stripping agent, reaction time 1hour     |
| <sup>42</sup> Cross-linked polyacrylamide and acrylic acid entrapping charcoal and iron oxide, 1-60 µm<br>(Cortex-Biochem)   | Cyanex 923 (trialkylphosphine oxide)<br>   | Th(IV), U(VI), Am(III) and Eu(III)   | Th(IV) and U(VI): ~10 <sup>4</sup> or less, Am(III) and Eu(III): ~100 or less   | nitric acid solutions  |
| <sup>157</sup> Cross-linked polyacrylamide and acrylic acid entrapping charcoal and iron oxide (Fe <sub>3</sub> O <sub>4</sub> ), 1-60 µm<br>(Cortex-Biochem)                      | N, N'-dimethyl-N, N'-dibutyl tetradecyl malonamide (DMDBT DMA)<br>                               | Pu(IV) > U(VI) > Am(III) > Eu(III) > Sr(II), Pr(III) > La(III) > Eu(III) > Tb(III) > Ho(III) > Er(III) > Yb(III) > Lu(III) | 1.58 mmol/g and 0.36 mmol/g for U(VI) and Eu(III)<br>5.0E3(Pu <sup>4+</sup> )<br>5.0E3(U <sup>4+</sup> )<br>31(Am <sup>3+</sup> )                           | nitric acid, 0.01M HNO <sub>3</sub> as a stripping agent               |

separation technologies of minor actinides due to the continually decreasing production cost of MNPs.<sup>45</sup>

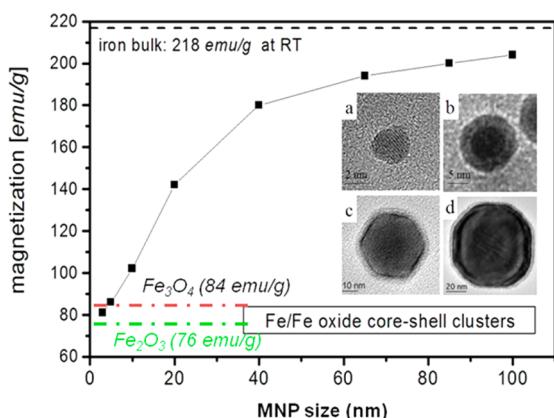
Generally the nuclear waste stream occurs in harsh acidic or alkaline conditions.<sup>46</sup> Therefore, the first important criterion for

MNP candidates is that they must be chemically stable during synthesis, in storage and while in use. Magnetic oxides, including iron oxides and other ferrites, are usually chemically stable with natural oxidization resistance. However, oxides

usually have low magnetic moments compared to metallic MNPs, where a high magnetic moment is required for effective magnetic separation. Metallic MNPs would therefore serve well, but since they are extremely reactive, they will oxidize immediately when exposed to air or dissolved in acidic conditions. To solve this difficulty, magnetic core–shell nanostructured particles with a metallic core and a protective oxide shell are used. They are chemically stable in addition to having high magnetic moments. Some common oxide particles suitable for the nuclear waste separation are first reviewed with regard to their magnetic properties and chemical stability. Then, typical core–shell structures are reviewed with regard to their applications for radioactive waste separation. At the end of this section, the main synthesis methods to prepare these particles are compared with respect to the nuclear waste remediation process.

**A. Oxides.** Superparamagnetic  $\gamma\text{-Fe}_2\text{O}_3$  (maghemite) and  $\text{Fe}_3\text{O}_4$  (magnetite) nanoparticles are commonly used for magnetic separation due to their well-established synthesis and surface functionalization processes.<sup>36,47</sup> The activation of oxide MNPs is driven by two factors: (1) the small particles ( $<100$  nm) have a larger surface area for transuranic (TRU) waste adsorption, and (2) oxide particle adsorbs hydroxide ions, through which the metal ions bond to the particle surface.<sup>31</sup>

**B. Core–shell Nanostructured Particles.** The core–shell structure consists of a dark Fe metal core region surrounded by a light gray oxide shell as shown in the inset transmission electron microscopy (TEM) image of Figure 2. Compared to



**Figure 2.** Specific magnetization of sputtered core–shell MNPs with various sizes. The inset figure is the TEM images of the core–shell MNPs. The MNPs is totally oxidized when the size decreased to  $<2$  nm.<sup>89</sup>

oxides, core–shell MNPs have a higher magnetization in the same size of MNPs that facilitates the magnetic separation of the conjugates after the radionuclide adsorption.

Iron release is also a problem for magnetite particles, which dissolve within seconds if released into concentrated HCl.<sup>48</sup> To preserve the high magnetic moment of MNPs in the nuclear waste stream, different types of surface coatings are used for stabilization. Since the particles are more susceptible to damage from acid degradation than gamma radiolysis, and the coating helps to shield the metallic part of the particle when in acidic/alkaline solution, the magnetic moment is preserved. The types of coating discussed here are polymer, silica, carbon, and gold.

**(a). Polymer Coating.** Properties of polymer coatings, including steric repulsion, prevent agglomeration of the MNPs allow the polymer coated particles to be stabilized in suspension. Polymers containing different functional groups, such as carboxylic acids, sulfates, and phosphates, can be immobilized or physically adsorbed on the particle surface.<sup>49</sup> The polymer layer can form a single or double layer depending<sup>50,51</sup> on the solution conditions, such as pH. This layer creates repulsive force, or steric repulsion, to balance the attractive forces such as magnetic and van der Waals forces, making the particles more stable in solution. The polymer coated MNPs can be synthesized by a single inverse microemulsion<sup>52</sup> or by using polyaniline<sup>53</sup> and polystyrene.<sup>54</sup>

In highly acidic conditions, the polymer layers are not stable and are easily leached into the solution,<sup>55</sup> which results in protonation of surface hydroxyl groups on the particle and degradation of the magnetic moment. Though surface modified polymer coated MNPs are intensively studied for drug delivery and as contrast agents for magnetic resonance imaging,<sup>56,57</sup> they are not strong enough barriers to prevent oxidation of particles in the very acidic medium of spent nuclear fuel. Also, the polymer coating of MNPs is very sensitive to temperature and loses its stability at high temperature. In that environment, a polymer coating is still effective to achieve a higher chemical affinity between the chelator and the MNPs,<sup>31</sup> but only after a different protective coating has been applied.

**(b). Silica Coating.** The benefit of silica as a coating material mainly lies in its high stability, especially in aqueous media, but other reasons include easy regulation of the coating process, chemical inertness, controlled porosity, ease of processing, and optical transparency. The main factors favoring the remarkable stability of silica sols are (i) van der Waals interactions are much lower than those involving other nanoparticles, and (ii) cations and positively charged molecules can be tightly attached to the characteristic polymeric silicate layer at silica–water interfaces under basic conditions.<sup>58</sup> Thus, this silicate layer can confer both steric and electrostatic protection on different cores and act as a dispersing agent for many electrostatic colloids. These advantages render silica an ideal, low-cost material to tailor surface properties. Moreover, this coating endows the cores with several beneficial properties, such as the possibility of subsequent surface functionalization, which can be obtained by modifying the hydroxyls on the silica surface with amines, thiols, carboxyls, and methacrylate; and colloidal stability over a much wider range of solution conditions, such as ionic strength, temperature, solvent polarity, and pH.<sup>59–62</sup>

Two approaches have traditionally been used to coat particles with silica. The first technique, described by Iler,<sup>63,64</sup> involves deposition of a thin layer of silica onto oxide particles by polymerization of silicic acid from supersaturated aqueous silicate solutions. A second technique, sol–gel coating, is based upon the StÖber method<sup>65</sup> for forming uniform silica gel microspheres.<sup>66</sup> Other, less common techniques include sodium silicate water glass methodology, the two step precipitation method, and water in oil microemulsions.

**(c). Carbon Coating.** Carbon-coated metal nanoparticles have received considerable attention for advantages over polymer and silica in high chemical and thermal stability.<sup>67–69</sup> Several preparation methods, such as arc-plasma,<sup>70</sup> thermal decomposition of organic complexes,<sup>71</sup> arc discharge<sup>72</sup> or chemical vapor deposition (CVD) have been employed. Though the arc discharge method is the most popular, high

yield and low costs coupled with simple procedure make the combustion CVD method<sup>73,74</sup> a good candidate for future industrial fabrication of carbon-encapsulated magnetic nanoparticles.<sup>73</sup> The well-developed graphitic carbon layers provide an effective barrier against oxidation and acid erosion. These facts indicate that it is possible to synthesize carbon-coated MNPs, which are thermally stable, and have high stability against oxidation and acid leaching. Though carbon-coated MNPs have many advantages, such particles are often obtained as agglomerated clusters, owing to the lack of effective synthetic procedures and a low degree of understanding of the formation mechanism. The synthesis of dispersible, carbon-coated nanoparticles in isolated form is one of the challenges facing this field.<sup>36</sup>

(d). *Gold Coating.* Precious metals can be deposited on the surface of MNPs to protect the cores against oxidation. Gold seems to be an ideal coating owing to its low reactivity and the ability of its surface to be further functionalized, especially with thiol groups.<sup>75</sup> This treatment allows the linkage of functional ligands which may make the materials suitable for catalytic and optical applications. Gold coated particles are stable only under neutral and acidic aqueous condition,<sup>76</sup> they dissolve in highly acidic medium such as aqua regia. Gold coated particles and thiol groups would not survive the strongly acidic environment of nuclear waste. In order to apply these particles in spent nuclear fuel separation, additional coatings that can resist<sup>77</sup> highly acidic environments are required to prevent the particles from dissolving in the medium. The cost of gold and extra work associated with additional coatings make this process very expensive and complex. Hence, the gold coated particles are not recommended for nuclear waste treatment.

**C. Synthesis of Magnetic Nanoparticles.** MNPs have been synthesized with a number of different compositions and phases, including iron oxides such as  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ ,<sup>78,79</sup> pure metals such as Fe and Co,<sup>80,81</sup> spinel-type ferromagnets such as  $\text{MgFe}_2\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$ , and  $\text{CoFe}_2\text{O}_4$ ,<sup>82,83</sup> and alloys such as  $\text{CoPt}_3$  and  $\text{FePt}$ .<sup>84,85</sup> Several popular methods including coprecipitation, thermal decomposition and/or reduction, micelle synthesis, hydrothermal synthesis, and laser pyrolysis techniques can all be directed at the synthesis of high-quality MNPs. Instead of compiling all this literature, the main techniques for MNPs synthesis (vapor condensation, solid-state processes, chemical synthesis, and coprecipitation) are discussed.

i. With vapor condensation, evaporation of a solid metal followed by rapid condensation forms nanosized clusters that settle in the form of a powder. Various approaches to vaporize the metal can be used and variation of the medium into which the vapor is released affects the nature and size of the particles.

Different cluster sizes ranging from 2 to 100 nm can be prepared using a cluster deposition system.<sup>86</sup> Nanoparticle size is controlled by changing the ratio of argon to helium gas, power, aggregation length, and temperature. The ionized Ar ions sputter atoms from the surface of a target. The sputtered atoms form nanoparticles in the aggregation chamber which then travel to the deposition chamber due to pressure difference. There, they react with a small amount of oxygen (~2 to 5 sccm) to form a protective oxide shell on the particles before finally landing softly onto a room-temperature substrate.<sup>87,88</sup> Figure 2 shows the magnetization of core–shell Fe MNPs as a function of particle size.<sup>89</sup> A major advantage of this method is that the particles have much smaller size

dispersion than grains obtained in any typical vapor deposition system.

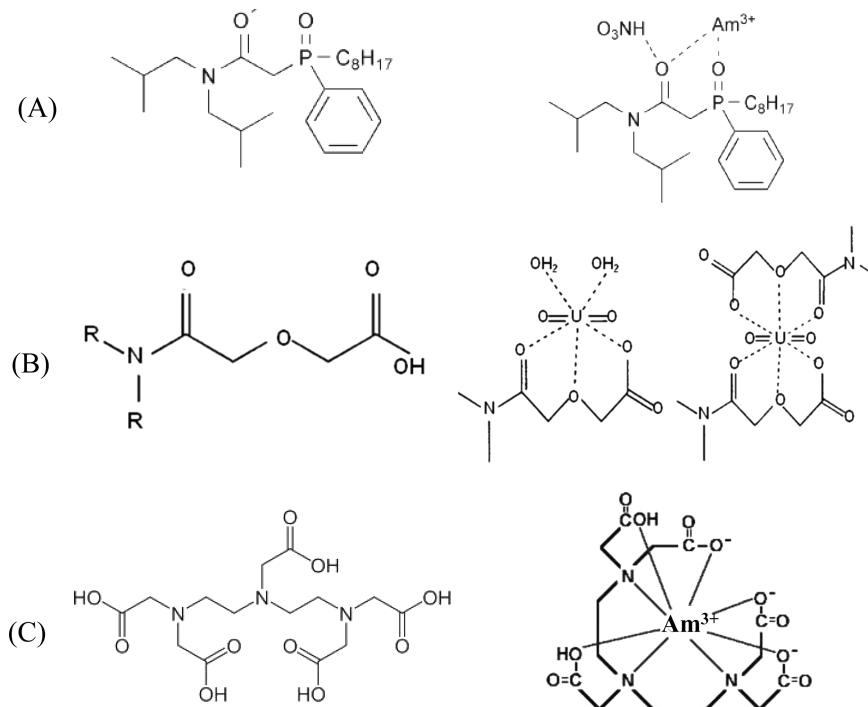
ii. In solid-state processes, grinding or milling can be used to create nanoparticles.<sup>90</sup> For example, high energy ball milling has been utilized to break particles into nanosized subparticles through high energy bombardment. The milling material, milling time, and atmosphere during milling affect the properties of resultant nanoparticles. This approach can be used to produce nanoparticles that are hard to synthesize from the chemical and gas aggregation methods. Contamination from the milling material can be an issue in this method. Though mechanical milling is a versatile technique to produce metallic micropowders, the particle size below 100 nm is not achievable that limit to get the high surface area nanoparticles.<sup>91</sup>

iii. Chemical methods<sup>92</sup> have been widely used to produce nanostructured materials due to their straightforward nature and their potential to produce large quantities of the final product. Particle sizes ranging from nanometers to micrometers can be achieved by controlling the competition between nucleation and growth during synthesis. It is well-known<sup>93</sup> that a short burst of nucleation followed by slow controlled growth is critical to produce monodisperse particles. Chemical synthesis methods are generally low-cost and high-volume, but contamination from the precursor chemicals can be a problem.<sup>90</sup>

iv. Coprecipitation<sup>36,94</sup> is a facile and convenient way to synthesize iron oxides (either  $\text{Fe}_3\text{O}_4$  or  $\gamma\text{-Fe}_2\text{O}_3$ ) from aqueous  $\text{Fe}^{2+}/\text{Fe}^{3+}$  salt solutions by the addition of a base under inert atmosphere, either at room temperature or elevated temperature.<sup>95</sup> The size, shape, and composition of the MNPs depend on the type of salts used (e.g., chlorides, sulfates, nitrates),  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio, reaction temperature, pH value and ionic strength of the media. Magnetic saturation values of magnetite nanoparticles are experimentally determined to be in the range of 30–50 emu/g, which is lower than the bulk value, 90 emu/g. Particles prepared by coprecipitation unfortunately tend to be rather polydisperse. Also, this method is limited to the synthesis of colloidal solution of iron-oxide particles.

### III. CHELATORS FOR SORPTION OF RADIOACTIVE ELEMENTS

Chelators, or ligands, are defined by American Society for Testing and Materials (ASTM-A-380) as “chemicals that can form soluble, complex molecules with certain metal ions, inactivating the ions so that they cannot normally react with other elements or ions to produce precipitates or scale”. Any reagent used in the separation process must be chosen to fulfill several challenging criteria.<sup>96</sup> The chelator must show a good level of selectivity for the actinides so that the separation process can be carried out in a relatively small number of extraction stages. The organic phase solubility of both the reagent and its extracted complexes should be high to minimize the possibility of third-phase formation or precipitation. The ligand must show a sufficiently high level of or acceptable resistance toward acidic hydrolysis and radiolysis, and any degradation products that form must not interfere with the separation process to any significant degree. Finally, the chelator should be able to extract from nitric acid ( $\text{HNO}_3$ ) solutions of low pH ( $\leq 4$  M  $\text{HNO}_3$ ) that are produced in the PUREX process. If possible, it should only be composed of the elements C, H, O, and N (CHON principle) so that any spent solid residues, solvent streams, or ligands may be degraded without producing corrosive products at the end of their



**Figure 3.** (A) Traditional CMPO chelator and the its chelation complex with Am;<sup>40</sup> (B) Environmentally friendly chelator DMOGA and its chelation complex with UO<sub>2</sub>.<sup>41</sup> (C) MNP coupled by DTPA chelator wraps around Am (III).

valuable life, reducing or avoiding altogether the generation of secondary waste. In order to make possible large-scale production of these ligands, the synthesis of the chelator should be as simple, cost-effective, and practical as possible.

Several European Union funded research projects studied a number of substituted diamide ligands such as

- i. *N,N'*-dimethyl-*N,N'*-dibutyltetradecylmalonamide (DMDBT DMA)<sup>97</sup>
- ii. *N,N'*-dimethyl-*N,N'*- diocetylhexyloxyethylmalonamide (DMDOHEMA)<sup>98</sup>
- iii. *N,N,N',N'*-tetraoctyl diglycolamide (TODGA)<sup>99</sup> for the DIAMEX (diamide extraction)<sup>100</sup> process

Trivalent actinide (III) ligands can be categorized into three major groups: O-donating ligands, S-donating ligands, and N-donating ligands.<sup>40</sup> The general rules of coordination chemistry state that soft donor atoms favor binding to soft metal ions, while hard donor atoms favor hard ions. The hard or soft character of a metal ion depends on oxidation state; for example, Fe(III) is harder than Fe(II) and Cu(II) is harder than Cu(I). Based on these general rules, oxygen is a hard donor atom that binds well to hard cations such as Ca(II) and Mn(II), sulfur is a soft donor atom that binds well to Cd(II) and Cu(I), and nitrogen is of intermediate hardness between oxygen and sulfur.<sup>101</sup>

**1. O-Donating Ligands.** This group of ligands covers a broad range of O-bearing functionalities (e.g., phosphonates, amides, ketones, and phenols). CMPO (octyl (phenyl)-*N,N*-di(iso-butyl)) and carbamoyl-methylphosphonates (CMPS) are well-known O-donating ligands. A derivative of CMPOs is presently used in the transuranium extraction (TRUEX) process.<sup>102,103</sup> Upon complexation with the metal cation, it forms a six membered chelate ring. CMPO chelator and its chelation complex with americium (Am) are shown in the Figure 3A.

The O-donor ligands are generally strong extractants owing to the hard nature of the oxygen atom. This type of ligands usually lack discrimination between the same oxidation state of Am(III) and Eu(III), which results in a relatively low separation factor<sup>104</sup>—one distribution ratio divided by the other. It is a measure of the ability of the system to separate two solutes. All successful aqueous processing options for group separation of fission product lanthanides from trivalent actinides have relied on the applications of ligand donor atoms “softer” than oxygen (N, S, Cl).<sup>105,106</sup> The appearance of hard donor oxygen atoms (resulting from degradation of the soft-donor extractant molecule) has been shown to significantly degrade the effectiveness of many soft donor separation systems.<sup>107</sup>

**2. S-Donating Ligands.** Cyanex 301 is a dialkyldithiophosphinic acid extractant containing C, H, P, and S. This sulfur-containing compound is a good example of an Am(III) chelator having a very high separation factor due to the preferable covalent binding of Am(III) to the relatively softer sulfur donor atom. The oxidation behavior of Cyanex 301 reduces its selectivity when it oxidizes to Cyanex 302, while it increases again when further oxidized to Cyanex 272. This characteristic minimizes its applicability in industrial processes. Wade et al. have discussed the application of soft donor ligands to the separation of trivalent actinides and actinides.<sup>108</sup> The S-donor, bidentate, dithiophosphinic acids were the first reagents that show very high selectivity for actinides over lanthanides.<sup>109–112</sup>

**3. N-Donating Ligands.** N-donor ligands are classified as an intermediate between the O-donor and S-donor ligands with respect to extraction efficiency and Am(III) selectivity. Due to the chelate effect, extraction efficiencies are also generally better for ligands having a higher valency. The nitrogen atom is integrated into an aromatic ring in most of the N-donor ligands. Such ligands are able to replace all coordinated water molecules, which is most likely one reason for its high

extraction efficiency. The first N-donor ligand found to selectively extract Am(III) from Eu(III) was tridentate aromatic nitrogen donor ligand 2,2':6,2''-terpyridine (TERPY).<sup>3</sup>

Tripyridyltriazine (TPTZ) is a terdentate N-donor ligand which can selectively extract actinide, An(III), from actinide and lanthanide solution when applied in synergistic combination with an organic cation exchanger.<sup>113,114</sup>

More information about recently developed ligands can be found in ref 3.

The choice of the ligand donor atom depends on the chemical nature of the metal. Actinides are considered to be hard Lewis acids<sup>115</sup> and will be preferentially bonded with either oxygen or nitrogen donors over sulfur donors.<sup>116</sup> Traditional ligand, such as CMPO, have phosphorus, while environmentally friendly ligands contain only of C, H, O, and N, alkyl-substituted amides, which have attracted more attention recently due to their more efficient separation process.<sup>41</sup> Also, stripping actinides from the organic amide-containing solvents is relatively easy. In contrast to the large amounts of liquid and/or solid radioactive waste generated in traditional organophosphorus-based separation processes, the amount of solid radioactive waste generated in the amide-based processes is significantly reduced. An environmentally friendly chelator, *N,N*-dimethyl-3-oxa-glutaramic acid (DMOGA)<sup>117</sup> and its complex with UO<sub>2</sub>, is shown in Figure 3C.

#### IV. CONJUGATION OF CHELATORS AND MNPS

An important consideration for applications of the MNP-Che conjugates is the absorption or binding strengths exhibited between the consequent coating and actinide specific chelators. Loss of interfacial integrity in either case under high level waste tank conditions is undesirable. To combine the chemical separation capability of chelators and the convenient magnetic separation of MNPs, strong conjugation is a key step to realizing nuclear waste remediation using MNP-Che conjugates.

The strong acidic medium of nuclear waste streams makes it necessary to protect the surface of the particles. In many cases the protective coatings not only stabilize the MNPs, but can also be used for further surface functionalization with, for instance, various ligands. Physical (or electrostatic) adsorption and chemisorption are the principal types of interaction between an organic ion (chelator/ligand) and the metal surface of a coated particle.<sup>118</sup>

**A. Physical Adsorptive Coatings.** Physical adsorption<sup>119,120</sup> is the result of electrostatic attractive forces between organic ions or dipoles and the electrically charged surface of the metal (particle). This type of interaction is known as hydrophobic or ionic. In the early report of the MACS process, the extractant was usually mixed with the magnetic particles and evaporated to obtain coated particles for waste treatment (plutonium and americium separation). The particles were prepared by coating iron or other ferromagnetic material with either an organic polymer or ion-exchange resin. The ion-exchange resin was attached to the particle by an adhesive or by direct bonding. The report found that organic solvents could be adsorbed onto the polymeric surface by contacting the particles with the solvent in volatile diluents that were subsequently removed by evaporation. Both coatings selectively separate contaminates onto the particles due to their chemical nature. Once loaded, the particles can be recovered from the tank using a magnet. The most reported magnetic particles are the Charcoal poly bis-acrylamide coated magnetite particles.<sup>33,34,121</sup>

Usually, particles coated by this method are only partially covered. Magnetite is soluble in nitric acid, thus the dissolution of magnetite prevents recovery of the particles and hinders the separation of radioactive waste.

**B. Covalent Bonded Coatings.** Another type of interaction between metal particles and organic ions, known as chemisorptions, forms a covalently bonded coating. This process involves charge sharing or charge transfer from the organic molecules to the metal surface in order to form a coordinate bond. Once the protective coating is on the MNP'surface, the particles can be covalently conjugated with actinide specific chelators. Such chemically modified particles should show increased long-term stability, since the ligands cannot be desorbed or leached.

The availability of specific functional groups on the polymeric coated particles enables them to chemically conjugate the chelators, such as CMPO and TBP. The selection criteria of polymers include structural similarity to and chemical affinity for the specific chelator, solubility, and melting point. A slightly porous polymer with different chemical affinity than phosphine oxides allows for greater acceptance of CMPO/TBP.<sup>51</sup> The vaporization method for impregnation of the solvent extractant CMPO yielded product that had a high sorption capability for radionuclide europium, as compared to product of the wet impregnation method.<sup>122</sup>

CMPO groups can be attached to the surface of MNPs by reaction of p-nitrophenyl(diphenylphosphoryl) acetate with the terminal amino groups of the coated MNPs. For example, the covalent attachment can take advantage of the preorganization of the chelating sites on various macrocyclic platforms like calix[4]arenes. The length and the number of linkers between the calixarene and the particle surface also affects the extraction capacity of chelator-functionalized MNPs. Linkers are used to provide a "chemical" spacer between the solid surface (particle) and the receptor that is anchored to the surface by an appropriate functional group. They spatially extend the receptor from the surface, increasing its accessibility by the solution ligand and removing any nonspecific adsorption. In general, increasing the chain length between the ligand and the calix[4]arene seems to reduce the selectivity while enhancing the distribution coefficients. However, for calix[6]arene substituted on the narrow rim, increasing the chain length between the ligand and the calixarene tends to reduce both the selectivity and the distribution coefficients. Structural representation of calix[4]arenes is shown in Figure 3B.

#### V. SORPTION OF THE NUCLEAR WASTE

After the selection of suitable MNPs and chelators, and completion of the conjugation process, the MNP-chelator complex is ready to be applied in the treatment of aqueous nuclear waste streams.

The distribution coefficient ( $K_d$ )<sup>34</sup> a measure of extraction, is usually used to assess the extractant in adsorption of nuclear waste. If a solute is introduced into any two-phase system, whether the system is gas/solid, gas/liquid, liquid/liquid, or liquid/solid, it will become distributed between the two phases. After equilibrium is reached, the solute distribution is defined by the distribution coefficient:<sup>#tab;</sup>

$$K_d = \frac{(C_i - C_f)}{C_f} \frac{V}{m}$$

where  $c_i$  and  $c_f$  are the metal ion concentrations before and after extraction,  $V$  is the volume, and  $m$  is the dry weight of the coated (or functionalized) MNPs.

A higher  $K_d$  value implies greater effectiveness of the chelator in capturing and holding the metal ions. The values of  $10^3$  mL/g are considered good, and those above  $10^4$  mL/g are outstanding.<sup>123</sup>

The sorption performance of chemical extractants depends on the pH and ionic strength of the waste stream, which is explained later in the text. These factors are closely related to the surface charge of the particles. Extractant concentration in turn affects the sorption through reaction kinetics. Due to the chemical coordination between the nuclear waste and the extractant, the effects of temperature and sorption time should also be considered.

The sorption process is generally studied by plotting a compound's concentration in the sorbent as a function of either its gas phase or solution concentration, all of which are measured at equilibrium and constant temperature. A classification of isotherms has been reported. Some of them, such as the Langmuir, Brunauer–Emmett–Teller (BET), and Gibbs models, often fail to adequately describe sorption data in the liquid phase. This leaves only Freundlich and linear models as usable fits to the sorption data.<sup>124</sup>

Some research results using MNP-Che processes are compared in Table I. The main process includes adding the MNP-Che complexes into the waste stream, which can be in the reaction chamber or *in situ* as some cases in tanks. To maintain particle suspension, the tank contents can be mixed by mechanical stirring, ultrasonication or other methods. After the required reaction time, physical separation of the particles from the solution can be achieved by using a magnetic field to collect the actinide adsorbed MNP-Che complexes. The left over uncontaminated stream can be removed for safe disposal. A small amount of strip feed is added to the MNP-Che-Actinide complex to separate the actinide from the MNP, allowing the latter to be recycled. Usually a volume reduction (processing waste materials to decrease the space they occupy by biological (composting), mechanical (compacting, shredding), or thermal (incineration, vitrification) means) factor higher than 100 can be achieved. With similar magnetic separation, the MNPs or MNP-che conjugates can be removed magnetically, leaving a condensed form of actinide waste that is ready for final disposal or recycling.

The key element of the technology is the particles' selective adsorption. These composite particles consist of a magnetic core, a polymer coating for durability, and either a "functionalized" resin coating or selective seed materials embedded in the polymer coating.

In this next section, the effects of important parameters on sorption are discussed in detail.

**A. Effect of MNPs and Chelators.** The chemistry between the chelator and the actinides plays a significant role in the sorption of radionuclides. High temperature, concentrated reactant, and catalysts all increase the reaction speed. As the chelator's contact area increases, more sorption sites become available to bind the actinides, consequently increasing the net efficiency of sorption. The sorption capacity of a given chelator may depend on a series of properties, such as particle-size distribution, cation exchange capacity, solution pH, and ionic strength.<sup>125</sup> Examining these properties will both help to predict the partitioning of the various radionuclides in a real system and provide a means to optimize the waste stream

separation using the open gradient magnetic separation (OGMS) system.<sup>126</sup>

OGMS is a type of high gradient magnetic separation system that consists of multiple magnetic field sources.

The sorption efficiency can be also optimized during the chelator conjugation process. As reported by Buchholz et al.,<sup>121</sup> the best  $K_d$  values for Am were obtained for extractants prepared with concentrations in the range of 1.0–1.2 M CMPO in TBP.<sup>121</sup> Particles prepared with lower concentrations produced less homogeneous coatings due to insufficient CMPO, whereas particles prepared with 1.5 M CMPO in TBP remained sticky after heating and did not disperse well. Therefore, coatings prepared with 1.0 and 1.2 M CMPO in TBP yielded high and consistent  $K_d$  values.

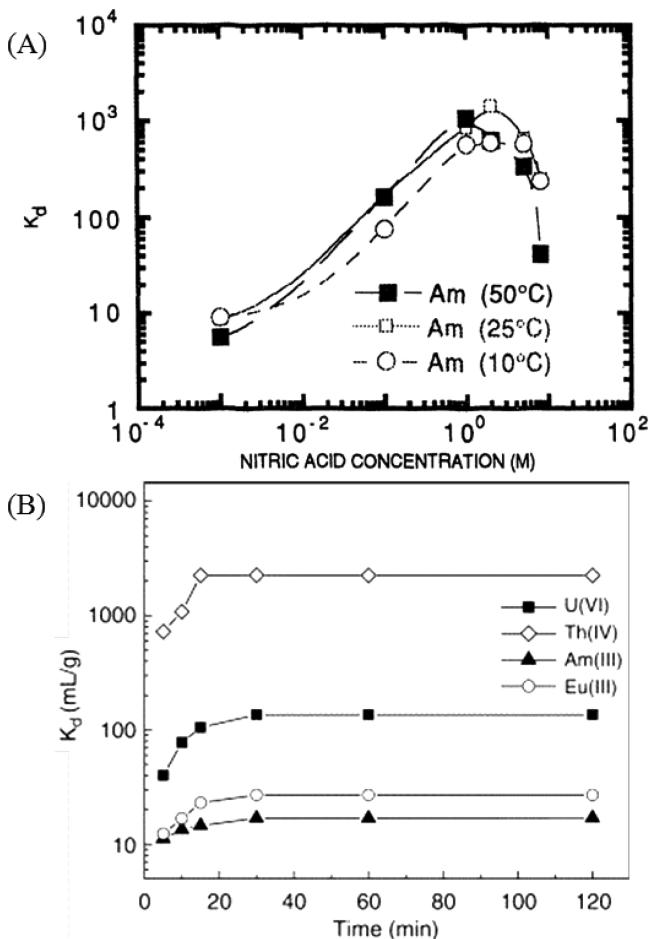
### B. Temperature and Extraction Time. 1. Temperature.

Generally, sorption coefficients decrease with increasing temperature.<sup>127</sup> However, some examples of increasing equilibrium sorption with increasing temperature<sup>128</sup> and no effect of temperature on sorption equilibrium were also found. Chiou et al.<sup>129</sup> observed that an inverse relationship<sup>130</sup> between sorption coefficients and solubilities exists for organic compounds. Lower  $K_d$  values are found at higher temperatures for most organic compounds for which solubility increases with temperature, while increased sorption at higher temperatures can be expected for compounds for which solubility decreases with temperature. Therefore, due to the dependence of both sorption coefficients and solubility on temperature, the measured effect of temperature on sorption isotherms is the combined result of sorption and solubility trends.

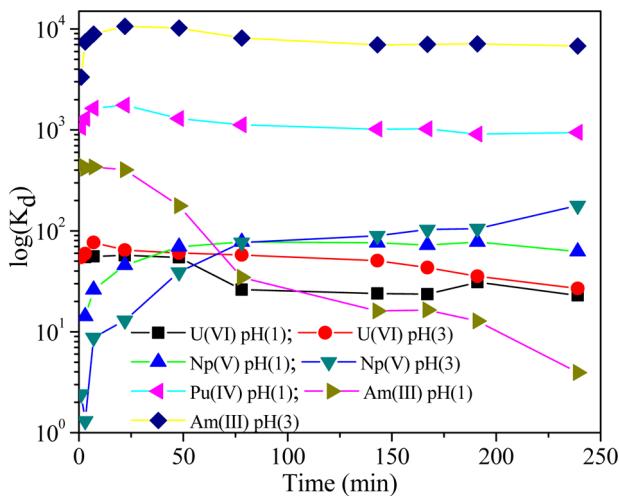
To make the MACS process applicable to wastes that have been stored in tanks for decades, the reaction temperature should be in the range of 20–50 °C. The extraction of americium by 1 M CMPO/TBP coating as a function of nitric acid concentration was analyzed at three different temperatures (10°, 25°, and 50 °C).<sup>31,131</sup> The extraction result of Am in Figure 4A shows that all  $K_d$  curves have the same general shape irrespective of temperature. On the other hand, the  $K_d$  value of many solvent extraction systems decreases with increasing temperature between 0 and 60 °C.<sup>132</sup>

**2. Extraction Time.** The amount of time required to complete extractions differed between solvent types.<sup>133</sup> The separation relies on the chemical reaction between the extractant and the extractor. The kinetics usually reach equilibrium within 1 h. Some extractors show slower kinetics for a certain extractant, which may be related to the viscosity and chemical reaction conditions. Due to these saturation phenomena, the  $K_d$  values are usually not constant and thus only values obtained under identical conditions (concentration in the liquid phase, amount of solid phase) can be compared. It can be seen from Figure 4B that the Cyanex 923-coated<sup>42</sup> magnetic particles exhibit slightly slower uptake kinetics for U(VI) (30 min), Am(III) (30 min), and Eu(III) (30 min) than for Th(IV) (15–20 min). The sorption efficiency of actinides remained the same after 30 min irrespective of contact time or extraction time.

The uptake for various actinides - Am(III), Np(V), Pu(IV) and U(VI) at pH 1, and Am(III), U(VI), and Np(V) at pH 3, by diethylene triamine pentaacetic acid (DTPA) chelator conjugated MNPs (DTPA-MNPs) shows maximum sorption efficiency for Am at pH 3 and Pu at pH 1 in Figure 5. The sorption reaches saturation in less than 7 min and remains stable until total extraction time reaches 4 h.<sup>134</sup>



**Figure 4.** (A) Extraction of Am as a function of temperature for 1 M CMPO/TBP coating;<sup>131</sup> (B) Contact time effect on the separation efficiency of the actinides with (A) Cynax923 and (B) CMPO/TBP.<sup>42,79</sup>



**Figure 5.** Distribution coefficient ( $K_d$ ) as a function of various actinides such as Am(III), Pu(IV), U(VI), and Np(V) by MNPs coupled through DTPA chelator.<sup>134</sup>

**C. Waste Stream Condition.** The separation depends on the pH and ionic strength of the waste stream.

**1. Effect of pH.** Solution pH is the single most important and dominant variable that influences the behavior of metals in the

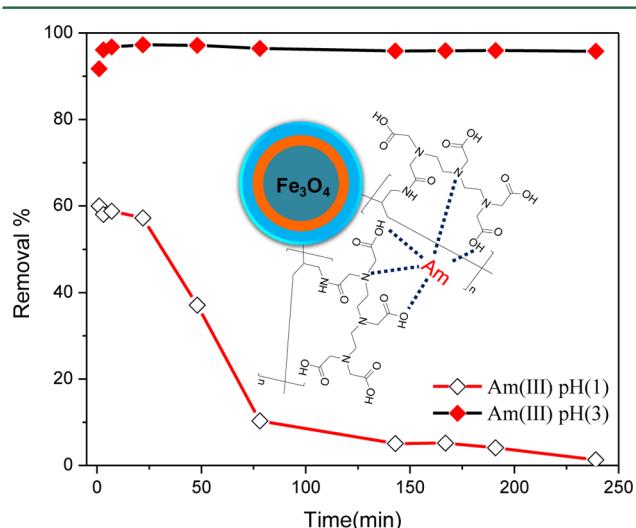
environment, uptake, and percent removal of metal ions from the waste solution, and adsorption rates. The pH determines the surface charge of the adsorbent (organic ion or chelator), the degree of ionization, and the specification of the adsorbate (metal ion). This is partly due to the fact that the hydrogen ion itself is a strong competing adsorbate.<sup>135,136</sup>

The hydroxyl groups present on the MNP's surface give it a cationic nature. As the pH of the solution decreases, the hydronium ion concentration increases, resulting in protonation of surface sites and a net increase in positive charge on the surface. On the other hand, as pH increases, the same surface sites deprotonate and cause the surface to be negatively charged. As a result, free metal cations exhibit near zero adsorption at low pH, and free metal anions exhibit 100% adsorption. Hydroxyl, carbonate, chloro-, etc., complexes change the size and charge (i.e., charge density) of the cation, and that affects the net adsorption efficiency.<sup>137</sup>

For pure mineral phases and natural sediments, U(VI) adsorption tends to increase with increasing pH from pH 3.5 to about 8. At pH > 9 the adsorption declines due to the formation of anionic carbonate/hydroxyl complexes. The increase in adsorption as the pH rises from acidic to neutral is attributed to the opening of sorption sites vacated by the correspondingly decreased proton concentration in clays and mineral surfaces.<sup>138</sup>

The chemistry of Pu is remarkably complex due to its many oxidation states (III, IV, V, VI) in solution, the tendency for Pu(IV) to disproportionate, and the slow rate of reaction of Pu-oxygen species (e.g., PuO<sub>x</sub> and PuO<sup>+</sup>).<sup>139</sup> The  $K_d$  value of Pu studied at four different pH values (8, 10, 12, and 14) shows the maximum at pH 12. Pu removal is decreases if the pH is below 11.5 or above 13.5.<sup>140,141</sup>

The influence of pH on the extraction of actinides like Am(III) at pH 1 and 3 by DTPA-MNPs shows lower removal of Am(III) in highly acidic medium as given in Figure 6.<sup>134</sup> It can be explained either by the degree of protonation of the carboxylate groups of DTPA, which is higher at lower pH (strong acid), or by the stability of the chelator conjugates of MNPs (DTPA-MNP), which might be lesser in high acidic medium.



**Figure 6.** Removal percentage of Am(III) by DTPA-MNPs as a function of sorption time at pH 1 and pH 3. The inset figure shows the MNP coupled by DTPA chelator wraps around Am (III).<sup>134</sup>

Dendrimer-coated magnetic silica particles with picolinamide derivative show strong dependence of Am and Eu extraction on the pH value. The  $K_d$  values for Am and Eu are extremely high at pH 3 compare to those at pH 1 and 2.<sup>142</sup>

Generally sorption increases as pH increases. In order to remove the sorbed species, the pH would need to be adjusted to the acidic range, provided that aging effects are minimal; the fate of sorbed species on oxide surfaces is not well understood, though it is believed that as time passes a slow reaction becomes important.

**2. Ionic Strength Effect.** In general, surface complexation is influenced by pH values, whereas ion exchange is influenced by ionic strength.<sup>143</sup> The ionic strength dependency of the magnetic separation process is important when applying this process to waste streams that carry a wide range of acidities.<sup>144</sup>

The ionic strengths of 0.001, 0.01, and 0.1 M NaNO<sub>3</sub> were chosen to investigate their effect on Th(IV) sorption onto Na-rectorite. The sorption of Th(IV) decreased with increasing ionic strength (Figure 7).<sup>145</sup> This phenomenon could be

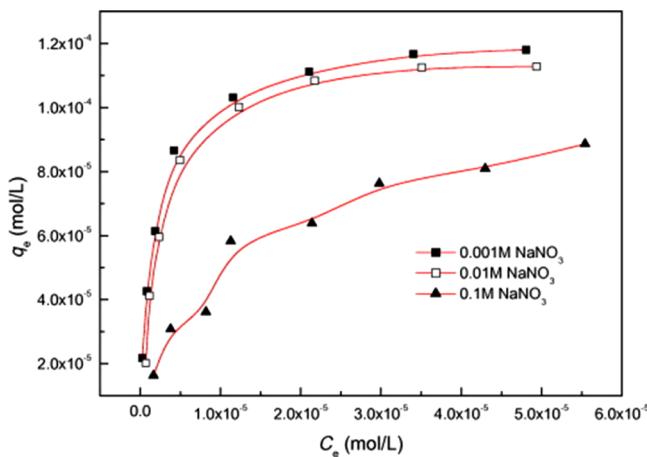


Figure 7. Isotherms of Th (IV) sorption at different ionic strength of NaNO<sub>3</sub>.<sup>145</sup>

attributed to two causes: (1) Th(IV) ions form electrical double layer complexes with Na-rectorite, which favor sorption when the concentration of the competing salt is decreased. This may indicate that the sorption interaction between the functional groups of Na-rectorite and Th(IV) ions is mainly ionic in nature, which is in agreement with an ion exchange mechanism; (2) ionic strength of the solution influences the activity coefficient of Th(IV) ions, which limits their transfer to Na-rectorite surfaces. The sorption of Th(IV) onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in the absence or presence of humic acid (HA)/fulvic acid (FA) was weakly dependent on ionic strength. Jakobsson<sup>146</sup> investigated the sorption of Th(IV) onto bare TiO<sub>2</sub> and found that the sorption was independent of ionic strength. Reiller et al.,<sup>147</sup> studied the sorption of Th(IV) onto hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and goethite ( $\alpha$ -FeOOH),<sup>148</sup> and also found that the sorption of Th(IV) was not strongly influenced by ionic strength in the presence of HA.

## VI. SEPARATION AND RECYCLING OF MNPS

There are two common and simple ways used to separate the complex conjugates of MNPs with actinides from the waste solution: centrifuge<sup>149</sup> and magnetic attraction.<sup>39,150,151</sup> Compared to the centrifuge, magnetic attraction that relies on permanent magnets or electromagnets is more energy efficient

for large quantity applications. After actinide extraction, the particles can be magnetically separated by one of the three methods:<sup>34</sup> (1) placing a magnetic field around the treatment tank, (2) pumping the colloidal solution through a magnetic filter (e.g., commercially available magnetic units), or (3) introducing an electromagnetic device into the tank.

**A. High Gradient Magnetic Separation (HGMS).** A HGMS<sup>30,152,153</sup> system generally consists of a column through which a particle suspension flows. This column is packed with a bed of wires and placed inside an electromagnet. The wires have a high magnetic susceptibility (diameter <50  $\mu$ m), so when a magnetic field is applied across the column, it dehomogenizes. The result is strong field gradients radiating from each wire that attract magnetic particles, trapping them to the wire surfaces. The effectiveness of this system depends on generating strong magnetic field gradients, as well as on the particles' size<sup>154,155</sup> and their magnetic properties.

The magnetic properties are highly dependent on the particle size.<sup>86</sup> Larger particles have higher saturation magnetizations and strong interparticle interaction that can lead to agglomeration. Until now, micrometer scale particles have been used for magnetic separation. Yamaura et al.<sup>156</sup> used silane coated magnetite particles for the sorption of Eu ions, Reddy et al.<sup>42,157</sup> used iron oxide particles (MagaCharc-AA) of size 1–60  $\mu$ m, and Gruttmann,<sup>142</sup> Verboom,<sup>158</sup> Matthews,<sup>159</sup> and Wang<sup>160</sup> et al used magnetic silica particles, whereas Nunez and Kaminski<sup>34,121</sup> used micrometer size cross-linked polyacrylamide entrapped charcoal and magnetite particles for the extraction and separation of lanthanides and actinides from nuclear waste streams. Compared to micrometer size particles, nano size particles have unique properties due to greater surface area relative to volume, which enhances the loading capacity of chelators, thereby extracting many more of ions from nuclear waste. The best particle size for magnetic separation depends on the type of magnetic nanoparticles. Coating and surface functionalization reduces the particles' saturation magnetization; hence the selection of particle size should balance the nonmagnetic coating on particles' surface and their magnetization. Superparamagnetic particles can experience reduction of their net magnetic moment if the thickness of the dead coating (protective coating/polymer/chelator) on the particles' surface exceeds its limit, because the magnetization is measured with respect to the total mass of the particle. The superparamagnetic size limit depends on the type of particles. It is categorized as single domain thermally unstable particles. The size of single domain of particles is given as <sup>161</sup>Fe = 14 nm, Co = 55 nm, Ni = 70 nm, Fe<sub>3</sub>O<sub>4</sub> = 128 nm. Therefore, a particle larger than its superparamagnetic limit is a suitable candidate for magnetic separation. Monodispersity of MNPs also counts for magnetic separation.

Both saturation magnetization and interactions between the particles increase with the size of the ferromagnetic particles. Larger particles interact more than smaller ones. Superparamagnetic particles are not a suitable candidate for magnetic separation because the particles' magnetization drops significantly after surface functionalization and silica coating. Core-shell particles exhibit a higher saturation magnetization and weak interaction between the particles. Even after surface functionalization, core-shell particles show high enough magnetization to magnetically separate out of the solution. Also, the oxide shell carries hydroxide groups that give a strong base to the silica coating.

For HGMS to succeed, the magnetic force attracting the particles toward the wires must dominate all other forces present, including forces due to fluid drag, gravitation, inertia, and diffusion. Typically, HGMS has been used to separate micrometer-scale or larger particles or aggregates. In some cases, MNPs have been used as separation agents; however, these nanoparticles have usually been present as micrometer-scale aggregates or encapsulated in larger polymer beads. Using a larger volume of these particles makes magnetic collection by HGMS (or other means) relatively straightforward.

**B. Stripping of the Actinide.** The physical separation (desorption) of actinides from the complex conjugate of surface functionalized MNPs after sorption is known as stripping. It is a key process to enable the reuse of MNP-Che for future separation of actinides from nuclear waste streams. Successful completion of the stripping process without adversely affecting the MNP-che's sorption efficiency is one of the most important criteria to make this separation method economical and cost-effective. Numerous studies have reported that the recycle of magnetic sorbents (particles) is possible by using appropriate stripping agents, such as strong acid solution<sup>42</sup> or deionized water,<sup>142</sup> to back-extract radionuclides from the particle surface. The stability and reliability of magnetic nanosorbents can be studied by performing sorption/stripping cycles.

In a series of experiments using deionized (DI) water, Eu was back-extracted from the particle surface by shaking the particles in 10 mL water three times, where each time was for 10 min in new water.<sup>142</sup> Generally, more than 90% of Eu activity was recovered by stripping the particles twice with DI water, and no significant decrease of the Eu extraction capacity was observed during 10 extraction/stripping cycles. The activity of extracted and back-extracted Eu at each step is represented in Figure 8.<sup>142</sup> These back-extraction studies demonstrate the feasibility of recycling the particles.

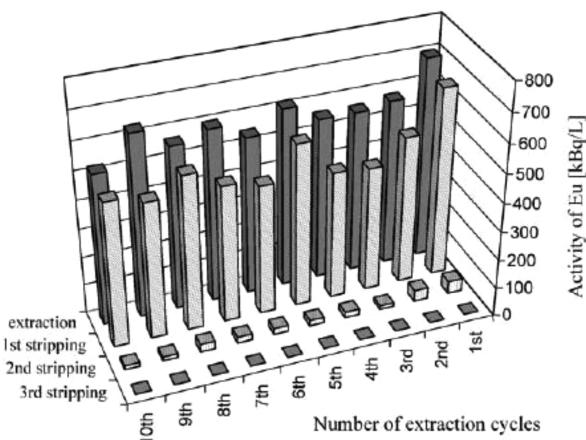


Figure 8. Activity of extracted and back-extracted <sup>152</sup>Eu during 10 extraction/stripping cycles with particles MC1.<sup>142</sup>

The reusability of the MNP-Che is checked using 50% Cyanex 923 coated MNPs<sup>42</sup> and 50% *N,N'*-dimethyl-*N,N'*-dibutyl tetradecyl malonamide (DMDBTDMA)<sup>157</sup> coated MNPs; it is found that after repeated extraction,  $K_d$  drops from 132 (I cycle) to 130 (II cycle) for Cyanex, and 27.94 (I cycle) to 25.90 (II cycle) for DMDBTDMA. These results demonstrate the stability and recycling capacity of the MNP-Che.

## VII. CURRENT STATUS OF SPENT NUCLEAR FUEL

Reprocessing spent nuclear fuel is a key component of nuclear energy, because recovered fissile and fertile materials provides fresh fuel for existing and future nuclear power plants. Russia Japan, and several European countries have policies in place to reprocess nuclear waste, by extracting residual plutonium and uranium and making it into usable fuel. The governments in many other countries have not yet addressed the various aspects of reprocessing or even whether or not to begin it.<sup>162</sup>

Currently, the recycling process is much more expensive than the production of new fuel, but it significantly cuts down on the amount of radioactive waste that must be disposed of. Additionally, recycling allows elements with particularly long half-lives present in the waste to be extracted and reused, ultimately making the waste's storage period much shorter. Research is being conducted in several countries to improve the efficiency and efficacy of reprocessing technologies.<sup>163</sup>

Removing uranium and plutonium from waste and converting the fuel cycle to shorter-lived fission products would eliminate most of the volume of radioactive material that currently requires disposal in a deep geologic repository and drastically diminish the long-term radioactivity in nuclear waste, respectively. However, the waste resulting from reprocessing would have nearly the same short-term radioactivity and heat as the original spent fuel, because recently reprocessed waste consists primarily of the same fission products that are responsible for the near term radioactivity and heat in spent fuel. Since heat is the main limiting factor on repository capacity, conventional reprocessing would not provide major disposal benefits in the near future.

To address that problem, various proposals have been made to further extract the primary heat-generating fission products (Cs, Sr) from high level waste for separate storage and decay.

Current U.S. policy favors direct disposal of high level waste instead of recycling or reprocessing it, because current recycling methods are cost-effective when compared to producing new fuel.<sup>164</sup> The Department of Energy strategy with respect to used nuclear fuel and high-level radioactive waste has two major components: a firm commitment to a once-through fuel cycle and a plan for legislative and administrative action to facilitate safe, permanent disposal. Important elements include institutional and public cooperation to arrange for waste transportation routes and storage facilities, development of a permanent geological disposal site, and a new agency to oversee it all to fulfill the federal government's 1985 contractual obligations.<sup>165</sup>

Now that the Obama administration has canceled plans to build a permanent, deep disposal site at Yucca Mountain in Nevada, spent fuel at the nation's 104 nuclear reactors will likely to remain onsite for years as it continues to accumulate. The Administration has, however, kept the door open to safer recycling methods as used in France.

## VIII. SUMMARY

Nuclear energy can be a safe and cost-effective energy source if the radioactive waste is handled properly. The extraction of primary elements (U, Pu) from waste for reuse can be cost-saving, but extraction of heat generating elements, including Am, Cm, and Np, is an essential first step to any disposal action. Without recycling these minor actinides, no significant reduction in the radiological hazard of the waste can be obtained, and unlike current processes, MNP-Chelator nano-

technology promises to do that. It is an efficient separation technology that uses chelator extractants, covalently bonded to the surface of MNPs, to remove the actinides from nuclear waste solution. The process is intended to (1) reduce the complexity of equipment required for reprocessing (2) facilitate scaling because of its simplicity, (3) target specific minor actinides with highly selective chelators, (4) ease separation, since MNP-chelator conjugates require only a small amount of magnetic field, and (5) recycle the MNPs. Magnetic separation nanotechnology has been summarized with respect to different types of MNPs, their synthesis processes, surface functionalization, sorption conditions, and stripping method.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*(Y.Q.) E-mail: youqiang@uidaho.edu.

### Notes

The authors declare no competing financial interest.

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