

Final Report  
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**Micelle Formation and Surface Interactions in Supercritical CO<sub>2</sub>.  
Fundamental Studies for the Extraction of Actinides from Contaminated Surfaces.**

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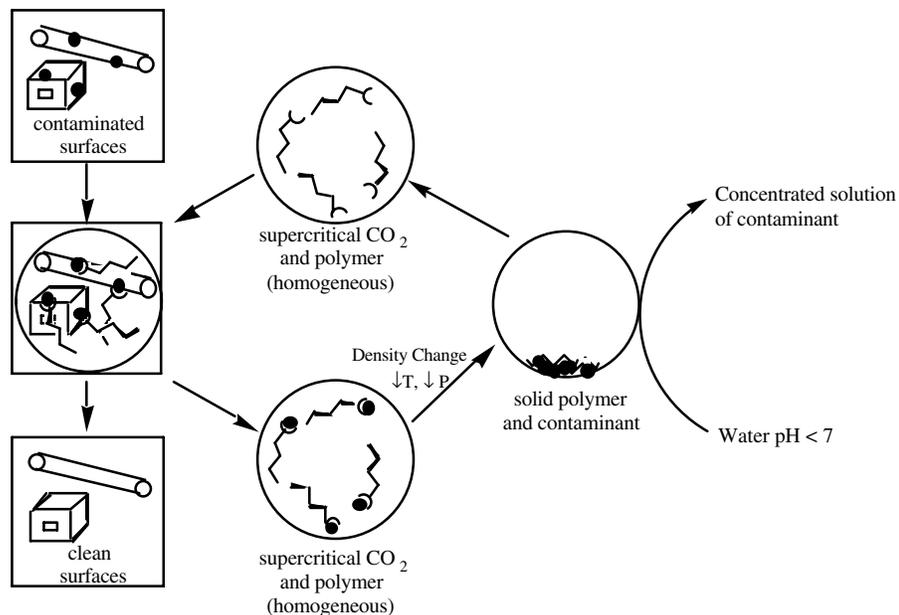
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**Executive Summary:**

This goal of this research was to build the fundamental understanding of microemulsion formation and mobility in supercritical CO<sub>2</sub> necessary to develop an innovative extraction system for selectively removing metals (actinides) from contaminated surfaces. Supercritical CO<sub>2</sub> has many advantages both for extraction from surfaces and minimization of the environmental impact of separation activities. The CO<sub>2</sub> solvent is an environmentally benign, inexpensive, radiologically and oxidatively stable extraction medium. We have studied reverse microemulsions that are comprised of nano-droplets of water (< 100 nm in diameter) suspended in CO<sub>2</sub> by a surfactant. The nano-droplets of water suspended in CO<sub>2</sub> take advantage of both the high solubility of metal ions in water and the high diffusivity of CO<sub>2</sub> to penetrate pores that might be inaccessible to bulk water to aid in the complete decontamination of complex heterogeneous surfaces. The ability to readily control solubility by changing the pressure allows for facile separation of the surfactant and bound metal from the CO<sub>2</sub> solvent, enabling both concentration of the waste and recycle of the carbon dioxide. This extraction scheme is particularly attractive for remediation of heterogeneous waste in which small amounts of metal contaminants are dispersed throughout a large volume of solid waste. Typically, such extractions require an amount of water or solvent proportional to the volume of solid material. With microemulsions, CO<sub>2</sub> is effectively used as a diluent and the amount of water need only be proportional to the amount of metal to be extracted, making it possible to decontaminate grams of waste with μL of water. The stake for new selective separations is very high, as deconstruction and decontamination activities tend to produce large amounts of solid TRU waste. The disposal of TRU waste can exceed thousands of dollars/barrel, resulting in millions

of dollars of added cost to D&D projects. Extraction of actinides from heterogeneous matrices, such as surface-contaminated rubble and debris, would greatly reduce the amount of TRU waste generated. Furthermore, the avoidance of organic or aqueous extractants through the use of  $\text{scCO}_2$  would lead to considerable cost savings through waste minimization of secondary streams.



During the course of the project we have demonstrated that metal ions can be extracted into microemulsions using  $\text{CO}_2$  soluble surfactants consisting of perfluoroether backbones with carboxylate or phosphate head groups. Experimentation has focused on two main issues: understanding the solubilization mechanism of metals into supercritical  $\text{CO}_2$  with regards to micelle formation, and studying the interactions between the extractants and surfaces. We have demonstrated that w/c microemulsions with two types of polyperfluoro- surfactants are capable of extracting copper and europium from a variety of solid substrates. The extractions are facile and result in high ion loadings within the water core. Extractions with microemulsions using only 60  $\mu\text{L}$  of water were shown to be more effective than 100 times the volume of 5% bulk

nitric acid in the case of a wood surface, demonstrating the ability of the microemulsions to penetrate porous materials. Regeneration of the surfactant without loss of capacity was demonstrated by controlling the pressure of the system. The system has slight selectivity for metals that bind to the surfactant relative to alkali metals; future research will focus on improving this selectivity through modifications of the surfactant head group. This new technique offers promise in remediation of solid materials contaminated with heavy metals or radioactive waste.

## Research Objectives:

The goals of this research program included:

- 1. Study solubility of extractants and formation of micelles.**
  - Do surfactants form micelles in scCO<sub>2</sub> and what is the mechanism of their formation?
  - Can the pressure/density of scCO<sub>2</sub> be used to alter surfactant solubility or micelle structure?
  - Can surfactant micelles be used to transport water based microphases?
- 2. Examine the solubilization of metals.**
  - What influence does metal binding have on the surfactant solubility or micelle structure?
  - What is the selectivity of metal binding in promising systems?
  - Are all solubilized metals bound to surfactant ligands or is an entire aqueous micro-environment solubilized by the surfactant/micelle?
  - Can metal species, as charged ions or neutral complexes, be insulated by fluorinated surfactants to enhance solubility in scCO<sub>2</sub>?
- 3. Explore surface interactions with the matrix and mobility of micelles.**
  - What factors affect wetting of heterogeneous matrices (*i.e.*, ligand type, CO<sub>2</sub> pressure)?
  - How deep can surfactants penetrate materials such as concrete?
- 4. Explore surface interactions with the actinide contaminant.**
  - Can surfactant based micelles be used to deliver acidic, aqueous microphases to the actinide surface?
- 5. Evaluate these new systems for metal extraction from a model contaminated surface containing radionuclides or surrogate metals.**
  - What is the rate of extraction?
  - What ratio of ligand to metal is required?

## Methods and Results :

### Introduction

There has been significant recent interest in utilizing supercritical fluids as unique media for a wide range of applications including separations, materials processing, and chemical synthesis. Supercritical fluids offer mass transfer rates that are an order of magnitude higher than liquid solvents. They have zero surface tension, allowing complete wetting of solid surfaces. When using a supercritical solvent, chemical solubility can be tuned across several orders of magnitude by isothermally altering the system pressure.<sup>1,2</sup> Supercritical carbon dioxide (sc CO<sub>2</sub>) is the most frequently used solvent in supercritical fluid technology<sup>3</sup> because it offers the transport and tunability properties of a supercritical fluid in an economic, environmentally benign form. CO<sub>2</sub> is inert, nontoxic, nonflammable and abundantly available at low cost. It is currently used as a replacement for organic solvents in a variety of applications, ranging from analytical extractions to industrial processes including the extraction of caffeine and hops.<sup>4</sup>

Our interest lies in using sc CO<sub>2</sub> as a solvent for metal extractions. Direct extraction of metal ions into sc CO<sub>2</sub> is not possible because of charge neutralization requirements and weak solvent-solute interactions. Because carbon dioxide is non-polar, highly soluble modifiers such as methanol or tri-n-butylphosphate have been used to increase solvent dielectric. Addition of such modifiers to supercritical CO<sub>2</sub> alters the polarity of the fluid phase, enhancing the extraction of metals.<sup>5,6</sup> Although the addition of polar modifiers can be effective for enhancing solubility, this reduces the environmental benefits of using carbon dioxide as a solvent.

Metal extraction with sc CO<sub>2</sub> can also be facilitated by converting metal ions into neutral metal complexes.<sup>7,8</sup> Complexing agents added to the supercritical fluid phase can neutralize the charge on the metal ion and successfully extract a wide range of metal species from both liquid and solid matrices.<sup>3,7-13</sup> Extraction efficiencies are often limited by poor solubility of ligands and ligand/metal complexes in sc CO<sub>2</sub>.<sup>3</sup> It has been shown that fluorination of ligands tends to enhance the solubility of both the ligand and metal/ligand complex.<sup>7</sup> More recently, Beckman and coworkers have shown that attaching moieties consisting of either highly fluorinated or polysiloxane oligomer groups to ligands can dramatically increase the solubility of the resulting metal complex.<sup>9,3,14</sup> It has been demonstrated that solubility of the metal ligand complex in supercritical fluids plays a more important role than the solubility of the ligand as long as

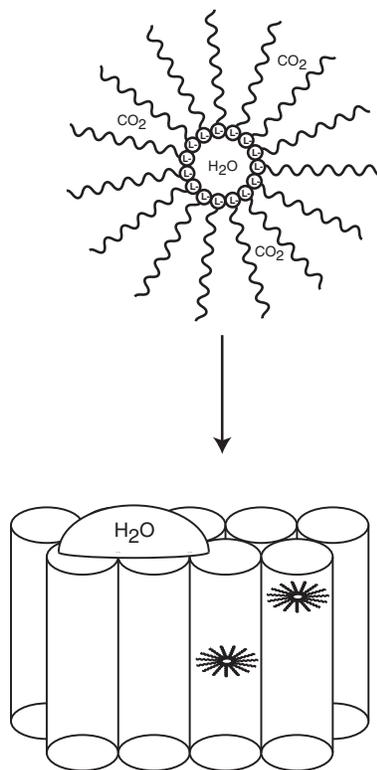


Figure 1. A water-in-CO<sub>2</sub> microemulsion with a negatively charged head group on the surfactant. The microemulsion penetrates pores of solid materials where the surface tension of a water droplet would keep it on the surface.

sufficient amount of ligand is present in the fluid phase.<sup>7</sup> These methods depend on directly enhancing complex solubility without compromising metal affinity (*i.e.*, though the addition of electronegative groups close to ligating heteroatoms).

Our approach is fundamentally different in that water-in-carbon dioxide (w/c) microemulsions are used to solubilize metals.<sup>15</sup> Perfluoropolyether ammonium carboxylate surfactants are known to stabilize water-in supercritical carbon dioxide microemulsion droplets.<sup>16</sup> The polyether surfactant associates in solution to form a reverse micelle with the hydrophilic carboxylic acid groups in the core. At certain temperatures, pressures, and surfactant concentrations, such micelles spontaneously self assemble and are thermodynamically stable in solution. At certain water-to-surfactant ratios ( $w_0$ ), water will be incorporated into the core of the micelle, generating a nanodroplet of water in a carbon dioxide solution. These droplets are extremely small, ranging from 1 to 10 nm in diameter,<sup>17</sup> meaning that the resulting microemulsion may retain the excellent diffusivity and transport properties of the supercritical fluid (Figure 1). The water is carried to surfaces by the supercritical fluid phase, allowing extraction of metals in a way not possible with an aqueous solution.

We describe the use of water-in-carbon dioxide microemulsions to extract copper and europium from filter paper, wood, cement, and activated carbon. The metal is concentrated into the nanodroplets of water, allowing easy separation of the metal from the spiked substrates. The microemulsions allow for contact even into small pores of the substrates not accessible to bulk water. Microemulsions are especially advantageous for the extraction of metals from heterogeneous waste, because the amount of water required is only proportional to the amount of metal to be extracted, not to the amount of waste to be cleaned. The result is that grams of waste can be cleaned with  $\mu\text{L}$  of water. The w/c microemulsions can also be readily broken by adjusting the  $\text{CO}_2$  pressure and adding additional water to the system, allowing phase separation of the extracted contaminant and the  $\text{CO}_2$ . This has the potential to provide an easy recycle system if the metal can be kept in the small water phase and the surfactant in the  $\text{CO}_2$  phase.

#### Experimental Section

**Materials.** Perfluoropolyether surfactants with the general formulas  $\text{CF}_3(\text{OCF}(\text{CF}_3)\text{CF}_2)_n\text{O}-\text{CF}_2\text{COOH}$  (PFPE-COOH, avg. MW = 650 amu) and  $\text{Cl}(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_n\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$  (PFPE- $\text{CH}_2\text{OH}$ , avg. MW = 600 amu) were obtained from Ausimont and distilled into three fractions:  $n = 1$  and 2,  $n = 3$ , and  $n = 4$ . The ammonium salts of the purified  $n = 3$  (MW = 678  $\text{g mol}^{-1}$ ),  $n = 4$  (MW = 844  $\text{g mol}^{-1}$ ), and of the undistilled carboxylic acid were synthesized based on the procedure by Johnston<sup>16</sup> by neutralization with excess 30 wt % aqueous ammonia, followed by vacuum rotary evaporation to remove residual ammonia and drying in a vacuum oven at 60°C for several days. The surfactant, Fluorolink 7004<sup>®</sup>, with the general formula  $\text{Cl}(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_n\text{CF}_2\text{COOH}$  (avg. MW = 600 amu) was obtained from Ausimont and used as received.

Copper (II) nitrate hemipentahydrate (FW = 232.59  $\text{g mol}^{-1}$ , Baker), copper (II) nitrate trihydrate (FW = 241.60  $\text{g mol}^{-1}$ , Strem), europium (III) chloride hexahydrate (FW = 366.41  $\text{g mol}^{-1}$ , Acros), anhydrous europium (III) chloride (FW = 258.32  $\text{g mol}^{-1}$ , Acros), europium (III) oxide (American Potash and Chemical), calcium chloride (Aldrich), sodium chloride (Acros), nitric acid (trace metal grade, Fisher), filter paper (Whatman Qualitative No. 5), activated carbon (Norit A powdered decolorizing carbon, Acros), and Portland cement were used as received. Wood dowels (1/8 in. diameter) were purchased at a local hardware store and used as received. Supercritical fluid grade  $\text{CO}_2$  (Matheson) was passed through Alltech oxygen, water and

hydrocarbon traps prior to use. Nanopure water (Barnstead >18 M $\Omega$ ·cm) was used in all experiments.

PFPE phosphonic acid (PFPE-PO(OH)<sub>2</sub>) was prepared from the n = 3 fraction of the PFPE alcohol (MW = 626 g mol<sup>-1</sup>) by first refluxing with a 1.5 molar ratio of thionyl chloride (Acros) for 48 h to form the alkyl chloride. This was converted to the diethyl phosphonate by reflux with a 4/3 molar ratio of triethyl phosphate for 24 h. The ether groups were removed by stirring with 3 equivalents of trimethylsilyl bromide (Acros) under argon for 16 h at room temperature and 3 h at reflux. The phosphonic acid was formed upon addition of water, forming a gel. Ethanol (Aldrich) and hydrochloric acid (Fisher) were added to dissolve the gel, then the phosphonic acid was extracted into trifluorotrichloroethane (Fisher). <sup>31</sup>P NMR and FT-IR were used to confirm the structure. The ammonium salt of PFPE phosphonic acid was prepared according to the same procedure as the carboxylic acid.

**Methods.** Water in carbon dioxide microemulsions were formed in a stainless steel variable volume view cell (2 in. outside diameter, 1 1/16 in. inside diameter, 28 mL total volume) fitted with a sapphire window (1 in. diameter, 3/8 in. thick) along the cell axis for visual observation.<sup>18</sup> One cell was equipped with two additional sapphire windows (5/8 in. diameter, 1/8 in. thick) perpendicular to the axis with 180° separation so that UV-Vis spectra of the cell contents could be collected.<sup>19</sup> Another cell was equipped with three 5/8 in. sapphire windows mounted perpendicular to the cell axis with 90° separation enabling collection of steady state emission and lifetime data.

Water or dilute nitric acid and PFPE surfactant were loaded into the view cell prior to sealing. Carbon dioxide was added to the cell with a computer-controlled syringe pump (ISCO, model 100DX). Pressure was controlled by the syringe pump with carbon dioxide as the pressurizing fluid behind a movable piston inside the view cell. Temperature was controlled by wrapping the cell with heating tape.

For extractions, the substrate (filter paper, activated carbon, wood, or cement) was loaded into a separate 3 mL extraction cell (ISCO, model EX-62030) which was also wrapped in heating tape. The pre-formed microemulsion from the view cell was circulated through the substrate in the extraction cell by an HPLC pump (Eldex, model AA-100-S). All experiments were conducted at 207 bar and 45°C. Following extraction, the extraction cell was flushed with at least 50 mL of neat CO<sub>2</sub> at 45°C to remove residual surfactant.

**Analytical Methods.** The substrates were digested in a CEM MDS 2000 microwave with nitric acid or aqua regia (activated carbon) according to CEM methods. Copper and europium concentrations in the digestates were determined on a Thermell Jarell Ash 61E Purge Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) using a modified EPA SW-846 6010B procedure. Extraction percents were calculated based on the ratio of metal remaining on the substrate to that of the spiked substrate. Spiked loadings were determined by averaging the results of multiple digestions of the spiked substrate. Results stated with an error indicate an average and standard deviation from three or more determinations.

NMR spectra were obtained on a 300 MHz Varian instrument. UV-Vis spectra were obtained on a Hewlett-Packard model 8453 spectrophotometer. FT-IR were collected on Nicolet Instruments Co. Avatar 360 ESP. Emission and lifetime data were collected on a Photon

Technology International GL-3300 fluorimeter with an R955 photomultiplier tube and a GL-302 nitrogen dye laser.

**Determination of the Extinction Coefficient and Copper Solubility.** To determine  $\lambda_{\max}$  and maximum solubility for copper in a w/c microemulsion, 100 mg of dry  $\text{Cu}(\text{NO}_3)_2$  were added to the view cell with  $n = 3$  PFPE- $\text{COO}^-\text{NH}_4^+$  (1.2 wt %) <sup>1</sup> and water ( $w_0 = 5$ ) <sup>2</sup> to form microemulsions in the presence of excess copper. UV-Vis spectra were taken at 15 min. intervals for 2.5 h. To determine the extinction coefficient, 10 mg of dry  $\text{Cu}(\text{NO}_3)_2$  was added to the view cell under the same conditions to give a known concentration of 2.8 mM  $\text{Cu}^{2+}$  in the front of the cell. A UV-Vis spectrum was taken after 1.5 h. All spectra were baseline corrected to account for light-scattering from the view cell.

**Europium Luminescence.** Microemulsions were formed with PFPE- $\text{COO}^-\text{NH}_4^+$  (1.2 wt %),  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  ( $w_0 = 5$ ), and 10 mg anhydrous  $\text{EuCl}_3$  (4 mM  $\text{Eu}^{3+}$ ). PFPE- $\text{PO}(\text{OH})_2$  (1.2 wt %) and 5 mg of anhydrous  $\text{EuCl}_3$  (2 mM  $\text{Eu}^{3+}$ ) was solubilized in 15 mL of sc  $\text{CO}_2$ . Steady state emission was observed from 570 nm to 650 nm with excitation at 394 nm. Luminescence lifetimes were monitored at 615 nm. All spectra were corrected for lamp intensity.

**Copper and Europium on Filter Paper.** One quarter sections of 7.0 cm Whatman 5 filter paper were spiked with 30.0  $\mu\text{L}$  of a 0.79 M  $\text{Cu}(\text{NO}_3)_2$  stock solution to yield 1.5 mg of  $\text{Cu}^{2+}$  (ICP-AES analysis of spiked filters indicated that the actual amount of copper deposited was  $1.4 \pm 0.1$  mg of  $\text{Cu}^{2+}$ ). The stock solution was added dropwise by syringe and the papers were dried in air at ambient temperature for at least 24 h. Microemulsions for extraction were formed with the  $n = 3$  or  $n = 4$  PFPE- $\text{COO}^-\text{NH}_4^+$  surfactant (1.2 wt %) and water ( $w_0 = 5$ ). Extraction proceeded for 1.5 h and was followed with UV-Vis spectroscopy.

Europium filters were spiked with 100  $\mu\text{L}$  of a 0.3 M  $\text{EuCl}_3$  stock solution to deliver 5 mg of  $\text{Eu}^{3+}$  (ICP-AES analysis of spiked filters indicated that the actual amount of europium deposited was  $3 \pm 1$  mg of  $\text{Eu}^{3+}$ ). The stock solution was added dropwise by syringe in two-50  $\mu\text{L}$  aliquots and the papers were dried in air at ambient temperature for at least 24 h. Microemulsions for extraction were formed with  $n = 3$  PFPE- $\text{COO}^-\text{NH}_4^+$  (2.0 wt %) and water ( $w_0 = 5$ ). Extraction was also attempted with PFPE- $\text{PO}(\text{O}^-)(\text{NH}_4^+)_2$  (2.0 wt %) and water ( $w_0 = 10$ ). Extraction proceeded for 2 h and was monitored by steady-state emission spectroscopy from 550 nm to 650 nm with excitation at 395 nm.

**Copper and Activated Carbon.** Activated carbon was spiked by mixing 15 g of the activated carbon with 98 mL of 0.05 M  $\text{Cu}(\text{NO}_3)_2$  in a shaker for 48 h. The carbon was removed by filtration and then dried in a vacuum oven. Analysis of digested carbon samples showed the actual loading to be  $25 \pm 2$  mg  $\text{Cu}^{2+}$  per gram. Microemulsions for extraction were formed with  $n = 3$  PFPE- $\text{COO}^-\text{NH}_4^+$  (1.4 wt %) and either water, 5%  $\text{HNO}_3$ , or 20%  $\text{HNO}_3$  ( $w_0 = 5$ ) and with Fluorolink 7004<sup>®</sup> (2.0 or 6.0 wt %) and either water or 20%  $\text{HNO}_3$  ( $w_0 = 3$ ). Extraction was conducted for 2 or 6 h from 150 mg samples.

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<sup>1</sup> Weight percent = grams surfactant  $\div$  (grams surfactant + grams  $\text{CO}_2$  + grams  $\text{H}_2\text{O}$ )

<sup>2</sup>  $w_0$  = moles  $\text{H}_2\text{O}$   $\div$  moles surfactant

**Europium and Wood.** 1.0 cm pieces of a 1/8 in wooden dowel were spiked by soaking in a 0.08 M  $\text{EuCl}_3$  stock solution for 100 h followed by drying in a vacuum oven at  $120^\circ\text{C}$  for 3h. The europium loading as determined by ICP-AES analysis was  $0.8 \pm 0.3 \text{ mg Eu}^{3+}$ . Microemulsions for extraction were formed with  $n = 3$  PFPE- $\text{COO}^-\text{NH}_4^+$  (1.5 wt %) and water ( $w_0 = 5$ ). Extraction was conducted for 2 h from a sample of three wood pieces.

**Europium and Cement.** Portland cement ( $3\text{CaO SiO}_2, 2\text{CaO SiO}_2, 3 \text{CaO Al}_2\text{O}_3, 4\text{CaO Al}_2\text{O}_3\text{Fe}_2\text{O}_3$ ) was spiked by taking 3.998 g of Portland cement and mixing it with 0.121 g of  $\text{Eu}_2\text{O}_3$  and 3 mL of  $\text{H}_2\text{O}$ . The mixture was left to harden for 24 h and then crushed into small pieces. The europium loading as determined by ICP analysis of three 100 mg aliquots of spiked cement was  $23 \pm 1 \text{ mg Eu}^{3+}$  per gram of cement. Extraction from 0.500 g of spiked cement was attempted for 24 h with PFPE- $\text{PO}(\text{OH})_2$  (1.5 wt %) and with undistilled PFPE- $\text{COO}^-\text{NH}_4^+$  (1.4 wt %) and 10%  $\text{HNO}_3$  ( $w_0 = 6$ ).

**Regeneration of Surfactant.** Microemulsions were formed with  $n = 3$  PFPE- $\text{COO}^-\text{NH}_4^+$  (1.5 wt %) and water ( $w_0 = 5$ ) and passed over 10 mg of dry  $\text{Cu}(\text{NO}_3)_2$  in the extraction cell for 3 h dissolving most of the copper. Circulation was stopped, isolating the dissolved copper in the view cell. To break the emulsion, 150  $\mu\text{L}$  of water was injected into the view cell and the pressure was slowly stepped down to 1514 psi upon which the aqueous phase and the surfactant-copper complex settled to the bottom of the cell. The uncomplexed surfactant was left in the upper  $\text{CO}_2$  phase. The copper was removed by venting the lower phases through a small port at the bottom of the view cell. The view cell was slowly depressurized, reloaded with water, and repressurized to 3190 psi to form a microemulsion with the remaining surfactant. The sample cell was loaded with 34 mg of  $\text{Cu}(\text{NO}_3)_2$ , reattached to the circulation line, and extracted for 4 h.

**Competition Experiments.** Competition between extraction of  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  from filter paper was investigated by further spiking three copper loaded filters with  $\text{CaCl}_2$  to yield molar  $\text{Cu}^{2+}$ :  $\text{Ca}^{2+}$  ratios of 1:1, 1:10, and 1:50 (120  $\mu\text{L}$  of 0.20 M  $\text{CaCl}_2$ , 120  $\mu\text{L}$  of 2.0 M  $\text{CaCl}_2$ , 240  $\mu\text{L}$  of 4.9 M  $\text{CaCl}_2$ ). The  $\text{CaCl}_2$  was added dropwise in 60  $\mu\text{L}$  aliquots and the papers were dried in air at ambient temperature for 24 h. The paper with a 1:50 loading was additionally dried in the vacuum oven for 2 h. The extraction procedure was the same as described above for filters.

Relative selectivity between  $\text{Eu}^{2+}$  and  $\text{Ca}^{2+}$  was determined by loading the extraction cell with a 1:10 molar ratio of the chloride salts (0.020 g  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ : 0.086 g  $\text{CaCl}_2$ , 0.020g  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ : 0.092 g  $\text{CaCl}_2$ ). A microemulsion with  $n = 3$  PFPE- $\text{COO}^-\text{NH}_4^+$  (1.2 wt %) and water ( $w_0 = 5$ ) was generated and pumped through the extraction cell for 2 h. Following extraction, the extraction cell contents were dissolved in 50 mL of 5%  $\text{HNO}_3$  and analyzed by ICP-AES.

## Results and Discussion

### *Intracellular Structure/ Localization of Metal Ions*

The extinction coefficient at 744 nm for  $\text{Cu}(\text{NO}_3)_2$  in the PFPE ammonium carboxylate microemulsion was determined to be  $43 \text{ M}^{-1}\text{cm}^{-1}$ . The maximum solubility of  $\text{Cu}^{2+}$  was determined to be 11 mM in 15 mL of  $\text{CO}_2$  or 0.66 moles  $\text{Cu}^{2+}$  per mole of surfactant. This corresponds to an effective concentration of 2 M  $\text{Cu}^{2+}$  within the water phase. The  $\lambda_{\text{max}}$  for

copper in a w/c microemulsion was found to vary from 732 nm to 761 nm, based on the concentration of copper in the microemulsion. Control experiments with copper dissolved in glacial acetic acid demonstrated that the copper absorption shifts rapidly toward the red as water is added. In glacial acetic acid  $\lambda_{\max} = 684$  nm, in a solution of 95 % acetic acid  $\lambda_{\max} = 710$  nm and in a solution of 90 % acetic acid  $\lambda_{\max} = 770$  nm; the  $\lambda_{\max}$  continues to shift to 808 upon

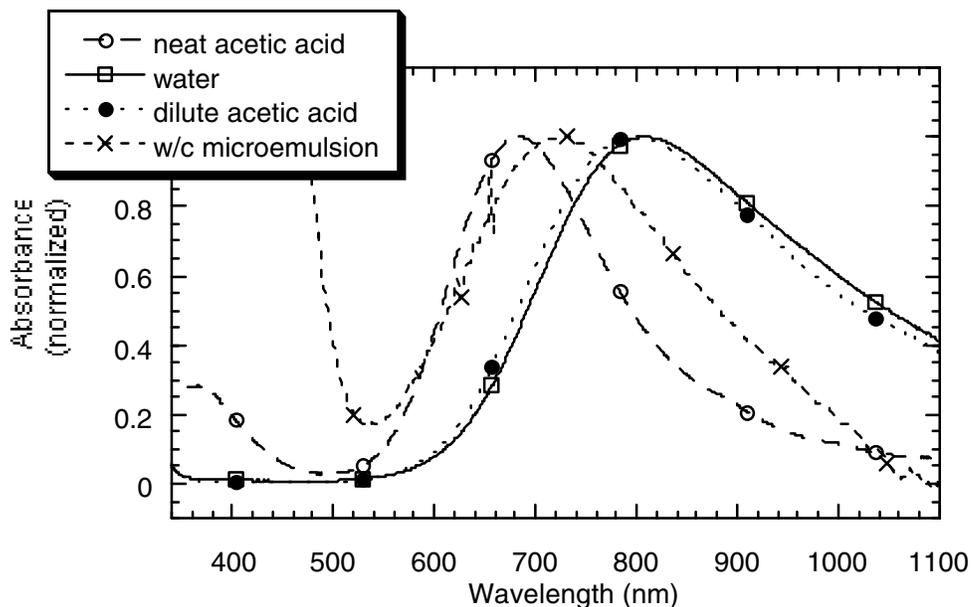


Figure 2. Normalized absorption spectra of copper nitrate in water, glacial acetic acid, dilute acetic acid, and a w/c microemulsion. The blue shift in the Cu absorption in the w/c microemulsion relative to water indicates that the copper is bound to the carboxylate groups on the surfactant.

further dilution (closed circles). At low concentrations of copper,  $\lambda_{\max}$  is closer to that of copper(II) dissolved in 95% acetic acid, while at higher concentrations it shifts to that of 90 % acetic acid (Figure 2). The changing  $\lambda_{\max}$  may be due to two populations of copper, one that is strongly interacting with the surfactant, and one that is in the aqueous core of the microemulsion. At higher copper concentrations, the excess copper must go into the aqueous phase because the number of acetate binding sites are limited. At low concentrations, there is a drop in absorbance of the 740 nm band with a correlated rise in absorbance of a higher energy band at 384 nm. The 384 nm band is also observed in the neat copper acetate spectrum (in glacial acetic acid) and not in any other copper spectrum.

To further probe metal ion interactions in the microemulsion, emission spectra and luminescent lifetimes were obtained for anhydrous europium chloride in a microemulsion with  $n = 3$  PFPE-COO<sup>-</sup>NH<sub>4</sub><sup>+</sup> and water,  $n = 3$  PFPE-COO<sup>-</sup>NH<sub>4</sub><sup>+</sup> and D<sub>2</sub>O, and PFPE-PO(OH)<sub>2</sub> alone. Figure 3 shows the emission spectrum of europium in a  $n = 3$  PFPE-COO<sup>-</sup>NH<sub>4</sub><sup>+</sup> w/c microemulsion compared to that of a aqueous europium solution at ambient conditions. The increase in emission intensity of the 615 nm band indicates that the center of inversion which is

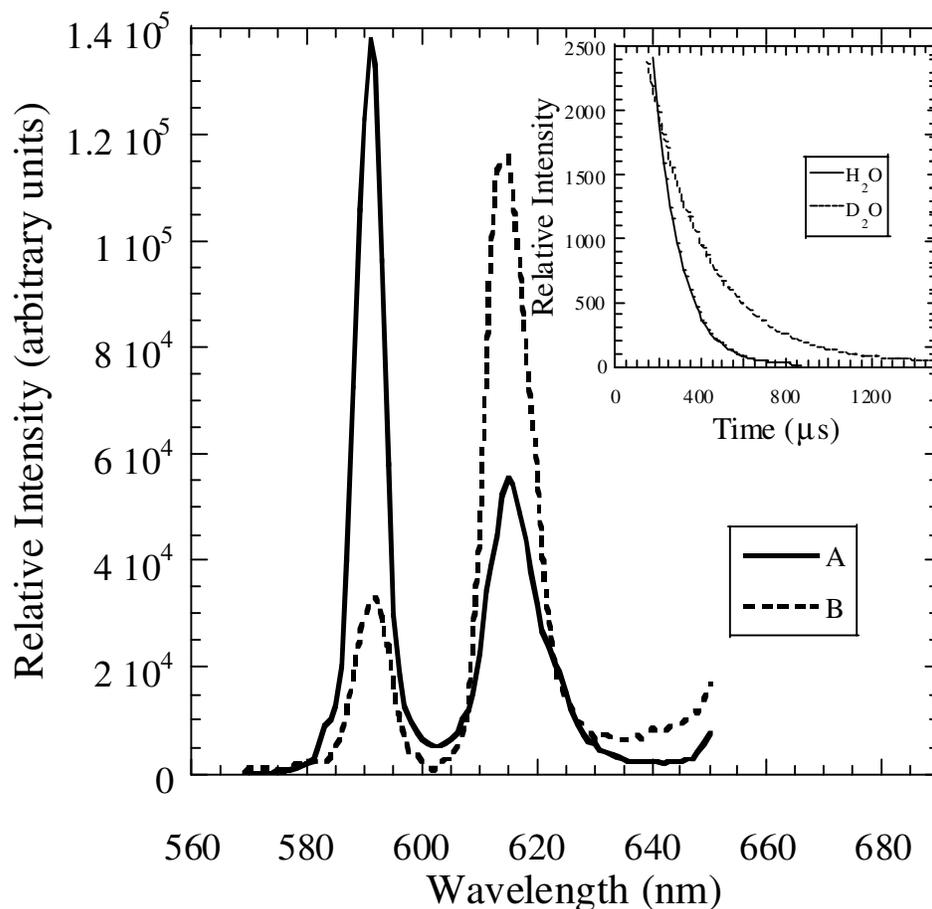


Figure 3. Emission spectra of europium (III) ion in: (A) H<sub>2</sub>O solution at ambient conditions, (B) the water/CO<sub>2</sub> microemulsion. The inset shows the fluorescence decay curves for Eu<sup>3+</sup> in the microemulsion formed with H<sub>2</sub>O and D<sub>2</sub>O.

present for the fully hydrated europium ion is gone due to displacement of water from the first hydration sphere.<sup>20, 21, 22</sup> The symmetry around the europium ion can only be broken by direct binding of the carboxylate head groups of the surfactant. Further evidence for such interactions comes from comparing the lifetime of europium in w/c microemulsions formed with H<sub>2</sub>O and D<sub>2</sub>O, as shown in the inset of figure 3. The lifetime of europium in the w/c microemulsion was found to be 120 μs; when D<sub>2</sub>O is used, the lifetime increases to 274 μs.<sup>15</sup> Using the equation:  $n = C^* (1/\tau_H - 1/\tau_D)$ , where  $n$  is the number of water molecules in the first hydration sphere,  $C$  is a constant (1.05 for Eu),  $\tau_H$  is the lifetime in H<sub>2</sub>O, and  $\tau_D$  is the lifetime in D<sub>2</sub>O,<sup>20,23</sup> the observed isotope effect indicates that approximately 5 water molecules are present for the europium ion in the w/c microemulsion as compared to 8 or 9 for the fully hydrated ion. This again supports the idea that at least two surfactant molecules are bound to the europium ion. When no water is present, as in the case of a dry micelle formed with PFPE-PO(OH)<sub>2</sub>, the lifetime increases to 2100 μs. The extended lifetime in the absence of an aqueous-based microemulsion indicates that there is deactivation in the microemulsion in addition to that provided by the O-H or O-D stretch.

The deactivation could be due to stretching of the PFPE- surfactant end group or to Eu-Eu effects in the forced proximity of the microemulsion.

### **Extractions: Filter Paper**

Almost complete extraction of both copper and europium from filter paper is accomplished with PFPE-COO<sup>-</sup>NH<sub>4</sub><sup>+</sup> (Table 1). The amount of metal spiked onto the filter paper was approximately one-tenth of the capacity of the microemulsion, resulting in a 0.3 M solution of copper in the microemulsion core. Extraction is complete in less than one hour, demonstrating

<b>Metal ion</b>	<b>Surfactant</b>	<b>w<sub>0</sub></b>	<b>Percent Extracted</b>
Cu <sup>2+</sup>	None (CO <sub>2</sub> alone)	0	0
	n = mixed PFPE-COO <sup>-</sup> NH <sub>4</sub> <sup>+</sup>	5	99.6 <sup>a</sup>
	n = 3 PFPE-COO <sup>-</sup> NH <sub>4</sub> <sup>+</sup>	0	26 ± 3
		2	98 ± 2
		5	99 ± 1
n = 4 PFPE-COO <sup>-</sup> NH <sub>4</sub> <sup>+</sup>	5	99 ± 1	
Eu <sup>3+</sup>	n = 3 PFPE-COO <sup>-</sup> NH <sub>4</sub> <sup>+</sup>	5	94 ± 2
	PFPE-PO(O <sup>-</sup> ) <sub>2</sub> (NH <sub>4</sub> <sup>+</sup> ) <sub>2</sub>	5 <sup>b</sup>	98

<sup>a)</sup> From reference 15

<sup>b)</sup> w<sub>0</sub> is approximate, solid particles remained in cell after microemulsion formation.

Table 1. Extraction of copper and europium from Whatman 5 filter paper using w/c microemulsions. The w/c microemulsion extracts the metal ions without wetting the filter paper.

excellent kinetics of contact between the water core and the paper substrate. This is in contrast to polymer-based ligands in CO<sub>2</sub>, which have very slow extraction kinetics, on the order of hours to days.<sup>24,25</sup> Remarkably, the water of the micelle core can interact with metals on the cellulose acetate filter, yet the water is not adsorbed into the filter matrix. All components of the w/c microemulsion are required for complete extraction. Not surprisingly, no copper is extracted in the absence of surfactant and water, as copper is not soluble in carbon dioxide. Only a small amount of copper, 26 %, is extracted in the absence of water. In this case, the surfactant serves simply as a ligand, solubilizing small amounts of copper in the CO<sub>2</sub> phase. The best extraction percentages are achieved in the presence of water and surfactant, when a droplet of water formed in the microemulsion generates a micro-environment that is compatible with high metal loading. Roughly the same extraction amount is seen for a w<sub>0</sub> of 2 as compared to a w<sub>0</sub> of 5. These results suggest that water is important for extraction from a solid matrix although only a minimum is required. The surfactant length did not influence extraction percentages. Extraction is unchanged at 99 % with the n = 3 or n = 4 ammonium carboxylate as compared to the undistilled surfactant.<sup>15</sup> As long as a stable microemulsion forms, extraction seems to be limited only by the number of charged species in the water core and the number of ligand sites.

Europium extraction with the ammonium carboxylate surfactant was not as complete as with copper, at 94 %. Replacement of the carboxylate end group with a phosphonate, which forms a more stable europium complex, increases the extraction percentage to 98 %. The phosphonate surfactant, however, did not form as stable a microemulsion as the carboxylic acid. The solution was not completely clear, indicating that some component was not solubilized into the microemulsion; possibly a by-product of the surfactant synthesis or small water droplets that were not stabilized in a microemulsion.

### Extractions: Activated Carbon

Activated carbon was chosen as a substrate for extraction as it represents a more challenging medium for environmental remediation applications in which the metal ions are chemically bound to the matrix. Table 2 shows the results of extraction from activated carbon using PFPE-COO<sup>-</sup>NH<sub>4</sub><sup>+</sup> and Fluorolink 7004<sup>®</sup> with different aqueous phases. With PFPE-COO<sup>-</sup>

Surfactant	Aqueous Phase	Number of Extractions	Percent Extracted
n = 3 PFPE-COO <sup>-</sup> NH <sub>4</sub> <sup>+</sup> (w <sub>0</sub> = 5, 1.4 wt %)	5% HNO <sub>3</sub>	1	16
	20% HNO <sub>3</sub>	1	25
		2	57
Fluorolink <sup>®</sup> (w <sub>0</sub> = 3, 2.0 wt %)	None	1	37
	H <sub>2</sub> O	1	39
	20% HNO <sub>3</sub>	1	37 ± 2
		1 (6 h)	51

Table 2. Extraction of copper from activated carbon using either water or various concentrations of nitric acid as the polar phase of the w/c microemulsion.

NH<sub>4</sub><sup>+</sup>, extraction increased from 16 % to 25 % of the loaded copper when using 5 % and 20 % nitric acid, respectively. The acid disrupts interactions between Cu<sup>2+</sup> and the carboxylate groups on the activated carbon. Two sequential extractions remove 57 % of the copper, implying that extraction is limited by the capacity of the microemulsion rather than the intractability of the copper in the activated carbon matrix. Higher wt % loadings of surfactant may result in better extraction percentages. However, when PFPE-COO<sup>-</sup>NH<sub>4</sub><sup>+</sup> w/c microemulsions are formed with acid rather than distilled water, a small amount of aqueous material remains outside the microemulsions. This water, which remains as a tiny droplet visible on the side of the high-pressure cell, obviously does not interact with the activated carbon and lowers the total extraction capacity of this system.

Fluorolink 7004<sup>®</sup> is a better surfactant for activated carbon extraction because it forms microemulsions with nitric acid at a w<sub>0</sub> of 3 with no water exclusion. Extraction with Fluorolink 7004<sup>®</sup> is increased to 37-39 % with either 20 % nitric acid, water, or even with no addition of water. Longer exposure times increase the Fluorolink extraction percentages to 51%; it is likely that under the best conditions even higher numbers could be achieved. With a -CF<sub>2</sub>COOH end group, the Fluorolink is significantly more acidic than PFPE-COO<sup>-</sup>NH<sub>4</sub>. Similar extraction results are likely observed with water and dilute nitric acid because the acidity within the water core is controlled by that of the surfactant, regardless of any initial acidity differences in the added aqueous phase. The filter paper results indicated that some water is necessary for extraction; it may be that additional water was not needed with the activated carbon because the activated carbon matrix retains water, and thus generated a microemulsion as the copper was extracted. Although the acidic water core will help disrupt metal binding to the activated carbon, it appears that it also interferes with the binding to the surfactant head group.

A control experiment using 5 mL of 20% nitric acid resulted in extraction of 96 % of the copper from the activated carbon. Although higher efficiencies are achieved with this bulk extraction than with the w/c microemulsions, the amount of secondary waste generated would be unacceptable. The w/c microemulsion extractions represent 100 fold decrease in the amount of aqueous material needed for remediation.

### ***Extractions: Wood***

Wood represents a challenging substrate based on its porous nature and is a realistic substrate to encounter in potential applications. Table 3 shows the results of europium extraction from spiked wood samples. A w/c microemulsion removed 84 % of the  $\text{Eu}^{3+}$  from the wood in 2

<b>Extraction Medium</b>	<b>Percent Eu Extracted</b>
w/c Microemulsion	84
Bulk Water	32
Bulk 5% Nitric Acid Solution	26

Table 3. A comparison of extraction of europium from wood by w/c microemulsion and bulk water or nitric acid solutions. The microemulsion penetrates into the wood more effectively than bulk water or nitric acid solutions.

hours. Leaching an identical sample in 5 % nitric acid or water for the same amount of time yielded only 26 % – 32 % extraction. This result dramatically demonstrates the potential advantages of the w/c microemulsions for extraction. The w/c microemulsion required only 60  $\mu\text{L}$  of acid to extract more material than 10 mL in a bulk system. Clearly the microemulsions are able to penetrate the porous wood structure much more effectively than a bulk solution.

### ***Extractions: Cement***

Portland cement is the most difficult substrate that we examined, because the cement was not simply doped with a solution of europium nitrate, but formed in the presence of europium, completely incorporating it into the cement framework. Furthermore, europium was in the insoluble-oxide form, not the easily ionizable chloride salt. Under our standard extraction conditions, no europium was removed from the cement using PFPE- $\text{COO}^-\text{NH}_4^+$ . The carboxylic acid group on the surfactant does not provide a selective interaction to solubilize  $\text{Eu}_2\text{O}_3$ . When the phosphonic acid surfactant, PFPE- $\text{PO}(\text{OH})_2$ , was used, 20 % of the europium was extracted. This corresponds to a 0.2 M solution of Eu within the microemulsion. Extraction was further hindered by competition from other metals in the cement matrix, as both microemulsion systems were shown to extract aluminum and iron.

### ***Extractions: Competition Experiments***

Table 4 shows the extraction percentages when a competing ion,  $\text{Ca}^{2+}$ , is also adsorbed onto the filter paper. With a 1:1 molar ratio of copper to calcium, the copper is preferentially

<b>Molar Ratio <math>\text{Cu}^{2+} : \text{Ca}^{2+}</math></b>	<b><math>\text{Cu}^{2+}</math> (mmol) Extracted</b>	<b>% <math>\text{Cu}^{2+}</math> Extracted</b>	<b><math>\text{Ca}^{2+}</math> (mmol) Extracted</b>	<b>% <math>\text{Ca}^{2+}</math> Extracted</b>	<b>Molar Ratio (Surfactant / Total Metal Extracted)</b>
1:1	0.021	97	0.019	79	4.5
1:10	0.016	74	0.084	36	1.8
1:50	0.0031	14	0.46	39	0.38

Table 4. The effect of calcium competition on the extraction of copper from filter paper using w/c microemulsions. The microemulsion extracts over 10 times as much metal in the presence of high calcium than with copper alone.

extracted, at 97 % extraction compared to 79 % for calcium. This result was expected given the ability of copper ions to form metal-ligand bonds with the carboxylate head group on the surfactant, which is a stronger interaction than the purely ionic attraction between the calcium

cation and the anionic surfactant. In the presence of excess calcium, extraction decreases to 74 % at a 1:10 ratio and to 14% at a 1:50 molar ratio. Total calcium extraction continues to increase, and at the highest Ca loading, the molar ratio of surfactant to metal extracted drops to 0.3. This indicates that the calcium ions must be in the water core, and not interacting with the surfactant head groups. Modification of the surfactant end group to a ligand with a stronger copper affinity than the carboxylate may mediate competition effects as such a ligand could bind copper selectively. Such modifications will be the subject of future research in this area.

To ensure that the matrix of the filter paper did not influence the selectivity of the extraction, solid chloride salts of europium and calcium were placed in the extraction cell in a 1:10 molar ratio. Under these conditions, 29 % of the europium is removed compared to 27 % of the calcium. Though total extraction percentage is low, it is significant that a greater percentage of europium is taken up in the presence of a ten fold excess of calcium.

### ***Regeneration and Reuse of Surfactant***

Surfactant recycle was demonstrated by generating a w/c microemulsion in the presence of copper and then using pressure changes to precipitate out the water droplet, allowing removal of the copper (Figure 4, Table 5). By following the absorbance of the copper at 750 nm, the amount of copper in the cell could be determined. The initial trace (closed circles) shows copper

	Initial Loading	After phase separation	Re-extraction			
			t = 0	t = 0.5 h	t = 2 h	t = 4 h
Copper in continuous phase (mg)	1.93	0.197	0.725	0.961	1.223	1.56
Relative to initial loading (%)	—	10	38	50	63	81

Table 5. Stripping and reuse of PFPE surfactant. Dropping the pressure to 2200 psi causes 90% of the copper in the water cores of the micelles to precipitate out of the continuous phase (phase separation). After the cell is reloaded with more CO<sub>2</sub>, water and copper, over 80% of the original capacity of the microemulsion is obtained.

dissolved in a w/c microemulsion. When the pressure within the cell was dropped to 1514 psi, copper-containing water droplets precipitated onto the sides of the cell, removing 90% of the copper from the bulk solution (closed squares). At this point, the cell was manually turned so that the water droplets were near the vent of the cell, and the water, with the copper, was vented from the cell. The same cell was again loaded with CO<sub>2</sub> and water (no additional surfactant) to generate a microemulsion and used to extract a second amount of solid Cu(NO<sub>3</sub>)<sub>2</sub>. UV-Vis shows that eighty one percent of the original copper uptake was obtained, indicating excellent recovery. The majority of the loss is likely due to engineering problems, as our cells are not designed to vent in this fashion. The likelihood of using the surfactant for multiple extractions is high.

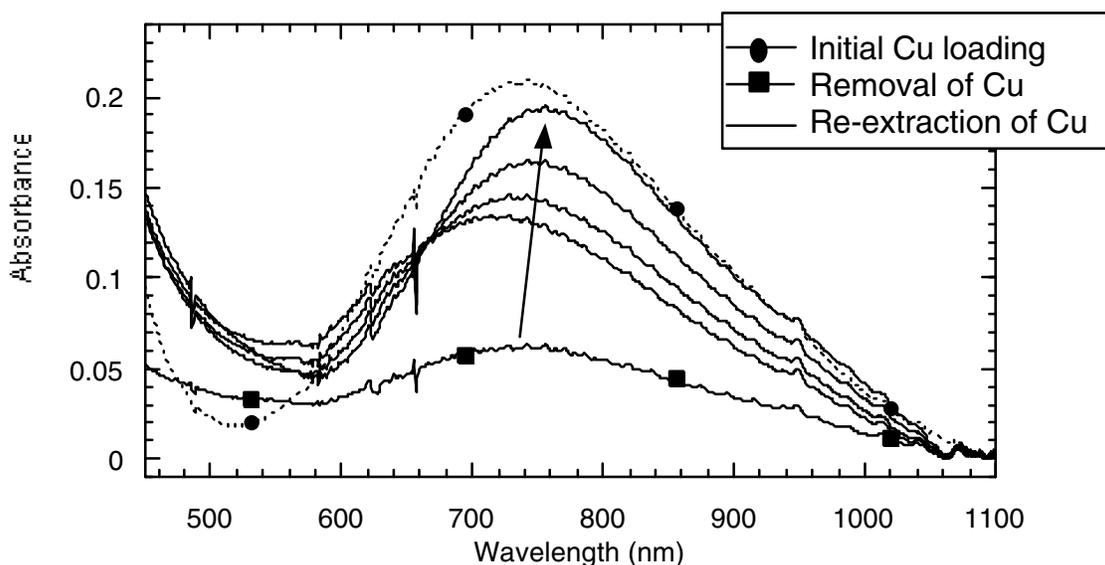


Figure 4. The absorption spectra during recycle of the PFPE surfactant. The initial loading (closed circles) is reduced 90% upon phase separation via a pressure drop (closed squares). Reloading the cell with CO<sub>2</sub>, water, and more copper, but not additional surfactant, shows that the surfactant is capable of extracting over 80% of the original loading into the new w/c microemulsion.

## Conclusion

We have demonstrated that w/c microemulsions with two types of polyperfluoro-surfactants are capable of extracting copper and europium from a variety of solid substrates. The extractions are facile and result in high ion loadings within the water core. Regeneration of the surfactant without loss of capacity is possible through controlling the pressure of the system. The system has slight selectivity for metals that bind to the surfactant relative to alkali metals; future research will focus on improving this selectivity through modifications of the surfactant head group. This new technique offers promise in remediation of solid materials contaminated with heavy metals or radioactive waste.

**Relevance, Impact and Technology Transfer:** This research has increased the understanding of how metals can be solubilized into supercritical CO<sub>2</sub> significantly. The impact of the work is already beginning to surface in the literature with extensions of our work looking at the applicability of water in CO<sub>2</sub> microemulsions to cleaning processes in the semiconductor industry. The idea of cleaning and dissolving metals using only very small amounts of water is highly attractive to this industry that is often criticized for its large water use. CO<sub>2</sub> is advantageous in the semiconductor industry since it does not add any contaminants and can be easily removed by reducing the pressure. IBM is currently beta-testing a CO<sub>2</sub> based cleaning process and working on the engineering aspects needed to develop a high throughput system that can cycle pressure quickly. Our work has greatly extended the understanding of how microemulsions might enable the solubilization of metals in supercritical CO<sub>2</sub>. The initial extraction results are very promising. The main hurdles to deployment are selectivity and the ability to control the acidity within the microemulsions.

**Project Productivity:**

The productivity was very high. We were able to demonstrate proof of principle for metal extractions from heterogeneous surfaces using water in CO<sub>2</sub> microemulsions. We succeeded in all of our research goals except one. Although we tested simple acidic microemulsions by using nitric acid instead of water, we did not have time to extend this to introducing an acidic environment using the head group of the surfactant. It should be possible to dissolve metal oxides by using surfactants with head that are highly acidic.

**Personnel Supported:**

Dr. T Mark McCleskey TSM at LANL

Dr. Eva R. Birnbaum TSM at LANL

Dr. Mathew Yates Postdoc - now assistant professor at Rochester University

Dr. Jeff Rack Postdoc - now assistant professor at the University of Ohio in Athens

Mary Campbell student – now a graduate student at Stanford University

BethAnne Parker student – finishing work on the carbonic acid equilibrium

Geoff Brown – technician at LANL

Deborah Appadoca – student and then technician – currently in private industry

**Publications:**

[Metal extractions using water in carbon dioxide microemulsions](#)

Yates MZ, Apodaca DL, Campbell ML, Birnbaum ER, McCleskey TM  
*CHEMICAL COMMUNICATIONS*, v. (#01) pp. 25-26 2001

[Metal extraction from heterogeneous surfaces using carbon dioxide microemulsions](#)

Campbell ML, Apodaca DL, Yates MZ, McCleskey TM, Birnbaum ER  
*LANGMUIR*, v. 17(#18) pp. 5458-5463 SEP 4, 2001

[Polymers with multiple ligand sites for metal extractions in dense-phase carbon dioxide](#)

Powell KR, McCleskey TM, Tumas W, DeSimone JM  
*INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH*, v. 40(#5) pp. 1301-1305 MAR 7, 2001

"Extraction of Metals from Soils Using Fluoro-supported Ligands in CO<sub>2</sub>"

Deborah Appadoca, Eva R. Birnbaum, T. M. Young and T. Mark McCleskey  
ACS Symposium series 778, 2000, 159-174.

**Interactions:**

[Water-in-carbon dioxide microemulsions for metal extractions.](#)

Birnbaum ER, McCleskey TM, Rack JJ, Yates MZ, Campbell ML

*ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY*, v. 222(pt.2) pp. U31-U31 AUG 2001

[Metal removal from contaminated surfaces using water/CO<sub>2</sub> microemulsions.](#)

Birnbaum ER, Yates MZ, Apodaca DL, McCleskey TM

*ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY*, v. 219(pt.1) pp. 154-IEC MAR 26, 2000

[Heterogeneous extractions using supercritical carbon dioxide.](#)

McCleskey TM, Birnbaum ER, Apodaca DL

*ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY*, v. 218(pt.1) pp. 114-NUCL AUG 22, 1999

The work was also presented at the Gordon Conference for Green Chemistry in England in 1999.

We had interactions with Professor Joe DeSimone at University of North Carolina, Keith Johnston at the University of Texas in Austin.

**Transitions:NA**

**Patents: NA**

**Future Work:** We submitted a proposal for continued funding last year, but it was not accepted. Future work would explore the mobility of micelles and surfactants into surface pores of cellulose, concrete, and plastic, and examine the possibility of using acidic “microphases” in CO<sub>2</sub> to dissolve relatively inert actinide surfaces such as UO<sub>2</sub> and PuO<sub>2</sub>. To really be useful it is necessary to demonstrate the ability to dissolve metal oxides more inert than europium oxide. In general, the dissolution of such materials requires highly acidic conditions in acidic media. Initial investigations showed that nitric acid based microemulsions were not highly stable, but it should be possible to introduce acidity through the head group of the surfactant. Selectivity for specific metal ions through control of the surfactant head group is another issue that would be explored.

## Literature Cited:

- <sup>1</sup> Kaupp, G. *Angew. Chemie, Int. Ed. Eng.*, **1994**, 33, 1452.A
- <sup>2</sup> Morgenstern, D.A.; LeLacheur, R.M.; Morita, D.K.; Borkowsky, S.L.; Feng, S.; Brown, G.H.; Luan, L.; Gross, M.F.; Burk, M.J.; Tumas, W. *Green Chemistry*, **1996**, v. 626, 132.
- <sup>3</sup> Yazdi, A.V.; Beckman, E.J. *Ind. Eng. Chem. Res.* **1997**, 36, 2368.
- <sup>4</sup> Dooley, K.M.; Brodt, S.R.; Knopf, F.C. *Ind. Eng. Chem Res.* **1987**, 26, 1267.
- <sup>5</sup> Wai, C.M.; Lin, Y.; Brauer, R; Wang, S; Beckert, W.F. *Talanta* **1993**, 40 No. 9, 1325.
- <sup>6</sup> Iso, S.; Meguro, Y.; Yoshida, Z. *Chem Letters* **1995**, 365.
- <sup>7</sup> Wai, C.M.; Wang, S.; Liu, Y; Lopez-Avila, V; Beckert, W. F. *Talanta* **1996**, 43, 2083.
- <sup>8</sup> Erkey C. *J. OF SUPERCRITICAL FLUIDS* , **2000**, 17(#3), 259.
- <sup>9</sup> Yazdi, A.V.; Beckman, E.J. *Ind. Eng. Chem. Res.* **1992**, 35, 3644-3652.
- <sup>10</sup> Laintz, K.E.; Wai, C.M. *J. Supercrit. Fluids* **1991**, 4, 194.
- <sup>11</sup> Lin, Y.; Laintz, K.E.; Wai, C.M. *Anal. Chem.* **1993**, 65, 2549.
- <sup>12</sup> Cross, W.; Akgerman, A.; Erkey, C. *Ind. Eng. Chem. Res.* **1996**, 35, 1765.
- <sup>13</sup> Lagalante, A.F.; Hansen, B.N.; Bruno, T.J.; Sievers, R.E. *Inorg. Chem.* **1995**, 34, 5781.
- <sup>14</sup> Yazdi, A.V.; Lefilleur, C.; Singley, E.J.; Liu, W.; Adamsky, F.A.; Enick, R.M.; and Beckman, E.J. *Fluid Phase Equil.* **1996**, 117, 297.
- <sup>15</sup> Yates, M.Z.; Apodaca, D.L., Campbell, M.L.; Birnbaum, E.R.; McCleskey, T.M. *J. Chem. Comm.*, **2001**, 1, 25.
- <sup>16</sup> Johnston, K.P.; Harrison, K.L.; Clarke, M.J.; Howdle, S.M.; Heitz, M.P.; Bright, F.V.; Carlier, C.; Randolph, T.W., *Science* **1996**, 271, 624-626.
- <sup>17</sup> Eastoe, J.; Cazelles, B.M.H.; Steytler, D.C.; Holmes, J.D.; Pitt, A.R.; Wear, T.J.; Heenan, R.K., *Langmuir* **1997**, 13, 6980-6984.
- <sup>18</sup> Lee, C.T.; Psathas, P.A.; Johnston, K.P., *Langmuir* **1999**, 15, 6781-6791.
- <sup>19</sup> Yates, M.Z.; Li, G.; Shim, J.J.; Maniar, S.; Johnston, K.P.; Lim, K.T.; Webber, S., *Macromolecules* **1999**, 32, 1018-1026.
- <sup>20</sup> Horrocks, W.D.; Sudnick, D.R. *J. Am. Chem. Soc.* **1979**, 101, 334-340.
- <sup>21</sup> Bunzli, J.-C.G.; Yersin, J., *Inorg. Chem.*, **1979**, 18, 605.
- <sup>22</sup> Bunzli, J.-C.G., in *Lanthanide Probes in Life, Chemical and Earth Sciences*, ed. J.-C.G. Bunzli and G.R. Choppin, Elsevier, Amsterdam, 1989, ch. 7, p. 219.
- <sup>23</sup> Grygiel, W.; Starzak, M., *Journal of Luminescence* **1997**, 71, 21-26.
- <sup>24</sup> Powell, K. R.; McCleskey, T.M.; Tumas, W.; DeSimone, J. M. *Ind. & Eng. Chem. Res.*, **2001**, 40(5), 1301.
- <sup>25</sup> Apodaca, D.L.; Birnbaum, E.R.; McCleskey, T.M.; Young, T.M., *ACS Symposium Series* **2000**, 778, Ch11, Editors Heineman, W.R. and Eller, P.G.

**Feedback: N/A**