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Project Title: **Micelle Formation and Surface Interactions in Supercritical CO₂ Fundamental Studies for the Extraction of Actinides from Contaminated Surfaces**

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Lead Principal Investigator:

Dr. T. Mark McClesky
Technical Staff Member
Los Alamos National Laboratory
MS J514
P.O. Box 1663
Los Alamos, New Mexico 87545
Telephone: 505-667-5636
e-mail: tmark@lanl.gov

Co Principal Investigators:

Dr. Nancy Sauer
CST-18
Los Alamos National Laboratory
MS J514
P.O. Box 1663
Los Alamos New Mexico 87545
Telephone: 505-665-3759
e-mail: nsauer@lanl.gov

Dr. Gordon Jarvinen
NMT-6
Los Alamos National Laboratory
MS E510
P.O. Box 1663
Los Alamos New Mexico 87545
Telephone: 505-665-0822
e-mail: gjarvinen@lanl.gov

Dr. Eva Birnbaum
CST-18
Los Alamos National Laboratory
MS J514
P.O. Box 1663
Los Alamos New Mexico 87545
Telephone: 505-667-5394
e-mail: evab@lanl.gov

William Tumas
Group Leader
Los Alamos National Laboratory
MS J514
P.O. Box 1663
Los Alamos New Mexico 87545
Telephone: 505-667-3803
e-mail: tumas@lanl.gov

Micelle Formation and Surface Interactions in Supercritical CO_2.
Fundamental Studies for the Extraction of Actinides from Contaminated Surfaces.

Mid-Year Progress Report

T. Mark McCleskey
Los Alamos National Laboratory

June 1, 1999

Goals of Project:
The goals of this research program for the three year period include:

1. **Synthesize new surfactants that have binding sites for metals.**
    - Can we make surfactants with metal binding sites that are CO_2 soluble?
    - Can these new surfactants form micelles with water cores?
    - Can we form micelles with highly acidic cores?
2. **Study solubility of extractants and formation of micelles.**
    - Do surfactants form micelles in $scCO_2$ and what is the mechanism of their formation? What effects do hydrogen bonding (aprotic vs. protic ligands) and ligand concentration (ligand sites per surfactant) have on micelle structure?
    - Can the pressure/density of $scCO_2$ be used to alter surfactant solubility or micelle structure?
    - How does water as an added cosolvent affect hydrogen bonding and subsequently micelle structure?
    - Can surfactant micelles be used to transport water based microphases?
3. **Examine the solubilization of metals.**
    - What influence does metal binding have on the surfactant solubility or micelle structure?
    - What are the energetics and 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 $scCO_2$?
4. **Explore surface interactions with the matrix and mobility of micelles.**
    - What factors affect wetting of heterogeneous matrices (*i.e.*, ligand type, CO_2 pressure, cosolvent)?
    - How deep can surfactants penetrate materials such as cellulose, polyethylene, and concrete?
    - What is the limiting pore size accessible to CO_2 soluble surfactants?
5. **Explore surface interactions with the actinide contaminant.**
    - Can surfactant based micelles be used to deliver acidic, aqueous microphases to the actinide surface?
    - Can addition of a CO_2 soluble oxidant help solubilize inert forms of metals such as UO_2 and PuO_2?
6. **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?
    - Are dynamic extractions in which the CO_2 pressure is changed during extraction better than static extractions?

Technical Description of Work:

This research seeks to build the fundamental understanding of micelle formation and mobility in supercritical CO_2 necessary to develop an innovative phase-transfer extraction system for selectively removing metals (actinides) from contaminated surfaces. We will extract metal ions into supercritical CO_2 ($scCO_2$) using CO_2 soluble extractants. The surfactants consist of perfluoroether and perfluoroalkyl backbones with phosphate head groups. Experimentation will focus on two main issues: understanding the solubilization mechanism of metals into supercritical CO_2 with regards to micelle formation, and studying the interactions between the extractants and surfaces. Surface interactions will include both those with the matrix surface and the surface of the actinide contaminants.

Supercritical CO_2 has many advantages both for extraction from surfaces and minimization of the environmental impact of separation activities. The gas-like properties of high diffusivity and low surface tension will enable penetration of the surfactants and micelles deep into surface pores, inaccessible by aqueous based systems, 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_2 solvent, allowing concentration of the waste and recycle of the carbon dioxide. The CO_2 solvent is an environmentally benign, inexpensive, radiologically and oxidatively stable extraction medium. Secondary waste streams are minimized since no toxic solvents are used. Most importantly worker contact with radioactive material is minimized compared to techniques such as sandblasting which can expose the worker to surface contamination.

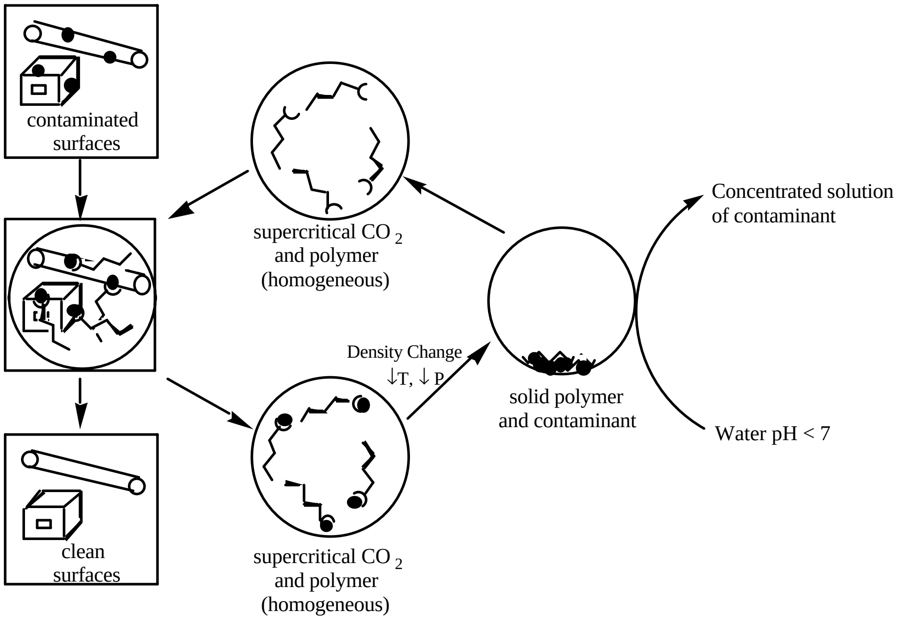


Figure 1. Process for extraction with supercritical CO_2. An initial wash with dense phase CO_2 removes organics. A second wash with a surfactant will solubilize and remove the metal ions. The metal can be back extracted to regenerate the surfactant.

Developing an understanding of surfactant solubility, micelle formation, and micelle mobility could lead to a novel extraction method for removing radionuclides from contaminated surfaces. 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 $scCO_2$ would lead to considerable cost savings through waste minimization of secondary streams.

This research will explore the fundamentals of solubilization mechanisms and surface interactions in supercritical CO_2 ($scCO_2$). We will probe how micelle formation and stability affects solubilization of metal ions (Eu^{3+}, Nd^{3+}, Pu^{4+}, UO_2^{2+}) in CO_2 as well as interactions of the supercritical phase components with surfaces. Surface studies will include interactions with the matrix surface and with the surface of the contaminant. We will explore the mobility of micelles and surfactants into surface pores of cellulose, concrete, and plastic, and examine the possibility of using acidic "microphases" (water based environments within a micelle) in CO_2 to dissolve relatively inert actinide surfaces such as UO_2 and PuO_2. The knowledge gained from this research will serve as a foundation for the development of a CO_2 extraction system for removing actinides from heterogeneous waste.

Our studies will initially focus on surfactants with perfluoroether and perfluoroalkyl backbones. The perfluoroether backbones are known to be highly soluble in CO_2 and have been shown to solubilize carboxylic acid head groups. We will first examine solubility of the surfactants in CO_2 as a function of CO_2 pressure and temperature. Micelle formation will be studied both in dry CO_2 and in the presence of small quantities of water by *in situ* spectroscopies such as IR, NMR and light scattering. Since the surfactants are composed of CO_2-philic perfluoro backbones and CO_2-phobic phosphate head groups, micelle formation is expected. The protic phosphates with the capacity for hydrogen bonding are more likely to form micelles, especially in the presence of water. Once characterized, we will examine these new surfactants for their potential to bind and solubilize a range of metal ions and metal complexes.

Initial solubilization studies will be done with simple metal salts as a function of CO_2 pressure/temperature in pure CO_2 and then with small quantities of water as an added cosolvent. Metals may be solubilized directly in CO_2 as surfactant-metal complexes, or within surfactant based micelles. Recent reports in the literature demonstrate that perfluoroether backbones with carboxylic acid head groups do indeed form micelles and these micelles are capable of solubilizing small microphases of water containing multiply charged proteins. We plan to study the mechanism of metal extraction to determine if metal solubility can be enhanced through formation of micelles. Microphases within the hydrophilic core of the micelle are particularly intriguing, because they may provide a mechanism for bringing highly acidic aqueous environments to the contaminant surface. Promising surfactants that solubilize metals will be used to study surfactant/micelle mobility into surface pores. Mobility studies will be done a variety of surfaces to ascertain how pore size and density of the material effect the surfactants' ability to penetrate the surface. We expect the low surface tension and high diffusivity of CO_2 will enhance wettability such that the surfactant/micelle will be able to access all potentially contaminated areas of a surface. Surface studies will then be extended to examine how the surfactant or micelle interact at the surface of the contaminant. Simple metal salts may be dissolved by binding the metal to a ligand on the end of the surfactant, but more inert forms will require chemistry at the metal surface to be solubilized. This chemistry can include acid/base or reduction/oxidation chemistry depending on the state of the metal. For many forms of the actinides an acidic environment is needed for dissolution. Studies of aqueous microphases will be done using either the perfluoroethers with carboxylic acid that are known to solubilize microphases of water or the analogous phosphate surfactants if they are shown to be capable of forming microphases. These aqueous microphases will have ligands available for the metal contaminant and should be highly acidic ($pH < 2$) based on the carbonic acid equilibrium of $H_2O + CO_2 \text{<--->} H_2CO_3$. We will examine the feasibility of using such acidic microphases to solubilize more inert metal forms such as UO_2 and PuO_2.

Creation of new surfactants, along with the fundamental understanding of their interactions, will allow us to develop a complete extraction system for selectively separating metal ions (actinides, fission products, and heavy metals) from a wide range of heterogeneous wastes found in the DOE complex, as depicted conceptually in figure 2. Optimized systems will be used for treatability studies on several actual DOE wastes, which we have identified at Los Alamos . The waste stream will initially be washed with pure compressed CO_2 to remove any CO_2-soluble organics present. Next CO_2 and surfactant will be introduced, under either liquid ($liqCO_2$) or supercritical ($scCO_2$) conditions. Pressure will be used to control solubility and interfacial interactions, enabling the selective ligands on the surfactant to bind the desired metal(s). The CO_2 phase with surfactant and bound metals will then be transferred to another vessel. At this point the metals can be back-extracted to regenerate the surfactant for reuse and isolate a concentrated waste stream for disposal, stabilization, or recovery.

This extraction system will capitalize on the unique features of $scCO_2$ such as density-dependent solvent properties, high diffusivity, and low surface tension. For example, controlling the density of the CO_2 solvent through pressure changes will allow us to control the formation of micelles, enhance surface interactions, and easily separate the surfactants from CO_2 after binding metals. The high diffusivity and low surface tension of $scCO_2$ will aid in facilitating transport and extraction of metals from complex heterogeneous waste. This novel approach of insulating the metal will allow development of a broad range of separation systems using $scCO_2$ as an environmentally benign, inexpensive, radiologically and oxidatively stable extraction medium. Other advantages of this process include: a) the surfactant supports are relatively inert fluorocarbon matrices; b) ligand/surfactant combinations allow flexibility to target specific metal ions; c) solubility and phase behavior can be controlled with $scCO_2$ density (surfactants and metal/ligand complexes can be separated by controlling $scCO_2$ solvent properties through pressure control, thus avoiding large volumes of secondary process wastes; d) the potential for multiple ligand sites on the surfactant backbone (to enhance binding through chelation).

Our program is based on the covalent attachment of ligands with high affinities for the target metals to perfluoroether and perfluoroalkyl backbones with high $scCO_2$ solubility. This approach is unlike previous work in that it does not depend on increasing the CO_2 solubility of the ligand moiety itself, but rather on utilizing CO_2-philic carriers. This concept allows use of a wide range of ligands without significantly perturbing the electronic structure of the ligands and the metal-binding specificity. Our work focuses on perfluoroether oligomers ranging from 3 to 13 repeating units as depicted in Table 1. These systems are ideal for the bulk of our work because much of the synthetic methodology for the backbones has already been developed and a number of synthetic options for incorporating functionality for ligand attachment are readily available. Some preliminary understanding of the solution structure and dynamics of the perfluoroethers is also available. These systems should be applicable to a broad range of waste types, and are stable in highly acidic or caustic environments.

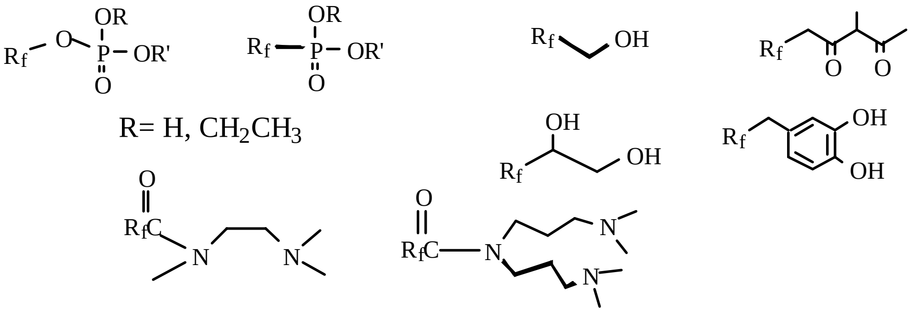
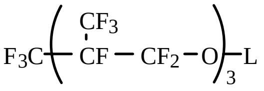
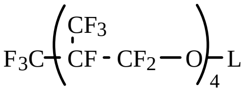
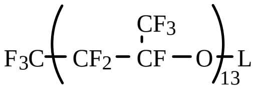
Targets	U, Np, Pu, Am
Ligands L	 R= H, CH_2CH_3
Backbones R_f	 $F_3C\left(\overset{CF_3}{CF}-CF_2-O\right)_3L$  $F_3C\left(\overset{CF_3}{CF}-CF_2-O\right)_4L$  $F_3C\left(CF_2-\overset{CF_3}{CF}-O\right)_{13}L$ $CF_3(CF_2)_7CH_2CH_2-L$ $CF_3(CF_2)_5CH_2CH_2-L$

Table 1: Ligand types and surfactant backbones.

Promising extractants will be studied in more detail because understanding the basic properties of these systems with respect to dynamics and phase behavior of the surfactants will be crucial to the development and implementation of this technology. The dynamics of these systems will be examined in terms of surfactant-surfactant interactions (micelle formation), surfactant-solvent interactions ($scCO_2$ pressure/density, introduction of water as a cosolvent), surfactant-metal interactions (conformational changes upon binding, thermodynamics), and surfactant-surface interactions (diffusivity of surfactant/CO_2 through porous heterogeneous materials, wetting of surfaces, interactions with inert metal forms). We will study the dynamics with a variety of spectroscopic techniques including *in-situ* UV-Vis, IR, and NMR spectroscopy, as well as light scattering. By comparing the observed dynamics of different surfactants with different ligands we will be able to investigate factors such as the effects of hydrogen bonding and ligand acidity. Studies as a function of CO_2 density will provide us with the knowledge of how we can control surfactant dynamics through changes in CO_2 pressure.

The knowledge gained from investigating the dynamics will be used to optimize extractions from actual contaminated surfaces. Waste generated at Los Alamos have been identified for potential treatability studies: heterogeneous trash from paint stripping operations (organics, lead, cellulose materials), and soil contaminated with uranium, lead, and beryllium from an internal firing site. Further experimentation will make use of our growing knowledge base to extract the metals back into a small aqueous volume and regenerate the surfactant. An aqueous back extraction will result in a minimum of concentrated metal solution that could be further treated (evaporation, reduction, precipitation) with essentially no waste generation to yield a pure metal stream.

Accomplishments to Date:

There has been a great deal of progress in this project already, and all initial results indicate that future milestones will be met with success. The following bullets summarize the goals that have been met.

- Synthesized fluoroether and fluoroalkyl surfactants
- Tested the solubility of the fluorinated based surfactants in supercritical carbon dioxide
- Formed surfactant based micelles in supercritical carbon dioxide with an acidic environment
- Demonstrated that microphases can penetrate polyethylene gloves with an acidic environment
- Extracted copper using surfactant based micelles
- Evaluated the fluorinated based surfactants and their ability to extract metals from surrogate heterogeneous surfaces without the formation of micelles

Synthesis of fluoronated surfactants

The fluorinated ether chain used in the synthesis of the chelating agents is commercially known as fomblin or perfluoropolyether vacuum-pump oil. The chelating groups that were synthesized and tested include a carboxylic acid (fomblin alone), two fluorinated amides and two fluorinated alkyl phosphates. The synthetic route for modification of the perfluoroether backbone is displayed in figure 6. Characterization of products was performed using a Magna-Infra Red 750 (IR) Spectrophotometer (Nicolet), a Nuclear Magnetic Resonance (NMR) Spectrometer (300 MHz Varian), and an inductively coupled plasma-atomic emission spectrophotometer (ICP-AES).

One set of polymers that was designed and synthesized for this project focused on remediation of actinides, specifically ^{238}Pu. Neodymium, a common surrogate for ^{238}Pu, was used in all extractions. A commercially available CO_2-philic polyfluoroether carboxylic acid was used as the starting material for all polymers that were developed. To target actinides such as ^{238}Pu or in our case neodymium, the polyfluoroether carboxylic acid was converted to an acid chloride. The acid chloride was then converted to an alcohol and then reacted with a phosphate ligand precursor to form an alkyl phosphate. The phosphorus oxy acids are protic ligands known to bind both plutonium and uranium. The alkyl phosphate was then reacted with hydrogen bromide to make a phosphate ligand that contained hydroxide groups. The alcohol was then converted to an alkyl chloride.

In addition to the actinide binding polymers that are described above, toxic metals such as cadmium, lead and mercury require the introduction of "softer" ligands such as amines. In this research, cadmium was used as the second target metal. The cadmium polymers were developed in a similar manner as the ones mentioned above. The fluorinated ether chain was converted to an acid chloride and then reacted with several ligand precursors to form two fluorinated amides. The other polymer that was tested in this research was the fomblin alone.

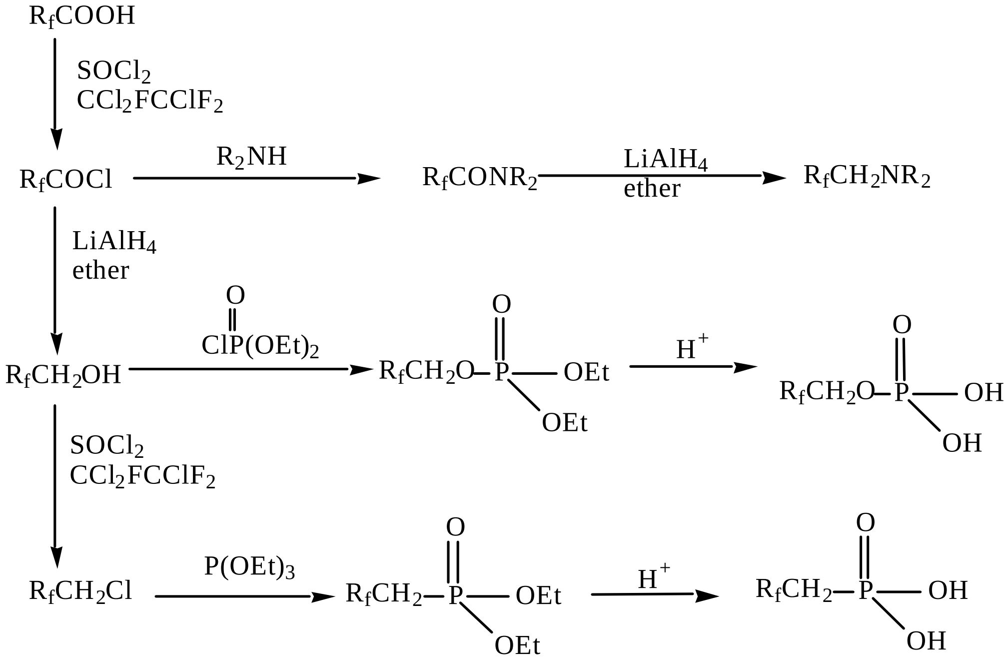


Figure 2. Synthetic route for modification of perfluoroether backbones

Solubility Tests

Solubility tests were performed on all of the surfactants. The solubility of the ligands in supercritical CO_2 as a function of pressure and temperature were tested. As the carbon dioxide pressure is decreased extractants will precipitate out at the “cloud point” (Table 1). If the surfactant is not soluble in supercritical CO2 it can visually be seen when the solution is taken to the critical temperature and pressure of carbon dioxide. All of the surfactants that were synthesized were soluble with the exception of one of the amides.

Table 1. Cloudpoints for fluoro supported surfactants at different temperatures and pressures (pressures are in psi)

	40^o Celsius	**50^o Celsius**	**60^o Celsius**
Perfluoroether Carboxylic Acid (Fomblin-3)	1098	1385	1571
Perfluoroether amide-2	1540	2112	2550
Perfluoroalkyl phosphate-1	1204	1486	1747
Perfluoroalkyl phosphate-2	1058	1390	1694
Perfluoroether amide-1	Not Soluble	Not Soluble	Not Soluble

Micellular Formation

All of the surfactants synthesized that show CO_2 solubility also from microemulsions with water. In some cases the microemulsions are actually more soluble than the surfactant itself. We have also started work on solubilizing acidic environments within the micelle core. Initial experiments with a 20% nitric acid solution show that microemulsions can be readily formed with an acidic microenvironment at the core. The acidity of the microenvironment was verified by solubilizing methyl orange, a pH indicator whose color changes from yellow at pH>4.4 to red at pH<3.2. Methyl orange is insoluble in pure CO_2, but can be solubilized in water based microemulsions using the Fomblin surfactants. When distilled water is used the CO_2 solution appears yellow indicating a pH > 4.4. When a 20% nitric acid solution is used the solution appears red indicating the acidic nature of the microenvironmnet. Measurements were made using in situ UV/Vis spectroscopy to identify the speciation of the methyl orange.

A preliminary experiment on the mobility of the acidic microenvironments has been done to determine if the microemulsions can penetrate plastic gloves. Methyl orange was placed within a polyethylene glove and the glove was then sealed using a heat knife. The glove was then placed in a CO_2 cell with the fomblin surfactant and some 20% nitric acid. When pressurized to supercritical conditions acidic microemulsions formed and extracted methyl orange from within the glove within minutes. This experiment shows that the acidic microemulsions are mobile enough to penetrate the polyethylene and are capable of solubilizing solids within the plastic.

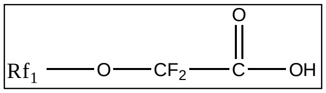
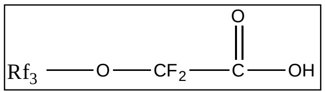
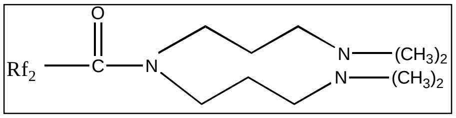
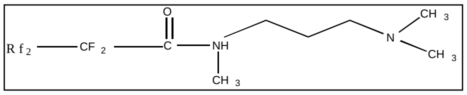
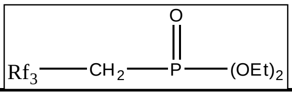
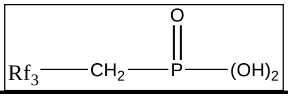
The first experiment on metal extraction has been done using copper chloride. Microemulsions with aqueous cores were formed using fomblin and distilled water in supercritical CO_2. These suspended microemulsions were then exposed to solid copper nitrate within the cell. Copper chloride rapidly began dissolving into the micelles as evidenced by the blue color of the solution and UV/Vis spectra. After two hours the concentration of copper within the CO_2 cell was 2 mM corresponding to 0.3M copper within the aqueous microenvironments. Control experiments showed that copper nitrate is completely insoluble in pure CO_2.

Metal extractions without the formation of micelles

One of the goals of this research was to test the ability of the fluorosupported surfactants to extract metals from surrogate soils. To date, all extractions have been done without the formation of micelles.

All extractions were performed at a pressure of 300 atm, temperature of $50^{o}C$ and a flow rate of 2 mL/min. Two different soils were spiked with each metal yielding four test soils. One soil is a fine, silty soil that contains 4.3% organic content and the other is a sandy soil with an organic content of 0.13%. The fomblin alone extracted an average of 37% of the Neodymium from the sandy soil using a ten-fold excess of polymer to metal ratio. When increased to a hundred-fold excess, extraction efficiencies increase to over 50% for the cadmium and an average of 25% for the neodymium. When a five hundred-fold excess of fomblin is used, 35% of the cadmium and an average of 18% of the neodymium are extracted. One of the fluorinated amides has cadmium extraction efficiencies of approximately 22% and neodymium extraction efficiencies of 18% using a ten-fold excess of polymer. The alkyl phosphates have not been successful at extracting cadmium or neodymium. No metal has been extracted from the fine, silty soil with higher organic matter content.

Table 2. Extraction summary for surfactants

Surfactant Number	Surfactant	Metal	Soil	Ratio	Replicates	Results (% Extracted)
1	**Fomblin 1**  $Rf_1 - O - CF_2 - \overset{\overset{O}{\|}}{C} - OH$	Cd	Wurtsmith	10X	2	1.1 0
		Nd	Wurtsmith	10X	2	47.6 26.26
		Cd	Wurtsmith	100X	2	69 54
		Nd	Wurtsmith	100X	2	22 34
		Cd	Forbes	10X	2	0.1 0
		Nd	Forbes	10X	2	0 1.1
		Cd	Wurtsmith	500X	2	34.16 107.52
		Nd	Wurtsmith	500X	2	30.51 21.5 4.44
2	**Fomblin 3**  $Rf_3 - O - CF_2 - \overset{\overset{O}{\|}}{C} - OH$	Nd	Wurtsmith	10X	1	0.28
		Cd	Forbes	100X	1	1.69
8	**Amide from Fomblin 2 and 3,3,-Iminobis(N,N-dimethylpropylamine) (Amide-2)** 	Cd	Wurtsmith	10X	4	1.1 32.8 20.1 14.42
		Nd	Wurtsmith	10X	3	18.85 5.89 15.02
		Cd	Wurtsmith	100X	2	8.71 3.25
		Nd	Wurtsmith	100X	2	17.78 1.9
		Cd	Forbes	10X	1	2
		Nd	Forbes	10X	1	0
13	**Amide from Fomblin 2 acid chloride using N,N,N-Trimethylene diamine (Amide-1)** 					
		Nd	Wurtsmith	100X	1	1.1
		Cd	Wurtsmith	100X	1	NA
10	**Alkyl phosphate from Fomblin 3 alcohol using diethyl chlorophosphate**  $Rf_3 - CH_2 - \overset{\overset{O}{\|}}{P} - (OEt)_2$					
		Cd	Wurtsmith	10X	1	3.3
		Nd	Wurtsmith	10X	1	1.8
		Cd	Forbes	10X	1	0
		Nd	Forbes	10X	1	0
11	**Alkyl Phosphate from Fomblin 3 alcohol after heating in 5% HBr solution (OH groups are attached)**  $Rf_3 - CH_2 - \overset{\overset{O}{\|}}{P} - (OH)_2$					
		Cd	Wurtsmith	10X	1	0
		Nd	Wurtsmith	10X	1	1.1
		Cd	Forbes	10X	1	0
		Nd	Forbes	10X	1	0

Projections:

At this stage all of the experimental work is progressing according to plan, and the results are very promising. We expect to make all of or milestones this year with no problems. Results have already been obtained that indicate many of next year's goals should be met with success. Currently we have demonstrated that acidic microemulsions can be made in CO_2 and are stable. These microemulsions can penetrate thin polyethylene layers and extract solid materials. We have also demonstrated that microemulsions can be used to solubilize copper in supercritical CO_2. All the results so far indicate that it should be possible to extract metals from heterogeneous surfaces.

Funding:

We are 69% spent at the end of May, which is on target for spending the full allocation without going over budget. We do not anticipate going over budget at this time.

Issues/Problems:

We have not encountered any problems at this stage that will require us to change strategy or indicate insurmountable barriers to obtaining the original goals of the proposal.

Corrective Actions:

NA

Additional Information: