

Project ID Number:

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

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Research Objective: We are examining the potential of water in CO₂ microemulsions as a new medium for the extraction of metal ions from contaminated surfaces with the ultimate goal of extracting actinides from heterogeneous waste to aid in decontamination and waste reduction.

Research Progress and Implications:

This report summarizes 1 ½ years of work on a 3 year program. We report here on using water in CO₂ microemulsions as a new medium for metal extraction from contaminated surfaces. The nano-droplets of water suspended in CO₂ take advantage of both the high solubility of metal ions in water and the high diffusivity of CO₂ to penetrate pores that might be inaccessible to bulk water. The pressure-dependent solvent strength of CO₂ can be used to control formation of the nano-droplets. As the CO₂ pressure is dropped, a cloud point is reached where the nano-droplets coalesce into a water phase that is no longer suspended in the CO₂, allowing easy separation of the metal solution. 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, CO₂ 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.

Extractions from Filter Paper - Extractions of copper from spiked filter paper were conducted to examine the effectiveness of the microemulsion in removing metal contaminants from solid surfaces. Greater than 99% of the copper is extracted in one step from the smaller pieces of filter paper. Extraction efficiency decreases when a larger piece of filter paper is used, but following with a second extraction again improves the efficiency to 83-99%. The kinetics of extraction from a spiked filter paper were followed by UV-Vis spectroscopy. The absorption from copper reached a maximum after 60 minutes of exposure to the microemulsion, with no further increase after an additional 90 minutes. The kinetics of extraction with microemulsions are much faster than those observed recently with CO₂-soluble polymers that required many hours to days for extraction. In addition to improved kinetics, the microemulsions have improved efficiency compared to previous studies with CO₂-soluble chelating agents. In general, past extractions have required a tremendous excess of ligand to achieve reasonable metal extractions (greater than 1000 fold). By comparison, at the maximum solubility of copper, the molar ratio of surfactant to copper in the microemulsion is approximately 3.

Luminescence Results - Europium fluorescence lifetimes and emission spectra were examined to probe ion solvation in the water in CO₂ microemulsions. The relative heights of the europium emission bands at 593 and 615 nm provide information on the first solvation sphere around the europium ion. When europium (III) is dissolved in water at ambient conditions, the ion is symmetrically hydrated by water and the transition at 615 nm is forbidden. In the microemulsion, the 615 nm band gains in intensity, indicating that the center of inversion around europium is gone, due to displacement of water in the first hydration sphere by another ligand. Two possible ligands are available in the microemulsion core: the carboxylate head group of the surfactant or carbonic acid, formed by CO₂ dissolved in the

aqueous phase. As a control, europium chloride was dissolved in D₂O and the headspace over the solution was pressurized to 3000 psi with carbon dioxide to introduce bicarbonate with no surfactant present. The europium emission spectra appeared the same as in water at ambient conditions, suggesting that the carboxylate head group of the surfactant is solely responsible for the changes in the emission spectra of europium ion dissolved in the microemulsion.

Further evidence for surfactant binding comes from lifetime experiments using H₂O- and D₂O-based microemulsions. The isotope effect provides a way to determine the number of water molecules surrounding the europium ion using the equation: $n = C^*(1/\tau_H - 1/\tau_D)$. The lifetime of europium (III) ion in the water in supercritical CO₂ microemulsion was found to be 120 μs and increased to 274 μs when the microemulsion was formed with D₂O. Using the above equation with the measured lifetimes gives approximately 5 water molecules in the first hydration sphere of the europium ions. As the fully hydrated ion has 8 to 9 water molecules, this result suggests that the surfactant displaces 3 or 4 water molecules from around the europium ion.

Extraction of Metal Oxides - Radioactive and heavy metal contaminants are often present as water-insoluble metal oxides in heterogeneous waste. To demonstrate the versatility of the microemulsion in metal extraction, the microemulsion was formed with a 20 wt% nitric acid solution instead of pure water. The increase in acidity was confirmed by dissolving methyl orange indicator in the microemulsion. The indicator appeared bright red when the microemulsion was formed with 20% nitric acid as opposed to orange when distilled water was used. The ability of the acidic microemulsions to extract metal oxides was examined with europium oxide. Based upon visual observation, ten mg of europium oxide completely dissolved into a microemulsion formed with 20 wt% nitric acid after stirring for one hour.

Conclusions - Water in supercritical carbon dioxide microemulsions are effective for extraction of metals from solids. At maximum solubility, a 3 molar solution of copper can be obtained within the microemulsion core. The nano-droplets offer the advantages of rapid and efficient extractions with a versatile environment. Making the microemulsion with 20 wt% nitric acid rather than pure water allowed europium oxide to be solubilized. Agents that oxidize low valent metal oxides or known, inexpensive, water-soluble chelating agents could also be introduced into the microemulsions to expand the types of metals that may be extracted and to provide selectivity in mixed metal extractions. This could greatly expand the potential of CO₂-based extractions by eliminating the need to develop novel fluorinated ligands for each new extraction. Metal is readily recovered by simply dropping the CO₂ pressure below the cloud point, causing the water to coalesce into a single droplet with all of the metal and some surfactant. We are currently exploring the possibility of recovering the surfactant by washing with CO₂ and by increasing the water concentration once the extraction is complete to the point at which the microemulsions are no longer stable. The ability of the microemulsion to concentrate the metal into a small volume of water makes it particularly attractive for extractions from contaminated solids that often have small amounts of metal dispersed over a large volume of solid waste.

Planned Activities:

During the remainder of the project we plan to:

- 1) Examine aspects of the surfactant that affect micelle formation such as chain length and charge.
- 2) Determine if water-soluble chelating agents can be added to promote specific metal extractions.
- 3) Control the pH within the microemulsion by changing the surfactant head group.
- 4) Characterize and test a newly synthesized phosphate based surfactant.
- 5) Extend extractions to look at depleted uranium, including uranyl and UO₂.
- 6) Explore extractions from a variety of matrices including cement and wood.