Metal Removal From Contaminated Surfaces Using Water/CO_2 Microemulsions

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Research Goals

- Develop a single extraction operation for remediation of radioactive and mixed solid wastes using micelles in supercritical carbon dioxide
  - Thousands of drums stored by DOE of TRU (> 100 nCi/g) waste with single isotope contamination (*i.e.*, 2000 drums of ^{239}Pu-contaminated solids at Rocky Flats alone)
  - Over 160,000 m^3 of mixed waste (rad + hazardous) in storage awaiting treatment and disposal at DOE facilities
  - 1,400 different mixed waste streams in inventory at 38 separate sites in 19 states

The Challenge – Heterogeneous Waste

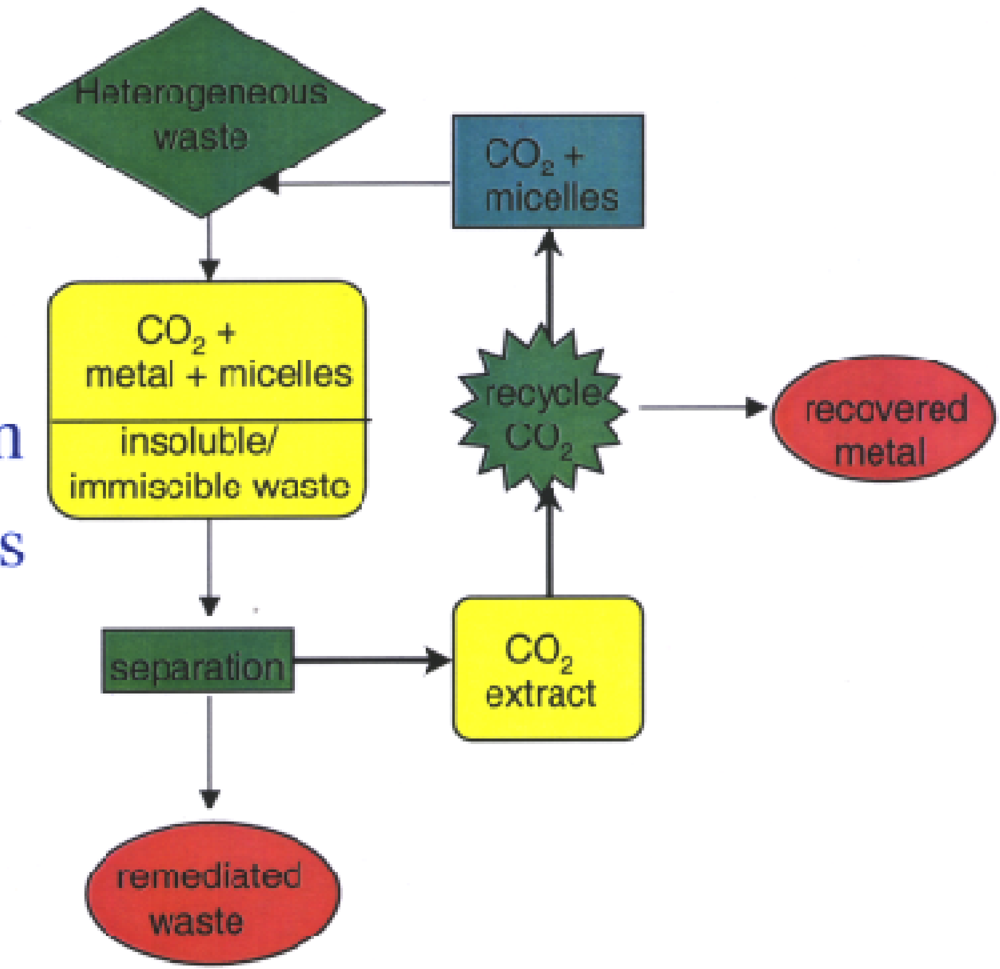
- Paper
- Plastics
- Cheesecloth
- Concrete
- HEPA filters
- Metal Parts

Mixed solids contaminated with small amounts of Pu

Drums of TRU waste slated for disposal at WIPP

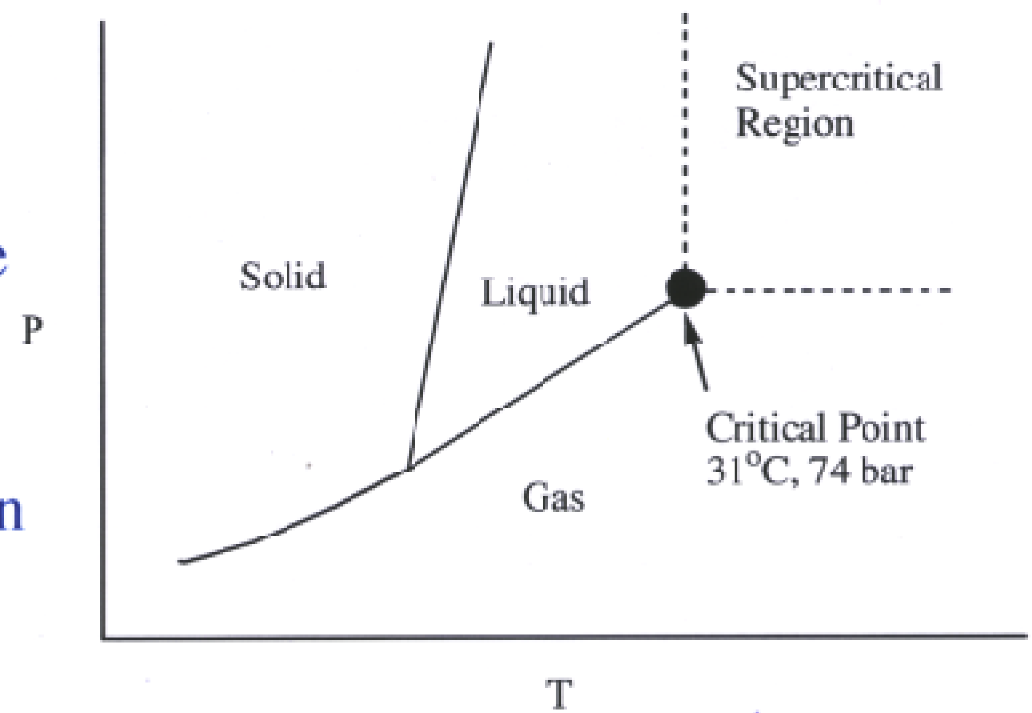
Decontamination Process

- Challenges
  - high surface area
  - dilute in metal
  - unknown speciation
  - small pore openings
  - secondary waste minimization



Carbon Dioxide as a Solvent

- Advantages
  - Environmentally benign
  - Chemically, radiolytically stable
  - Fast diffusion
  - High mass transfer
  - Zero surface tension
- Disadvantage
  - Nonpolar solvent



Current commercial applications of SC CO_2

- Cleaning of semiconductors, weapons parts
- Extractions
  - Coffee decaffination
  - Hops isolation
  - SFE (supercritical fluid extraction and chromatography)
- Dry cleaning
- Catalysis (on the R&D level)

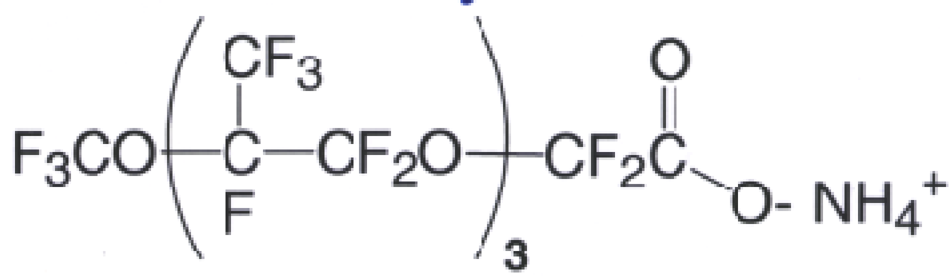
Disadvantages of Previous Metal Extractions in SC CO_2

- Addition of co-solvents
  - Often toxic (TBP, methanol)
- Addition of ligands
  - Low solubility (of ligands or metal complexes)
- Fluorination of ligands
  - Improved solubility, but
  - Decreased ligand strength, increased volatility
  - High ligand to metal ratios required

J.A. Darr, M. Poliakoff. *Chem. Rev.*, **1999**, 495.
C.M. Wai, S. Wang. *J. Chrom. A.*, **1997**, 369.

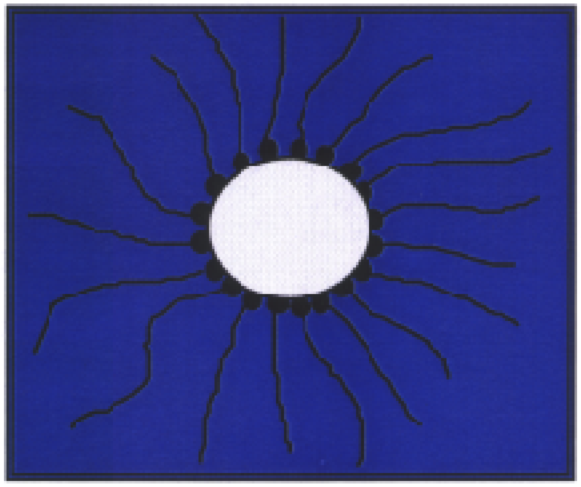
Fluorinated Polymers

- Attach ligands to CO_2-soluble polymers
  - Solubility driven via polymer
  - Selectivity driven via ligand
- Perfluoropolyether (Fomblin; PFPE)
  - Commericially available (pump oil)
  - Able to functionalize via carboxylic acid
  - Nontoxic
  - Inert backbone



AV Yazdi & EJ Beckman, *Ind. Eng. Chem. Res.*

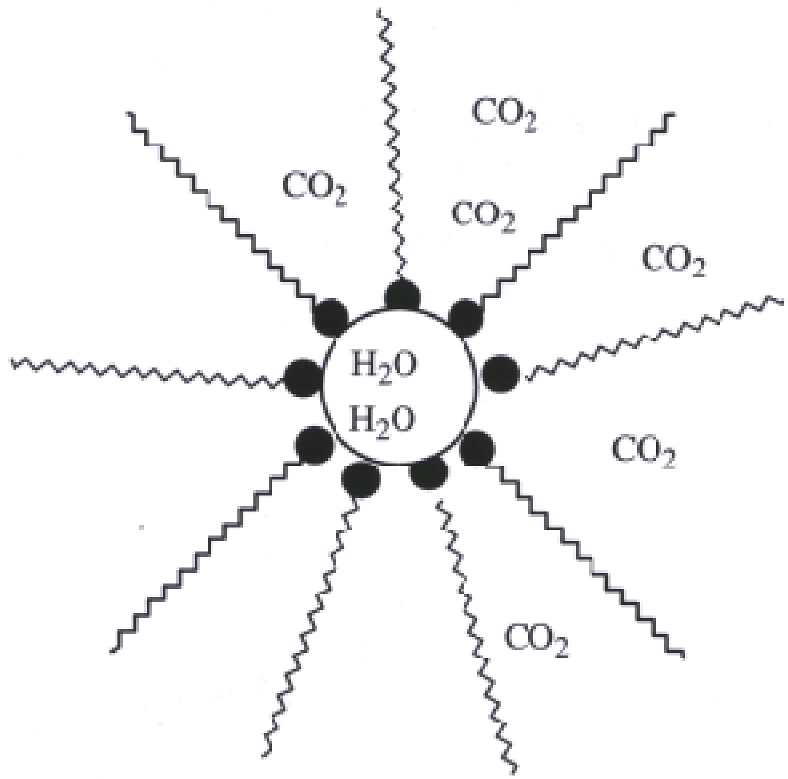
Surfactants and Micelles

Tail		**Head**
CO_2-philic		*CO_2-phobic*
Fluoroacrylates *Fluoroethers* *Siloxanes*		*Lipophilic* *Hydrophilic*

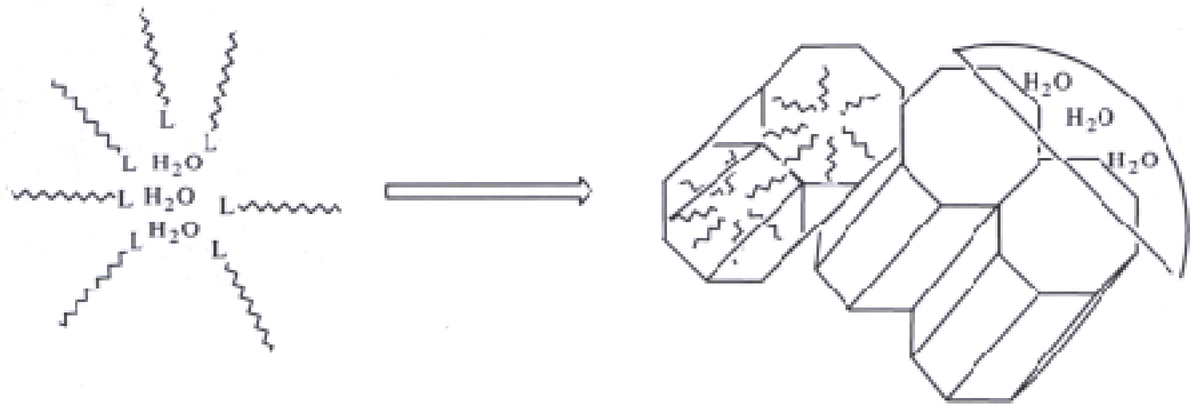
Use a bi-functional surfactant to form a micelle in SC CO_2. Can higher metal solubility be achieved in the micelle core than in bulk CO_2?

Microemulsions

- Small / mobile
  - 20-100 Angstroms
- Thermodynamically stable
- Ease of separation
- Control
  - ligand
  - surfactant length
  - water environment



Extraction from Solids



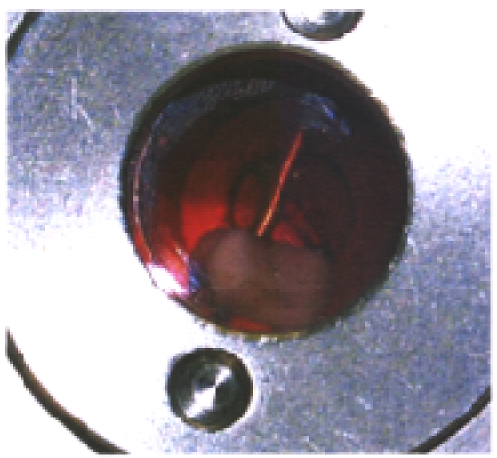
- Microemulsions can:
  - penetrate small pores
  - bring a water environment to places inaccessible to bulk water
  - compete to extract metals from surfaces

Microemulsion Generation -- Control of Microenvironment

- Microemulsions are clear. The addition of an pH indicating dye (methyl orange) shows that using water vs. nitric acid can change the pH of the water in the micelle core.

20% nitric acid

pH <3.2



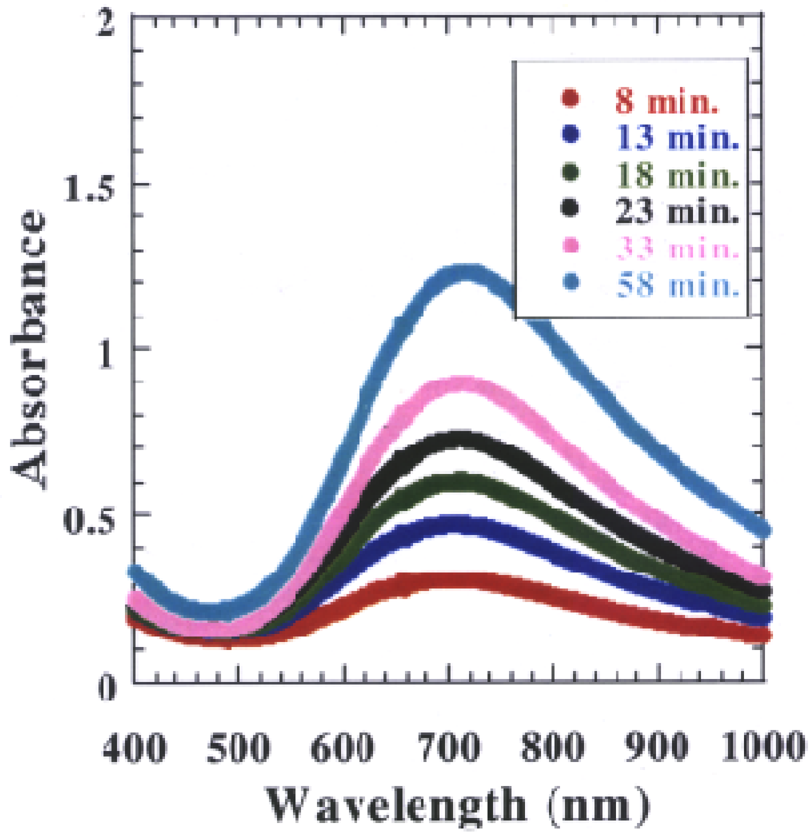
Distilled Water

3.2 < pH < 4.4

Water/surfactant (W_o)= 5; 3000 psi CO_2, 1.2% surfactant

Solid Metal Dissolution

UV-Vis of Cu uptake into microemulsion

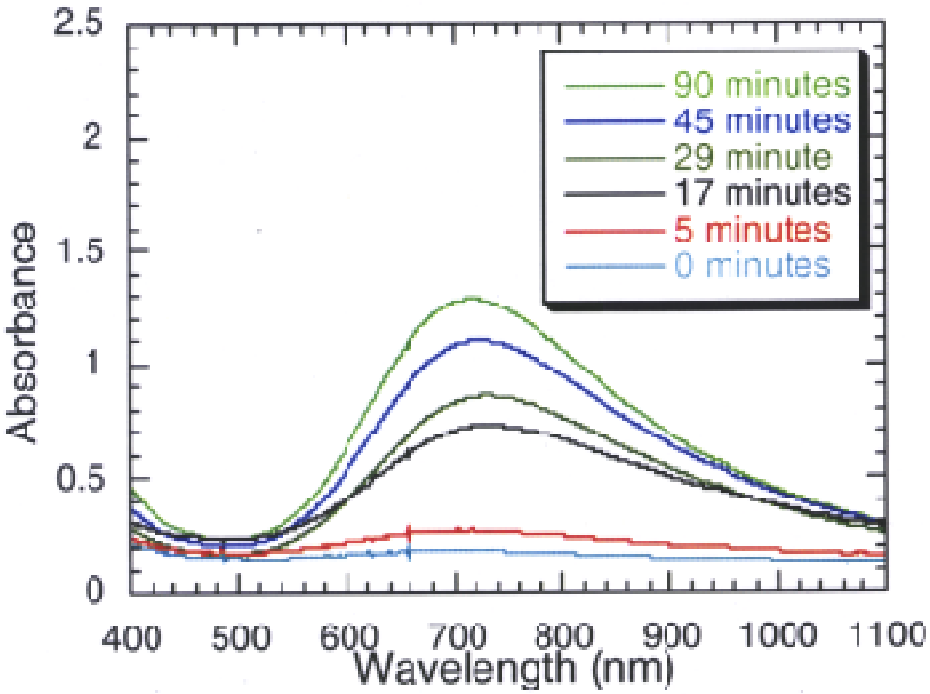


- Solid $Cu(NO_3)_2$ is dissolved into the microemulsion
- [Cu] = 15 mM in CO_2; 3 M in the water phase
- Low surfactant to metal ratio (2:1)

Water/surfactant (W_o)= 5; 3000 psi CO_2, 1.2% surfactant

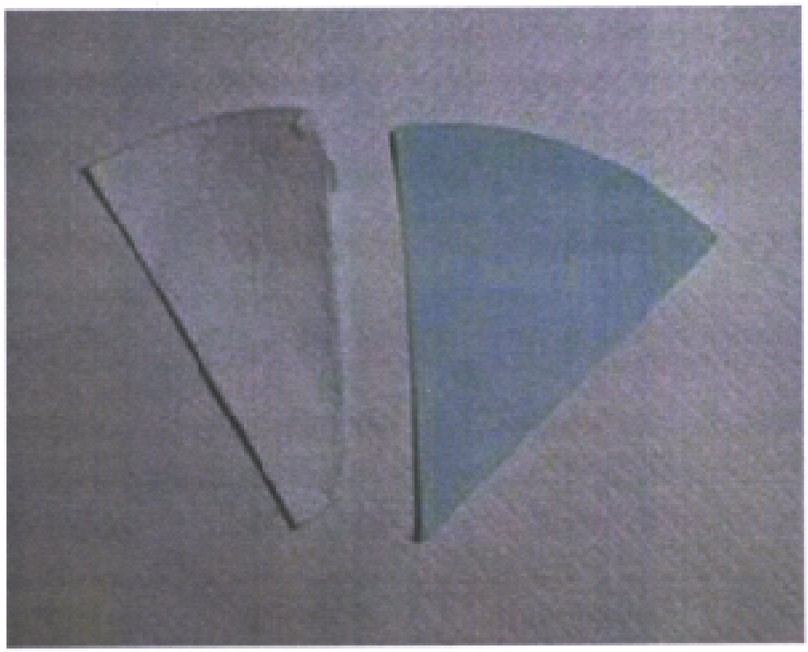
Copper Extraction from Filter Paper

UV-Vis of Cu uptake into microemulsion from filter paper



- Kinetics monitored *in situ* with UV-Vis
- Fast extraction
- Conditions:
  - 40 to 60 µL water
  - 45 °C, 207 bar
  - 10 g CO_2

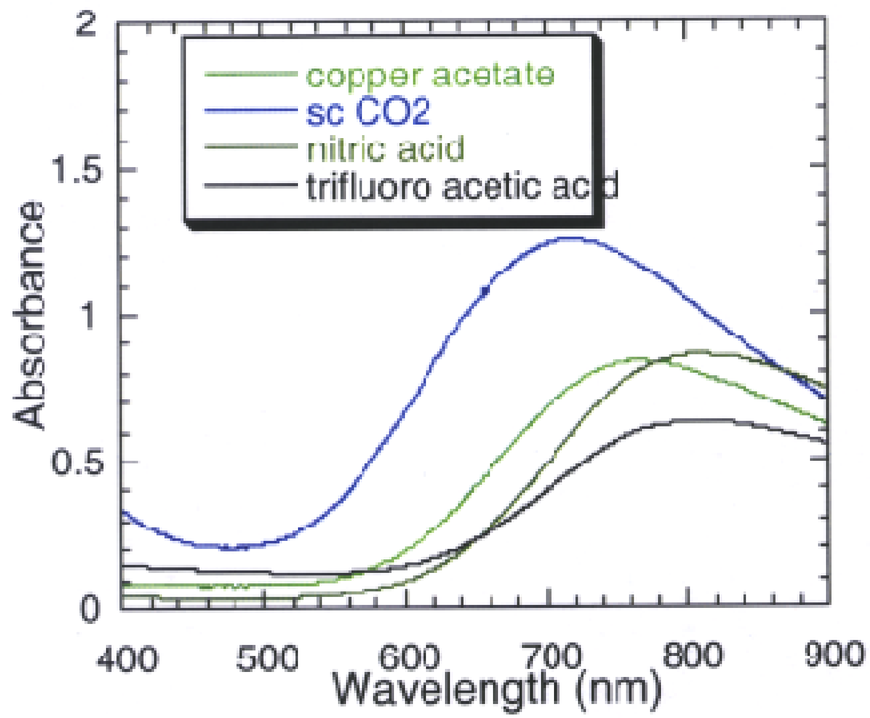
Cu Extraction From Filter Paper



After Before

# extractions	Filter paper (g)	Initial [Cu] (ppm)	% extracted
One	0.018	81400	99.65
One	0.019	81400	99.53
One	0.384	3430	60.2
Two	0.386	4090	98.0
Two	0.238	6630	82.8
Two	0.96	16500	99.7

Micelle Environment

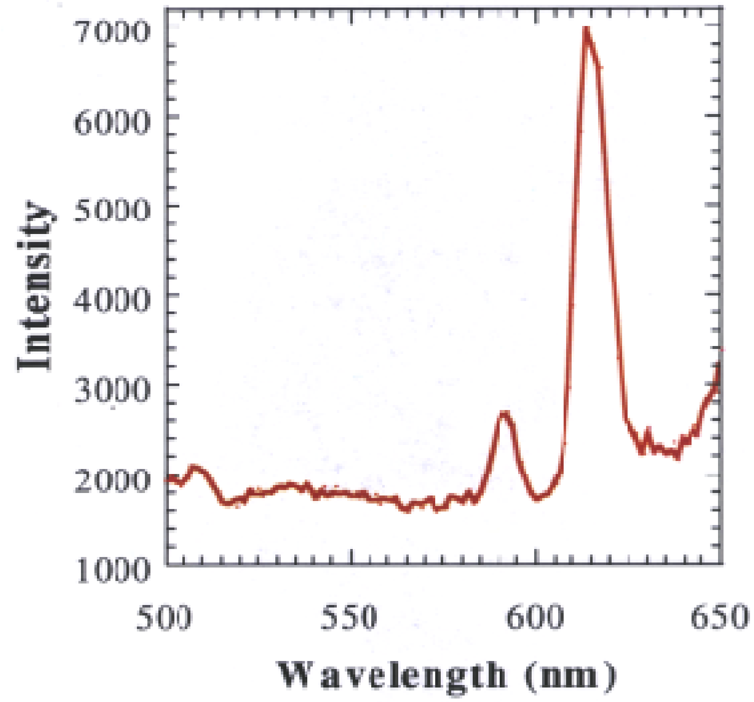


- Micelle environment affects copper spectrum
- Band shifts to higher energy and epsilon increases
- Increase in the ligand field strength

Dissolution of Metal Oxide

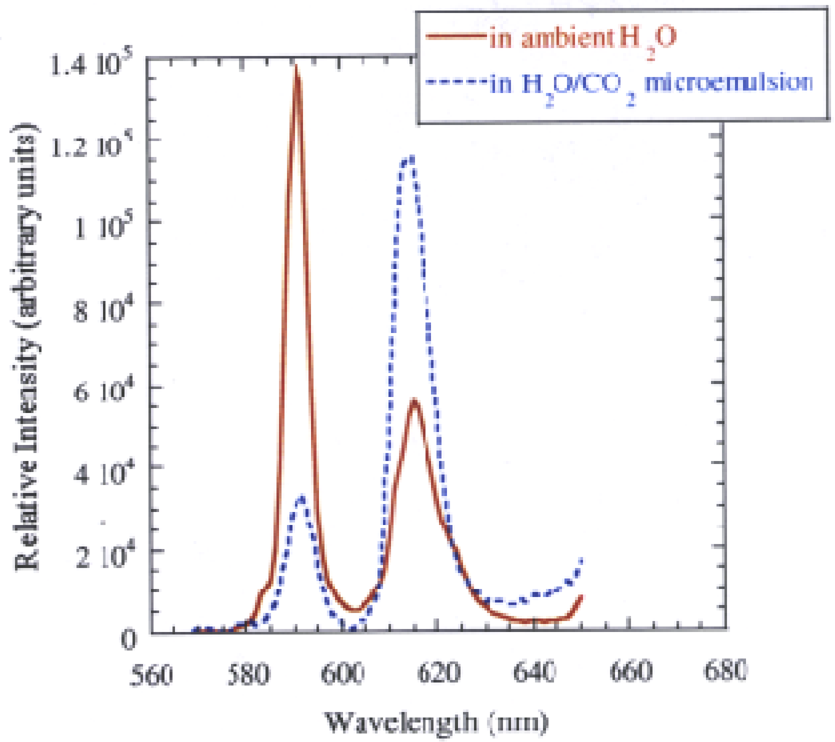
- Solid Eu_2O_3 powder dissolves into a nitric acid microemulsion
- Dissolution of U or Pu oxides may be possible

Emission spectrum of Eu_2O_3 powder in the presence of a microemulsion



Metal Interactions

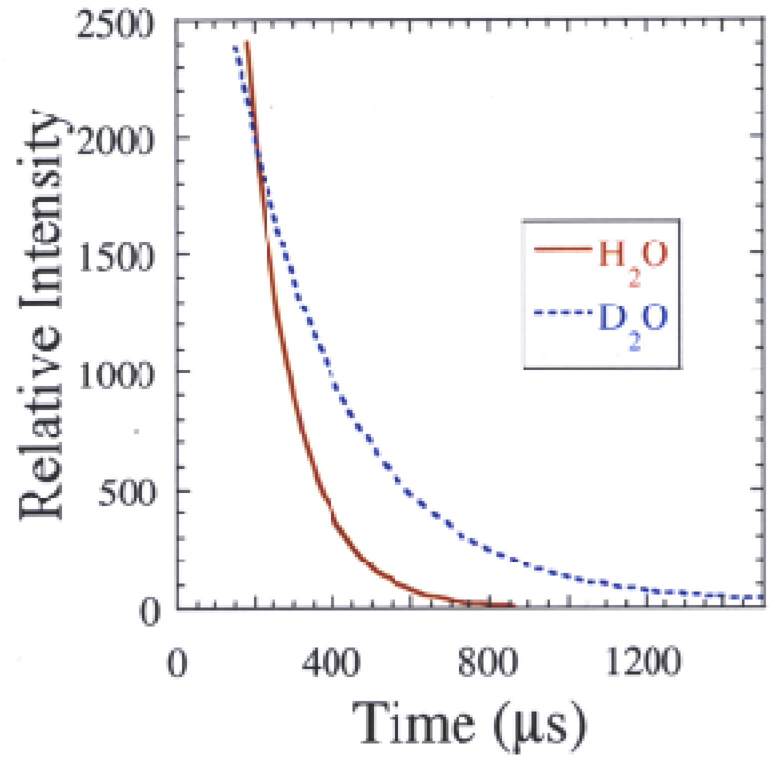
- Eu emission is highly sensitive to the metal environment
  - Intensity increase of 615 nm peak indicates symmetry decrease around Eu ion
  - Water ligands removed
  - Controls indicate no binding of Cl^- or HCO_3^-
- **Eu must be binding to surfactant**



Eu lifetime measurements

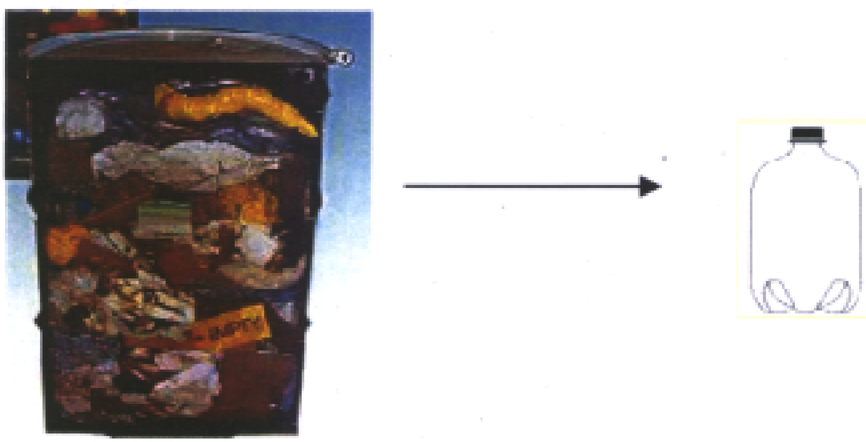
- Lifetime is sensitive to the number of bound water ligands
- Lifetime increases from 120 to 274 ns
- Indicates that only 5 water ligands are bound to Eu

Emission lifetimes of Eu in microemulsions



Potential scale up

- 55 gallon drum of waste
- 2 Kg of surfactant
- 1.2 L of water
- Potential for extracting >200 g Pu



Based on Cu extraction numbers

Conclusions

- Microemulsions rapidly remove metal nitrates from solid surfaces
- Reproducibly removed >99.5% copper nitrate from filter paper in 90 minutes
- Metal oxides may be dissolved with nitric acid into the microemulsion
- Copper and europium interact with carboxylate head group of surfactant

Acknowledgements

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