Fundamental UNEX Chemistry Project #81895

R. S. Herbst, D. R. Peterman, T. A. Luther
Idaho National Engineering & Environmental Laboratory

V. A. Babain, I. V. Smirnov
Khlopin Radium Institute, St. Petersburg, Russia

E. S. Stoyanov
Institute of Catalysis, Novosibirsk, Russia

Background

- ***UNEX is a solvent extraction technology for the simultaneous removal of the major fission products (Cs and Sr), actinides, and lanthanides from radioactive wastes.***

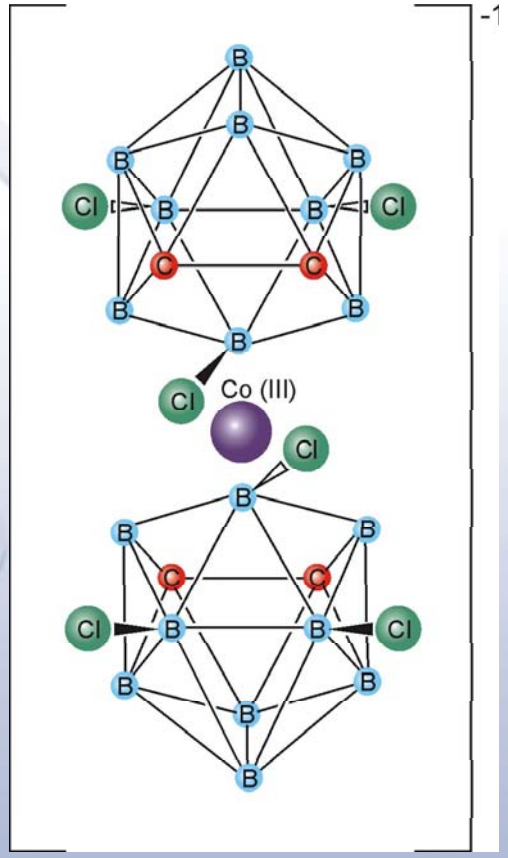
- ***The UNEX Process was initially developed collaboratively by the INEEL and KRI under the auspices of the DOE's TFA and ESP programs – now EMSP.***

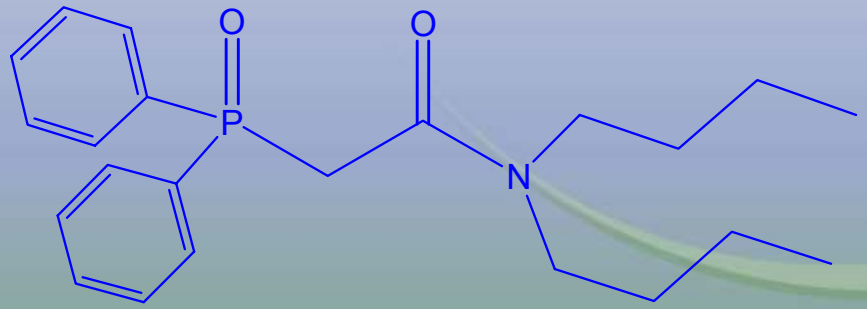
- ***Concept has been demonstrated at the laboratory and pilot scale in countercurrent tests with actual and simulated wastes.***

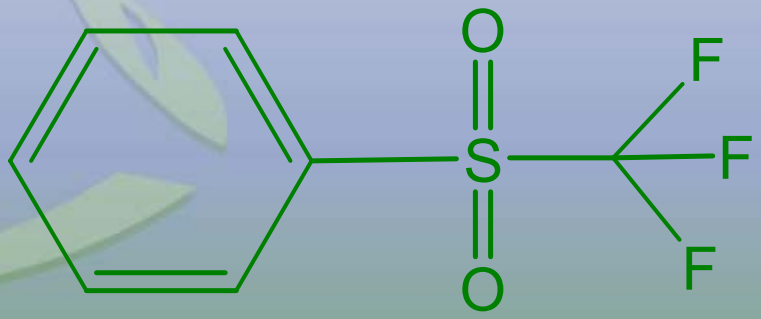
- ***Recoveries of 99.99% for ^{137}Cs, 99.995% for ^{90}Sr, and 99.96% for total α have been obtained from INEEL actual waste samples.***

The UNEX solvent combines:

- *Chlorinated Cobalt Dicarbollide (CCD) for Cs extraction.*
- *Polyethylene glycol (PEG-400) for Sr extraction.* $HO(CH_2CH_2O)_{8\text{-}10}H$
- *Diphenyl-N,N'-di-n-butylcarbamoyl-methylphosphine oxide (DiϕCMPO) for actinide extraction.*
- *Current diluent is phenyltrifluoromethyl sulfone (FS-13).*







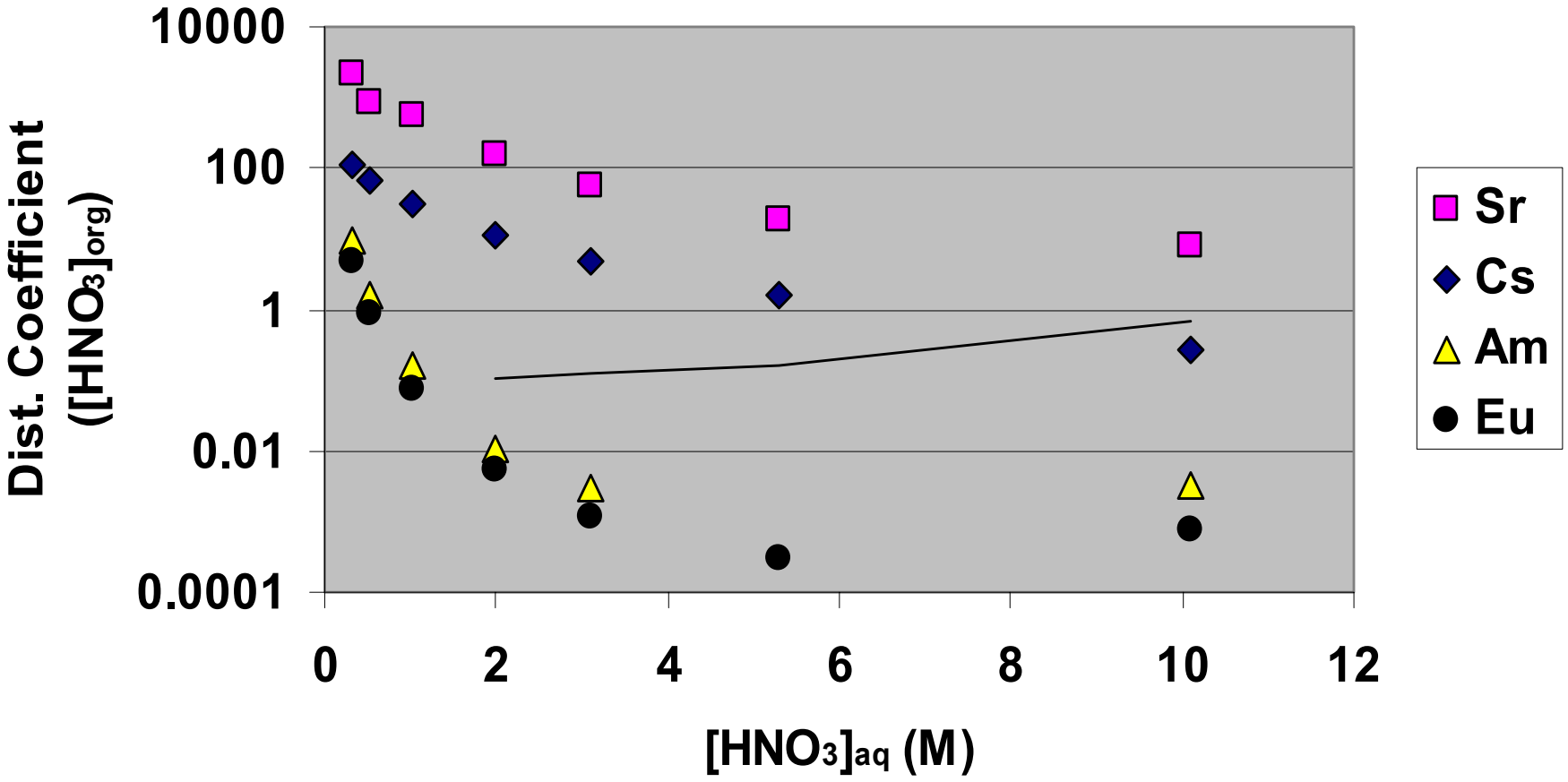
Research Goals

- ***UNEX Process indeed works, but how? - What fundamental chemistry is responsible for the extraction process?***

- ***The purpose of this project is to define the underlying chemical phenomena (mechanisms) operative during the extraction process including-***
  - ***diluent effects***
  - ***role of water, nitrate, and acid***
  - ***stoichiometry of extracted species***

Extraction Dependency on Aqueous [HNO_3]

0.08 M CCD + 0.016 M PEG-400 in FS-13 (25C)



Diluent Effects

- ***Physical properties of over 25 different organic diluents have been evaluated thus far.***
- ***Simple correlations between D_{Cs} and diluent properties (ε, MR_D, Δv $(OD)_{CD_3OD}$) have not been observed.***
- ***Collection of additional diluent data and evaluation of multi-parameter correlations is planned.***

Diluent Effects

Diluent	0.06 M CCD		
	D_{Cs}		
	3M HNO_3	3M $NaNO_3$	3M $LiNO_3$
nitrobenzene	8.5	26	46
FS-13	3.7	4.7	14
dichloroethane	1.4	14	14

Diluent	0.06 M CCD + 0.03 M PEG-400				
	D_{Cs}			D_{Sr}	
	3M HNO_3	3M $NaNO_3$	3M $LiNO_3$	3M HNO_3	3M $NaNO_3$
nitrobenzene	2.5	5.5	32	94	4.4
FS-13	1.1	1.3	12	160	4.3
dichloroethane	0.55	4.9	6.8	150	26

Diluent Effects (cont)

0.06 M CCD + Diluent	D_{Cs} 3M HNO_3	MR_D	ε	Δv (OD) in CD_3OD
2,2'-dichlorodiethyl ether	0.07	32	21	71.5
dichloroethane	0.55	20.9	10	21.7
2-nitroanisole	0.77	37.3	4.8	32.9
FS-13	1.1	43.4	29	21.3
2-nitrotoluene	2.7	37.4	27	23.3
nitrobenzene	2.5	32.9	35	28
3-nitrobenzotrifluoride	3.9	37.3	22.3	23.3
4-chloro-3-nitrobenzotrifluoride	4.3	42.4	13.1	9.8

Organic Phase Strontium Complex

- *IR spectroscopic studies of the organic phase:*
  - *Sr^{+2} saturated solution of 0.05 M CCD in DCE (w/o PEG):*

    $[Sr^{+2} \bullet 8H_2O]\ CCD^-_2$

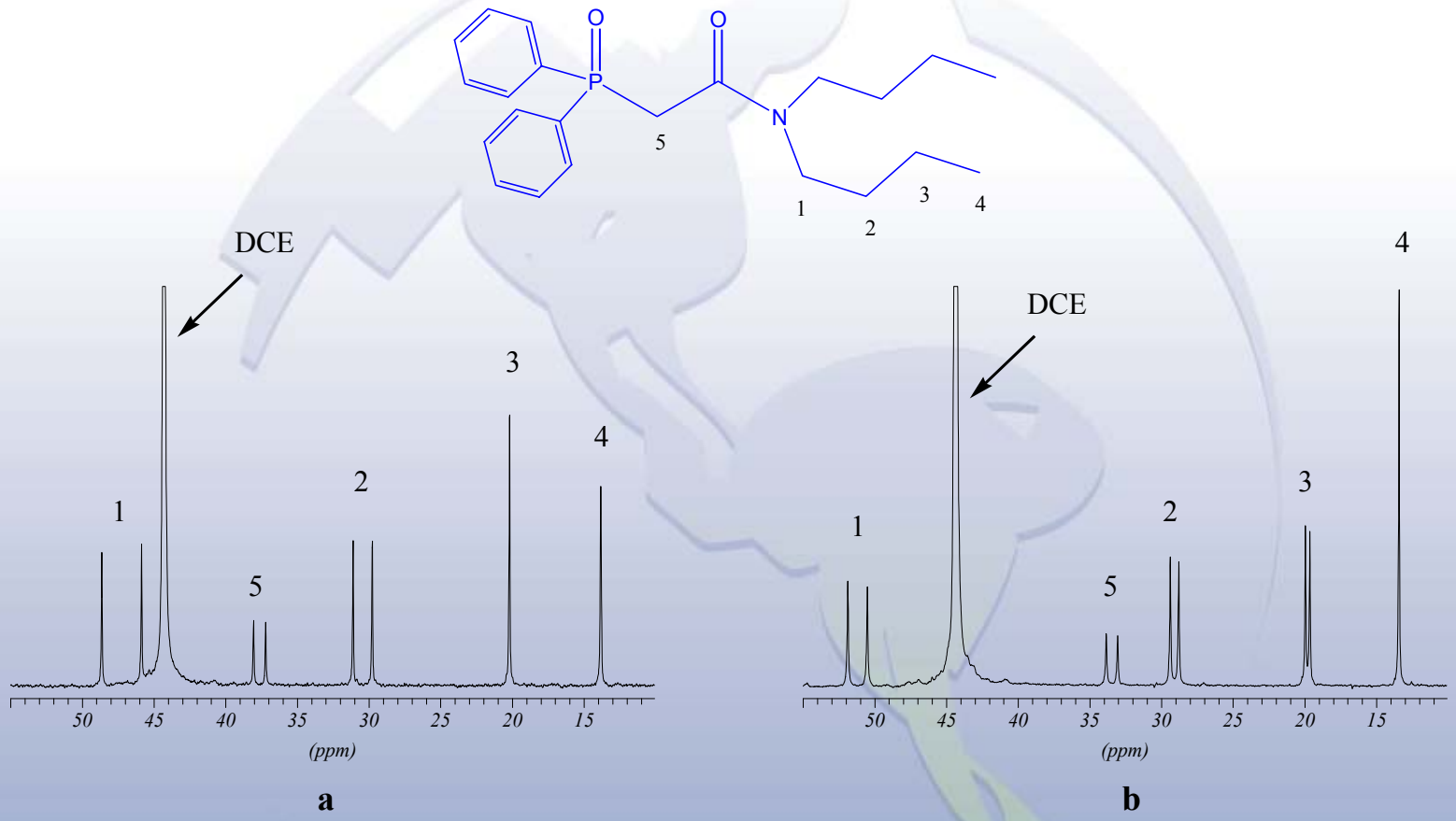
  - *Sr^{+2} sat'd sol'n of 0.05 M CCD & 0.05 M PEG-400 in DCE:*

    $[Sr^{+2} \bullet PEG]\ CCD^-_2$ *1:1 complex*

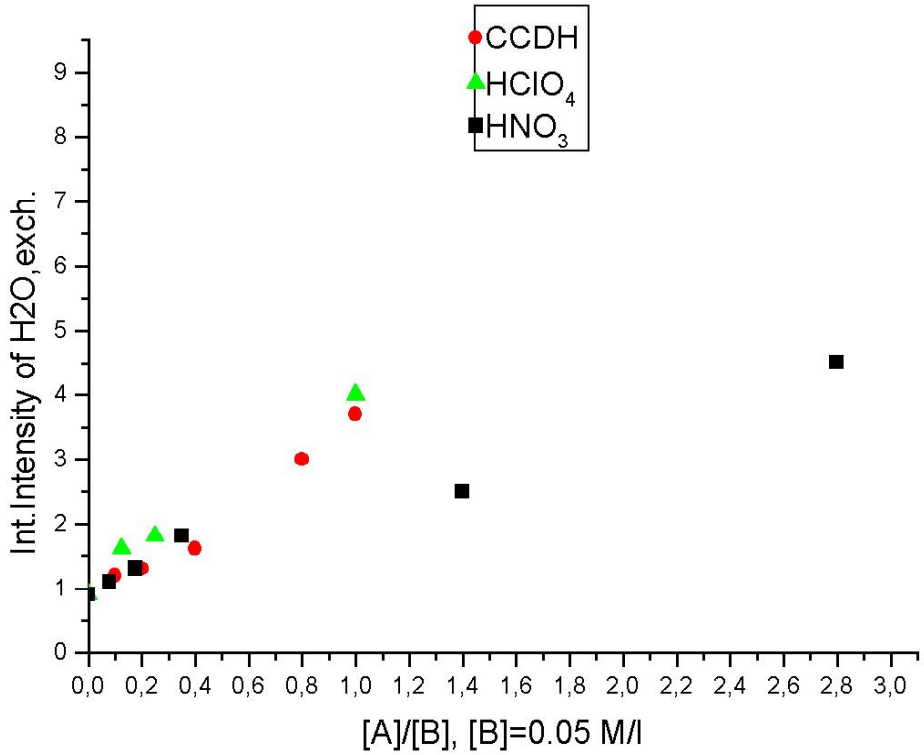
- *Etheral oxygen's in PEG displace 8 H_2O molecules from 1st coordination sphere. Consistent with Sr^{+2} extraction data vs. PEG size:*

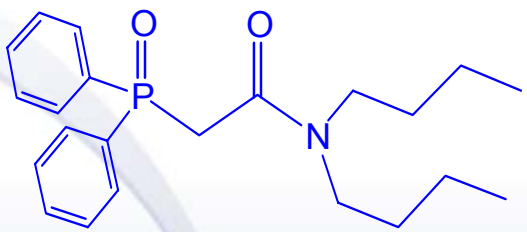
$HO(CH_2CH_2O)_n H$

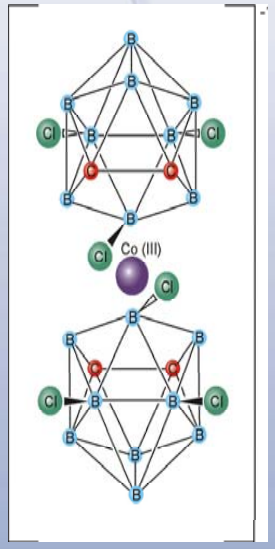
	Ave. n	D_{Sr}
PEG-300	6-7	4.0
PEG-400	9	4.1
PEG-1500	33-34	0.6



^{13}C NMR spectra of CMPO in 1,2-dichloroethane (a) and after contact with 11M $HClO_4$ (b).







Dependence of water intensity in H^+A – CMPO systems versus concentration of acid. In all cases the concentration of CMPO is constant at 0.05 M in 3-nitrobenzotrifluoride.

- ***Strong acids, such as $HClO_4$ or HCCD form new complexes with CMPO by protonation of the nitrogen nuclei.***

^{13}C NMR spectra exhibit significant downfield chemical shifts and a decrease in the diastereotopic nature of the carbon nuclei resonance in the butyl groups adjacent to the nitrogen.

	δ CH_2 (ppm)	$\Delta\delta$ (ppm)
"wet"	48.6, 45.9	2.7
6M $HClO_4$	49.9, 47.8	2.1
8M $HClO_4$	50.7, 49.0	1.7
11M $HClO_4$	51.9, 50.5	1.4

^{1}H NMR spectra indicate the water content in the organic phase increases (based on integration) with increasing acid strength:

	δ (ppm)	Intensity
"wet"	2.35	2.05
6M $HClO_4$	9.10	2.62
8M $HClO_4$	10.65	2.61
11M $HClO_4$	11.58	3.99

Continuing Research Directions

- Continue efforts to correlate extraction distributions to physical properties of the diluent – multi-parameter correlations.
- Evaluation of organic phase structures via IR and NMR spectroscopic techniques.
- Ultimately verify structures using EXAFS.

Site Needs - INEEL

- *The UNEX process is one viable option for the treatment and disposal of INEEL's calcine waste.*
- *Data necessary to support calcine treatment technology selection in 2007.*
- *Current data indicate the UNEX treatment option for INEEL calcine potentially saves $1.8B net cost avoidance over direct vitrification of calcine.*
- *Also anticipated to provide a potential payback of ~100 return on development investment.*