Removal of Radioactive/Toxic Cations and Anions from Polluted Water Using Ligand-Modified Colloid-Enhanced Ultrafiltration

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RESEARCH OBJECTIVES

Optimize removal of uranium, thorium, plutonium, strontium, lead, cadmium, & chromium from contaminated water using ligand-modified colloid-enhanced ultrafiltration (LM-CEUF).

Optimize recovery of colloid and ligands for reuse in the process.

Develop design parameters for scale-up of process for field demonstration

TECHNICAL APPROACH

Water-soluble colloid, along with ligand, is added to contaminated water

Ligand selectively complexes target metal ion(s)

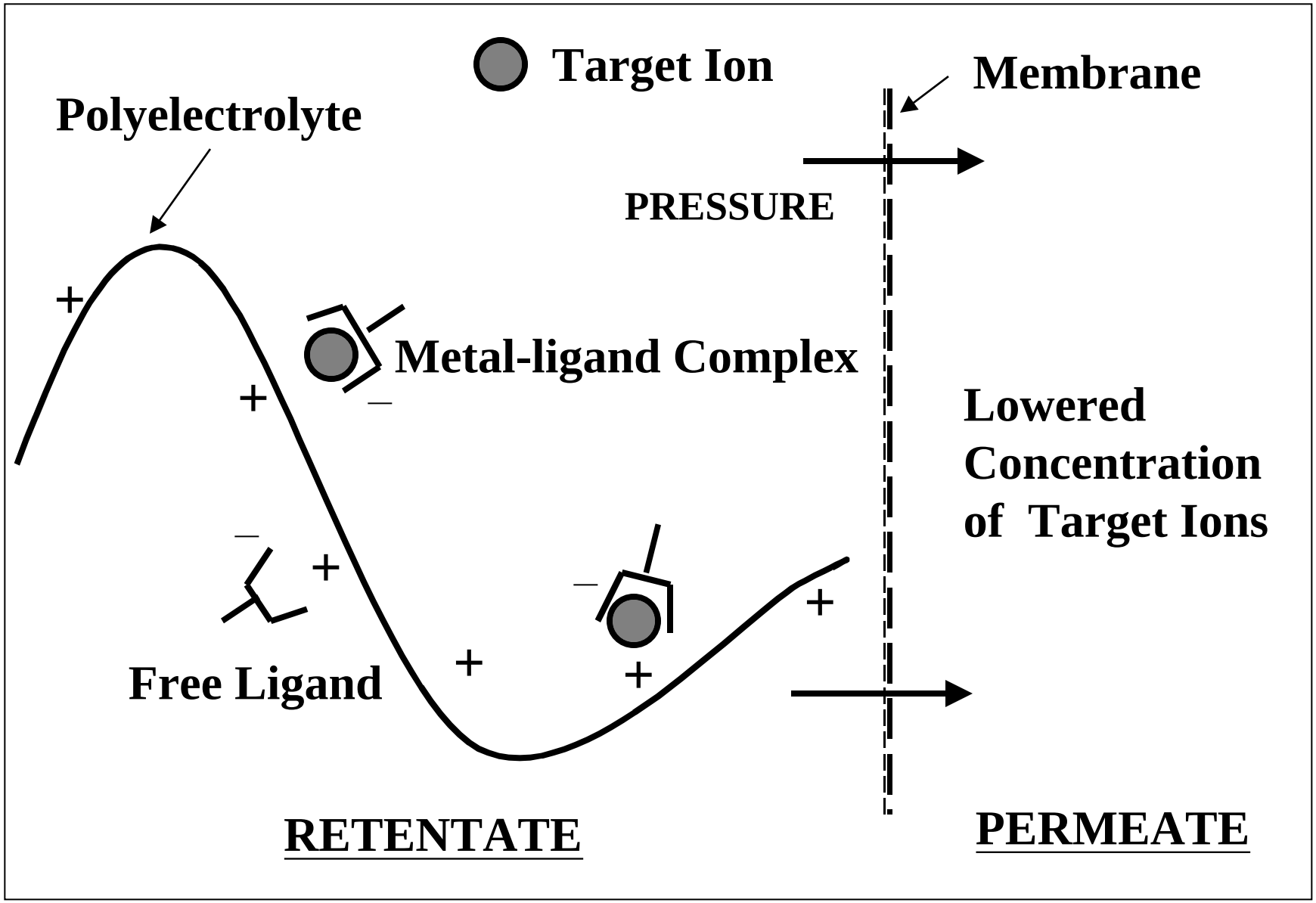
Metal-ligand complex partitions into colloid

Ultrafiltration produces:

<u>a highly-concentrated solution</u> of target metals, ligands, and colloid **(RETENTATE)**

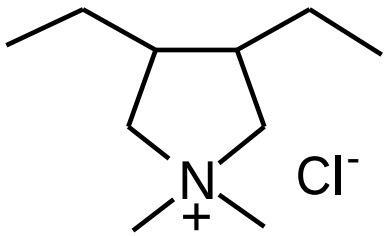
<u>a purified solution</u> passing through the membrane **(PERMEATE)**

LM-PEUF


Target Ion
Membrane
Polyelectrolyte
PRESSURE
Metal-ligand Complex
Lowered
Concentration
of Target Ions
Free Ligand
RETENTATE
PERMEATE

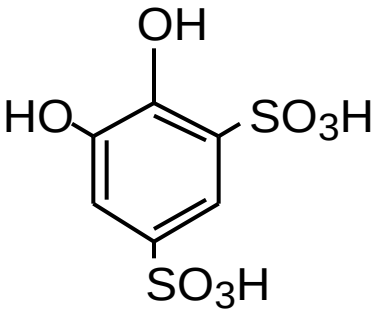
COLLOIDS:

$CPNO_3$
Cetylpyridinium nitrate

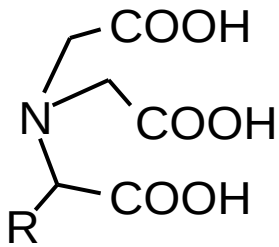


PDADMAC
Polydiallyldimethyl-
ammonium chloride

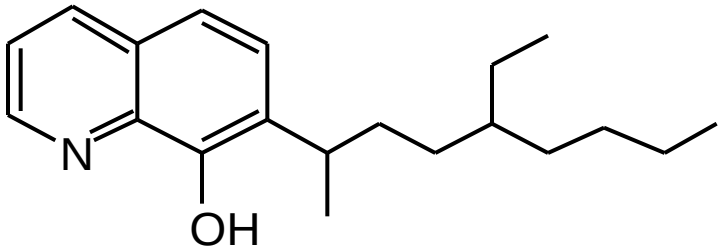
LIGANDS:



DHBSA
dihydroxy-
benzenedi-
sulphonic acid

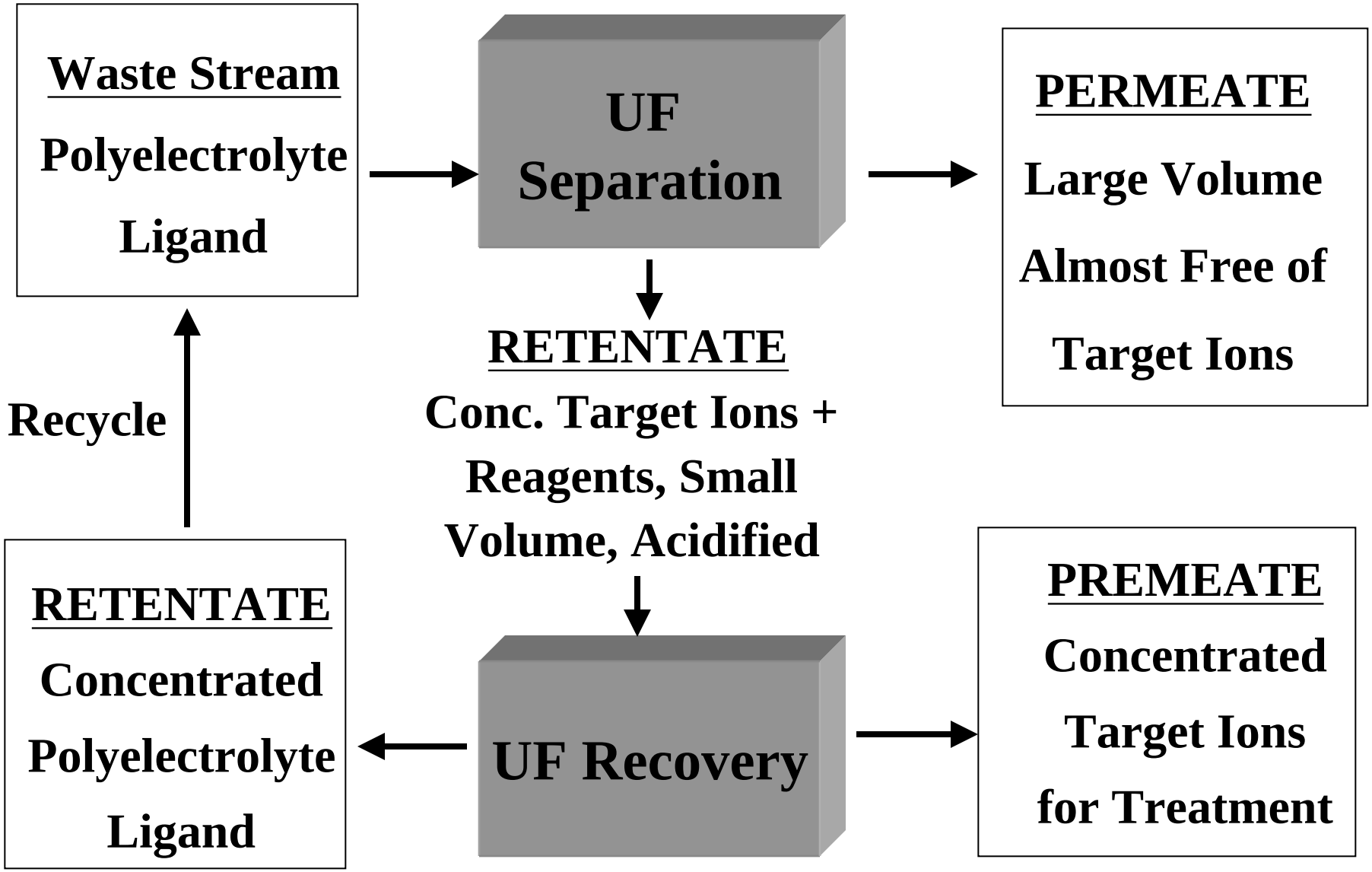


RNTA
nitrilotriacetic
acid; R = $C_{10}H_{21}$
R = CH_2SO_3H



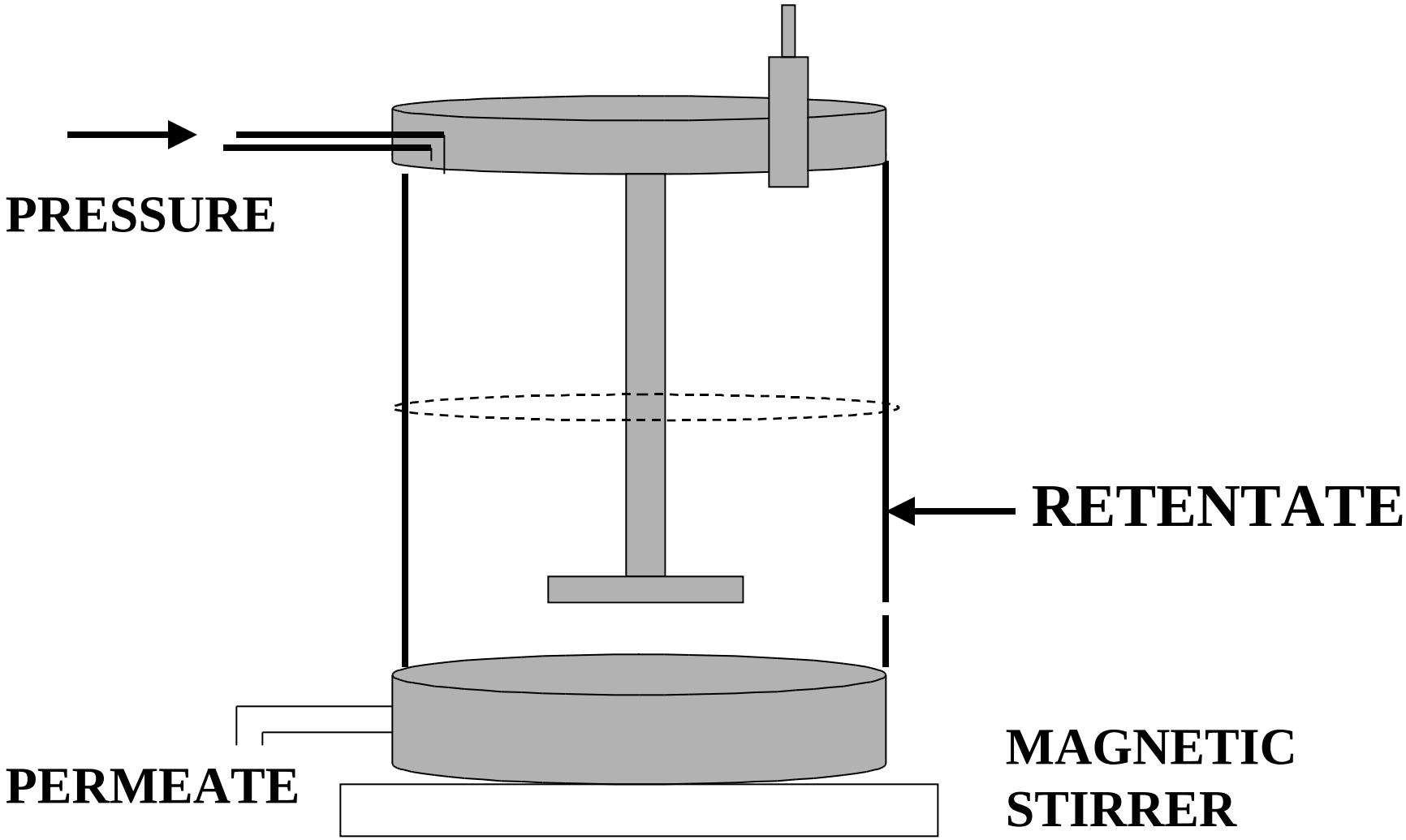
8-HQR
$C_{11}H_{23}$-(8-hydroxyquinoline)

LM-PEUF PROTOCOL



STIRRED CELL ULTRAFILTRATION

rejection: $R_X(\%) = (1 - [X]_{per}/[X]_{ret}) \times 100\%$



Research Status - Systems Studied

Metal	Ligand	Colloid
Pb^{2+}	Nitrilotriacetic acid derivatives	$CPNO_3$, PDADMAC
Cd^{2+}	8-Hydroxyquinoline	$CPNO_3$
UO_2^{2+}	Carbonate	PDADMAC
UO_2^{2+}, Th (IV)	Dihydroxybenzene-disulfonic acid	PDADMAC
CrO_4^{2-}	- - - - - -	PDADMAC

Summary: Pb^{2+} - RNTA

Ligand/Colloid	Rejection	Conditions
DNTA / $CPNO_3$	99.7 - 99.9 %	low salt
($C_{10}H_{21}$-NTA)	99.4 - 99.5 %	50 mM salt
SNTA / PDADMAC	99.0 - 99.9 %	low salt
($^{-}O_3SCH_2$-NTA)	50 - 55 %	50 mM salt

Ligand Recovery

DNTA	85 %	pH ~3.5
SNTA	96 %	+ oxalate

Summary: Cd^{2+} / 8-HQR / $CPNO_3$

Ligand	Rejection	Conditions
8-HQR	99.0 - 99.7 %	low salt, pH 9.0
	99.5 - 99.6 %	+10 mM NaCl
	99.4 - 99.7 %	+10 mM Ca^{2+}

Ligand Recovery	
~88 %	pH ~ 6.0

Summary:
UO_2^{2+} - Carbonate - PDADMAC

Rejection	Conditions
99.91 - 99.95 %	low salt
96.0, 82.1 %	10, 20 mM NaCl

Ligand Recovery	
~30-40%	pH 2.0, UF
~60 %	pH 2.0, ED

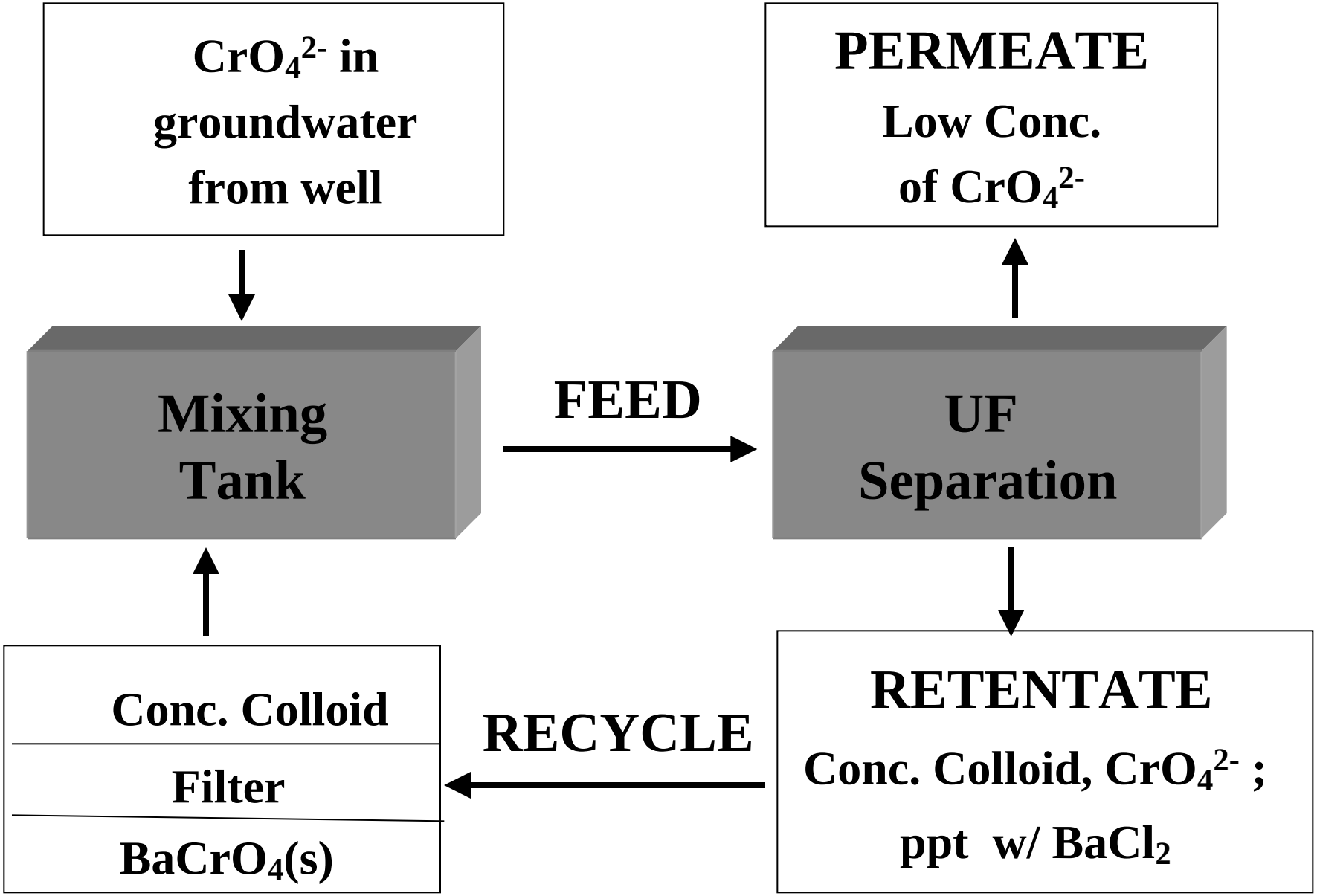
Summary: UO_2^{2+}/Th(IV) - DHBSA

Metal	Rejection	Conditions
UO_2, Th	≥ 99.9 %	low salt
UO_2	99.8 %	20 mM NaCl
Th	99.5 %	20 mM NaCl

Ligand Recovery

UO_2	40-50%	pH 2.0
Th	50 %	pH 1.3

FIELD TEST : Chromate - PEUF



CrO_4^{2-} Removal Using PDADMAC

System	Scale	Rejection (%)	Conditions
CrO_4^{2-} (alone)	lab	94.8 - 99.4 % 88.1 - 96.7 %	0 NaCl 6-10 mM NaCl
CrO_4^{2-} (+ ions)	lab	96.0 - 99.1 %	± Cu^{2+}, H_nDTPA^{n-5}
CrO_4^{2--} (ground-water)	field test	82.2 - 91.7 %	~500 ppm salts

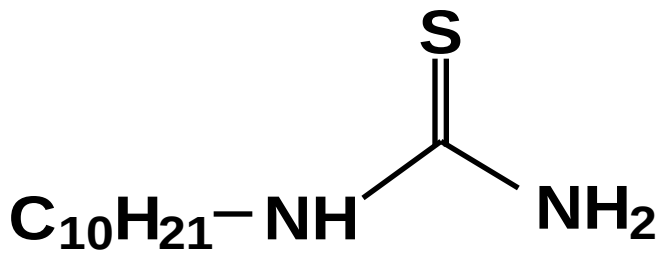
Summary - Rejection (%)*

Metal - Ligand	Rejection
UO_2^{2+} - Carbonate	$96.1 - 99.9_8\%$
UO_2^{2+} - DHBSA	$99.7_8 - 99.9_7\%$
Th(IV) - DHBSA	99.7 - 99.9%
Cd^{2+} - 8-HQR	99.0 - 99.7%
Pb^{2+} - RNTA	99.0 - 99.9%
CrO_4^{2-} - PDADMAC	82 - 92%

*Rejection (%) = 100 x (1-[permeate]/[retentate])

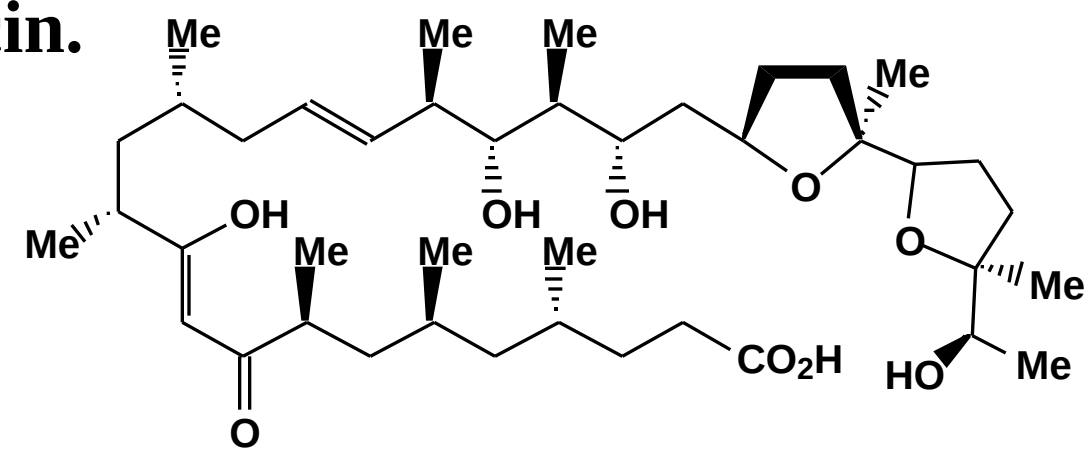
Recent Results / Preliminary Studies

Selective Hg^{2+} removal using *n*-decylthiourea with $CPNO_3$ as colloid; $R_{Hg} \geq 99.5\%$.



Decylthiourea (DTU)

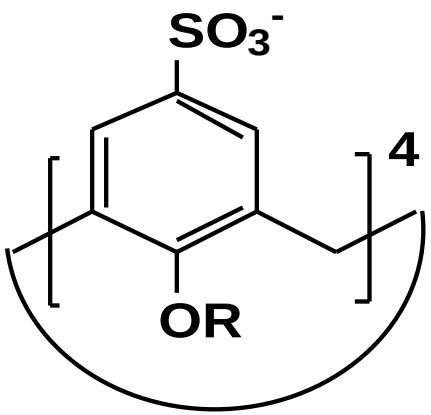
Selective transport of Pb^{2+} across membrane by polyether ionomycin. Selectivity ≥ 1000 ($S_{Pb} = J_{Pb}/J_M$) for M = Ca^{2+}, Sr^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}.



Ionomycin

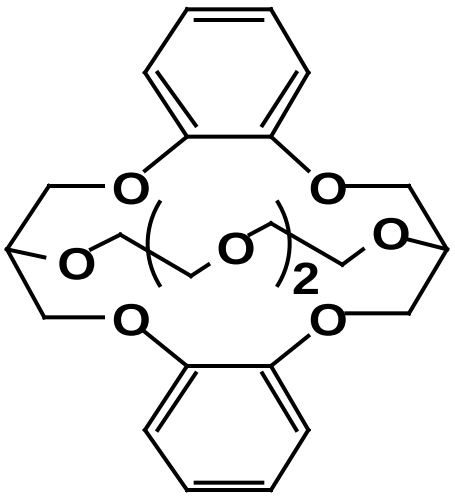
Recent Results / Preliminary Studies

Calix-[4]-arene(SO_3^-)$_4$ tested with PDADMAC. $R_{clx} \geq 99.5\%$ even in 0.5 M NaCl. Derivatives may be useful ligands for LM-PEUF where high concentrations of electrolyte are present.



Calix[4]arene-(SO_3^-)$_4$

$C_2B_2B_4$ complexes Sr^{2+} Selectively relative to other alkali and alkaline -earth ions. Log K_{ML} : 5.4_0 (Ca^{2+}), 7.6_3 (Sr^{2+}), 5.4_0 (Ba^{2+}), 5.7_6 (Na^+).



CRYPTAND $C_2B_2B_4$

Potential Applications

Removal of metals from existing contaminated water at DOE site.
-(ID-7.2.1, SR00-4014, ID-2.1.28, ID-2.1. 36)

Clean-up of solutions resulting from decontamination and decommissioning operations.
-(SR00-4015, ID-7.2.24, RL-DD026-S, ID-S.2.06, RL-DD021, OH-AB-0110)

Remediation of subsurface contamination
-(CH-SS01-99, RL-SS07, RL-SS04, ORHG-15)

SITE NEEDS: Removal of metals from existing contaminated water at DOE sites

Reactor Canal Water Cleanup - Cd, Cr, Pb, Co, Ba, Cs (ID-7.2.1; DDFA)

Basin Cleanup Technology - Sr, Cs (SR00-4014; DDFA)

Hg, Sr and Cs Removal from Liquid Wastes (ID-2.1.36, ID-2.1.28; TFA)

SITE NEEDS: Clean-up of solutions resulting from D& D operations.

Decontamination of Small Components
(SR00-4015; DDFA)

Decontamination of Metal Debris
(ID-7.2.24; DDFA)

Removal of Tc-99 from Soil Washing Leachate
(OH-AB-011; SCFA)

Metal Decontamination - Basic Science & Technol.
(RL-DD026-S, ID-S.2.06, RL-DD021; DDFA)

SITE NEEDS: Remediation of contaminated groundwater (and soil)

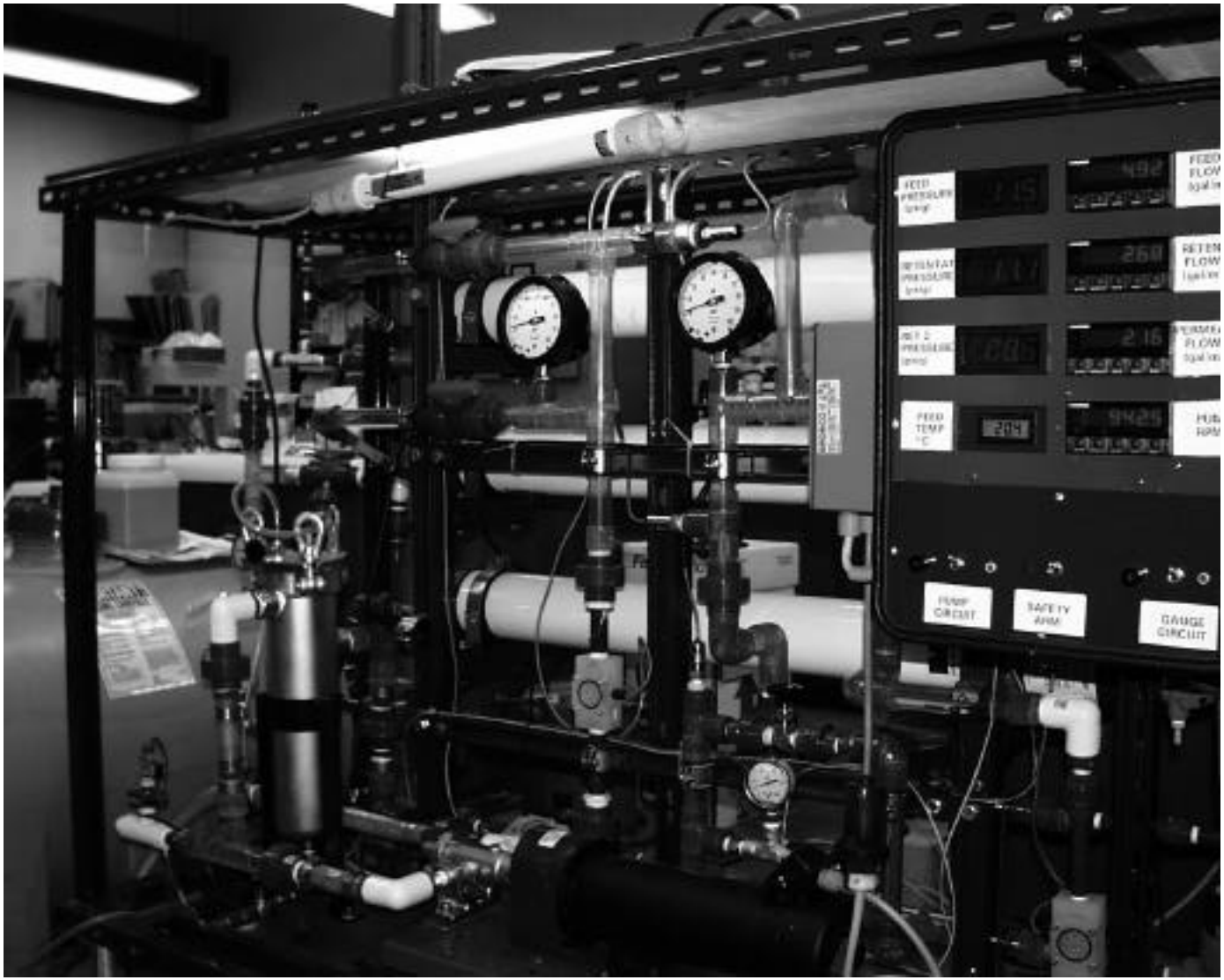
Remediation of Sr-90 Contaminated Groundwater (CH-SS01-99, RL-SS07; SCFA)

Remediation of Hg in Groundwater and Surface Water (ORHG-15; SCFA)

In Situ Remediation of Cr(VI) in Groundwater (RL-SS04; SCFA)

Remediation of Subsurface Water Contaminated by U, Tc, and TCE (OH-AB-006; SCFA)

FIELD TEST - Camp Lejeune, NC: Ultrafiltration unit used to recover colloid in groundwater treatment



Summary

High percent removal of uranium, thorium, cadmium, lead, and chromate, with large reduction in volume.

Excellent efficiency in presence of moderate electrolyte concentration.

Integrated process for metal removal and ligand / polyelectrolyte recovery.

Continuous, low-energy process.

Ultrafiltration with added colloids demonstrated in the field.

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