Utilizing combinations of co-precipitation, solvent extraction and chromatography to design efficient analytical and preparative scale separations

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Eichrom Technologies and PG Research Foundation

RRMC
Radiobioassay & Radiochemical Measurements Conference

RRMC 2013
Rohnert Park, California
October 21 -October 25, 2013

Separation Toolbox

(Selective) Dissolution

Precipitation

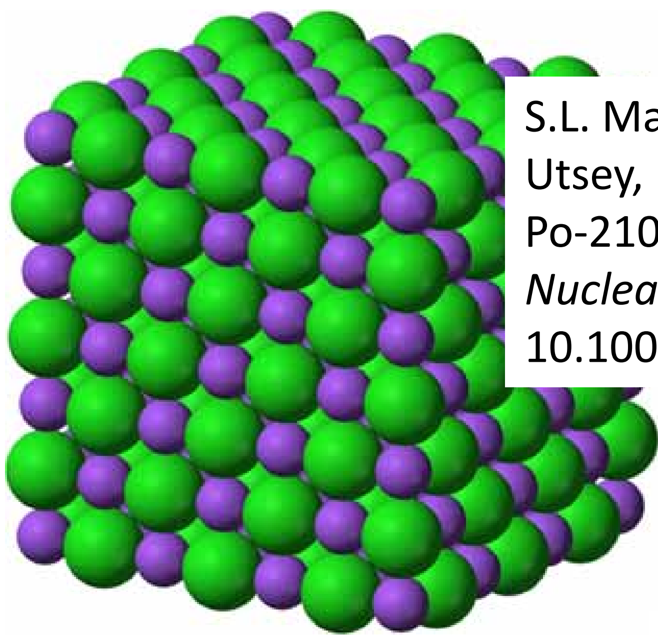
Solvent Extraction

Chromatography

(Co)Precipitation

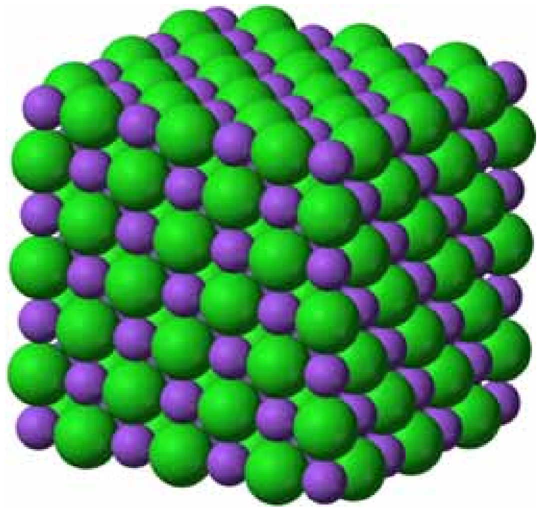
Preconcentration Matrix Removal Source Preparation

AgCl	BaSO4	PbSO4	CaCO3	BaCO3
CeF3	Fe(OH)3	Calcium-Phosphate		MnO2
Hydrous Titanium Oxide		Ca-oxalate	BiPO4	



S.L. Maxwell, B.K. Culligan, J.B. Hutchison, R.C. Utsey, D.R. McAlister, "Rapid Determination of Po-210 in Water Samples," *Radioanalytical and Nuclear Chemistry*, in press, (2013) DOI: 10.1007/510967-013-2644-2.

Library.lanl.gov/radiochemistry/elements.html



Additional ppt

Complete Recovery of analyte(s)

Solvent Extraction

Compatibility with Matrix

Chromatography

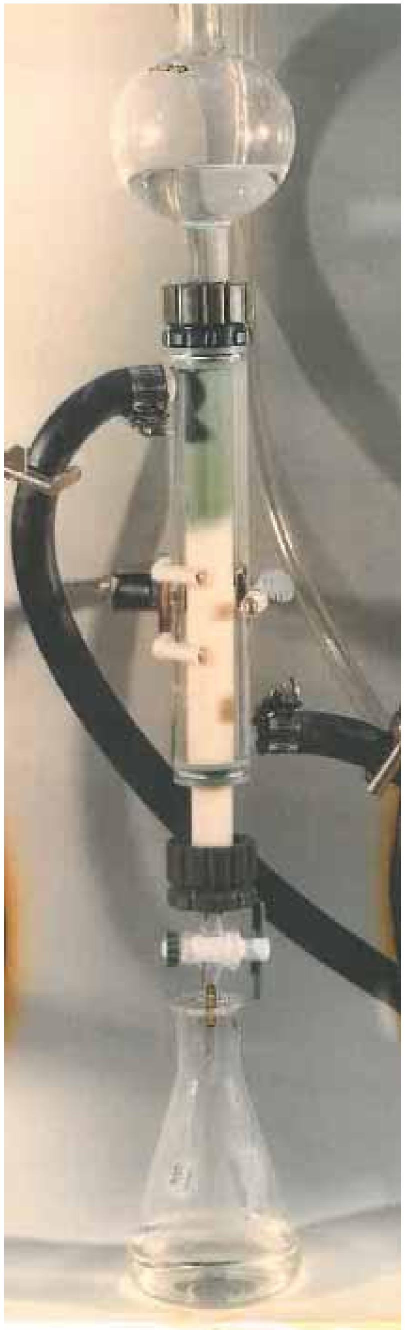
Redissolve?

Compatibility with Separation Methods

Decontamination?

"Matrix and High Loading Effects on EXC Resins," D.R. McAlister, E.P. Horwitz, Eichrom Workshop at 58th Annual Radiobioassay and Radiochemical Measurements Conference, Fort Collins, CO, October 29 to November 2, 2012.

Chromatography



Ion Exchange

Relatively Cheap Reagents

Moderate Selectivity

Moderate Capacity

Extraction Chromatography

Resins more Expensive

Superior Selectivity

Limited Capacity

Solvent Extraction

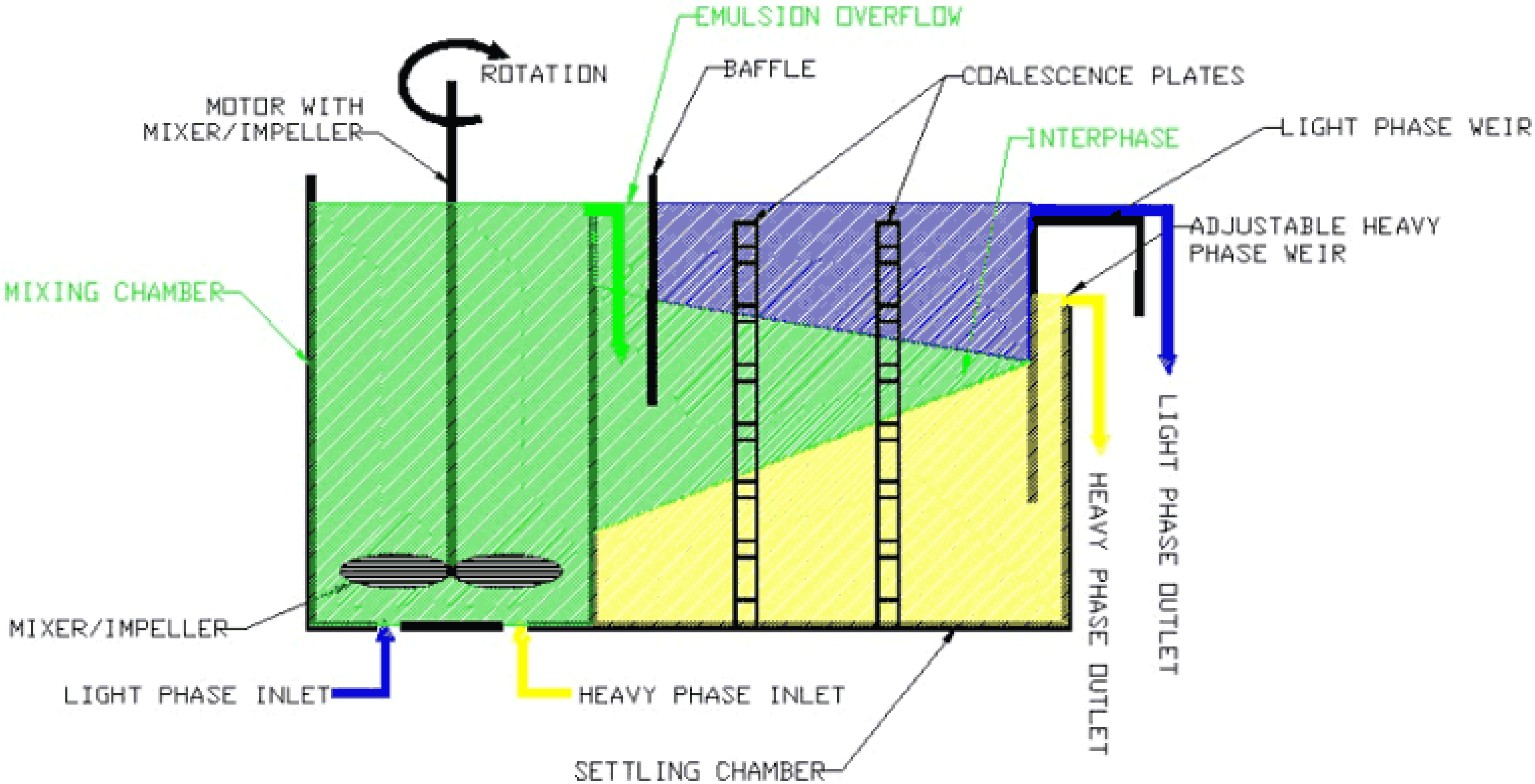
Relatively Cheap Reagents

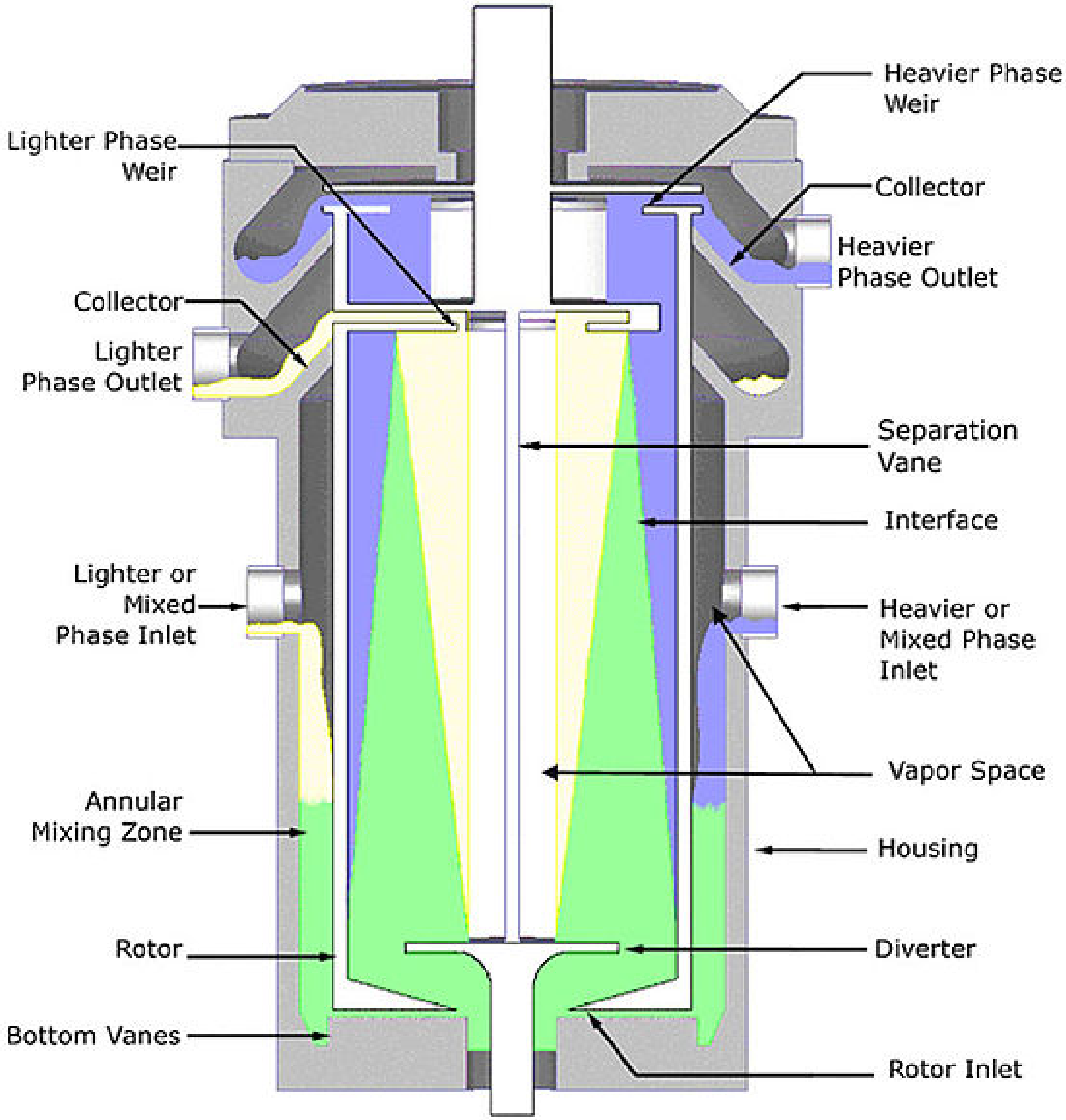
Higher Capacity/Throughput

Stage Efficiency Limited by Entrainment

Third phase, Interfacial CRUD, solvent degradation

LABORATORY MIXER-SETTLERS:

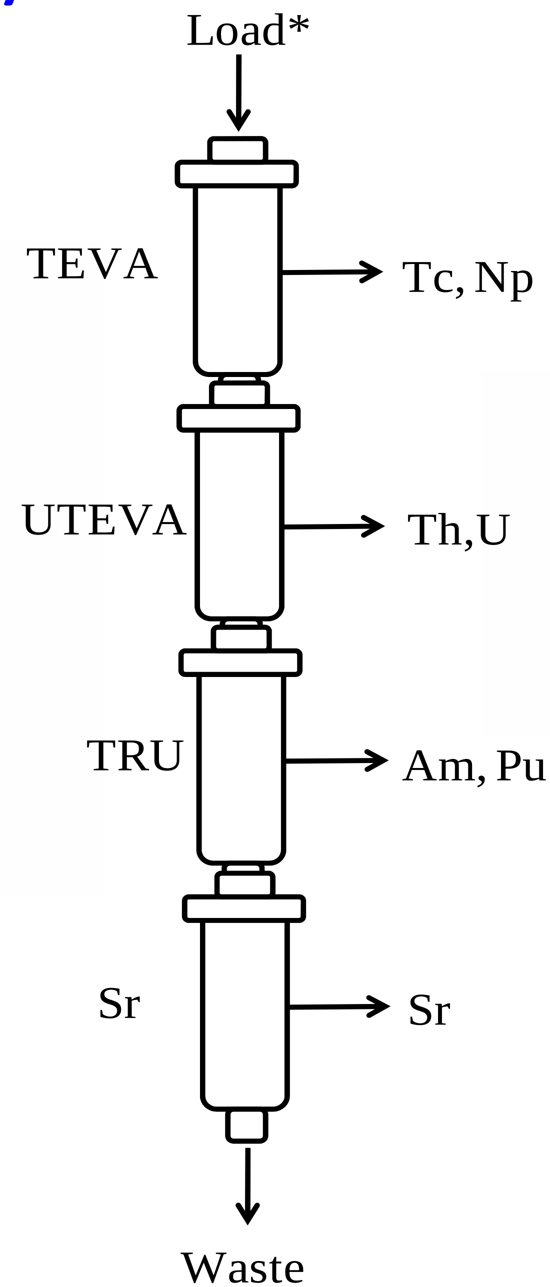



Heavier Phase Weir
Lighter Phase Weir
Collector
Heavier Phase Outlet
Collector
Lighter Phase Outlet
Separation Vane
Interface
Lighter or Mixed Phase Inlet
Heavier or Mixed Phase Inlet
Vapor Space
Annular Mixing Zone
Housing
Rotor
Diverter
Bottom Vanes
Rotor Inlet

Analytical

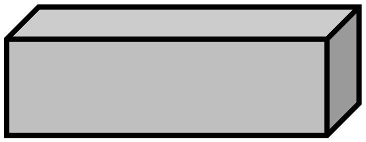
Sample

Load Solution

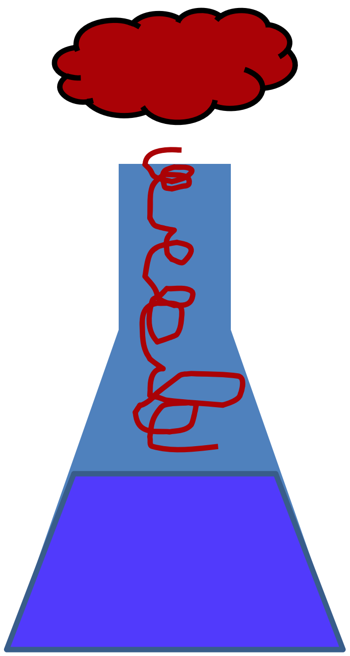


counting

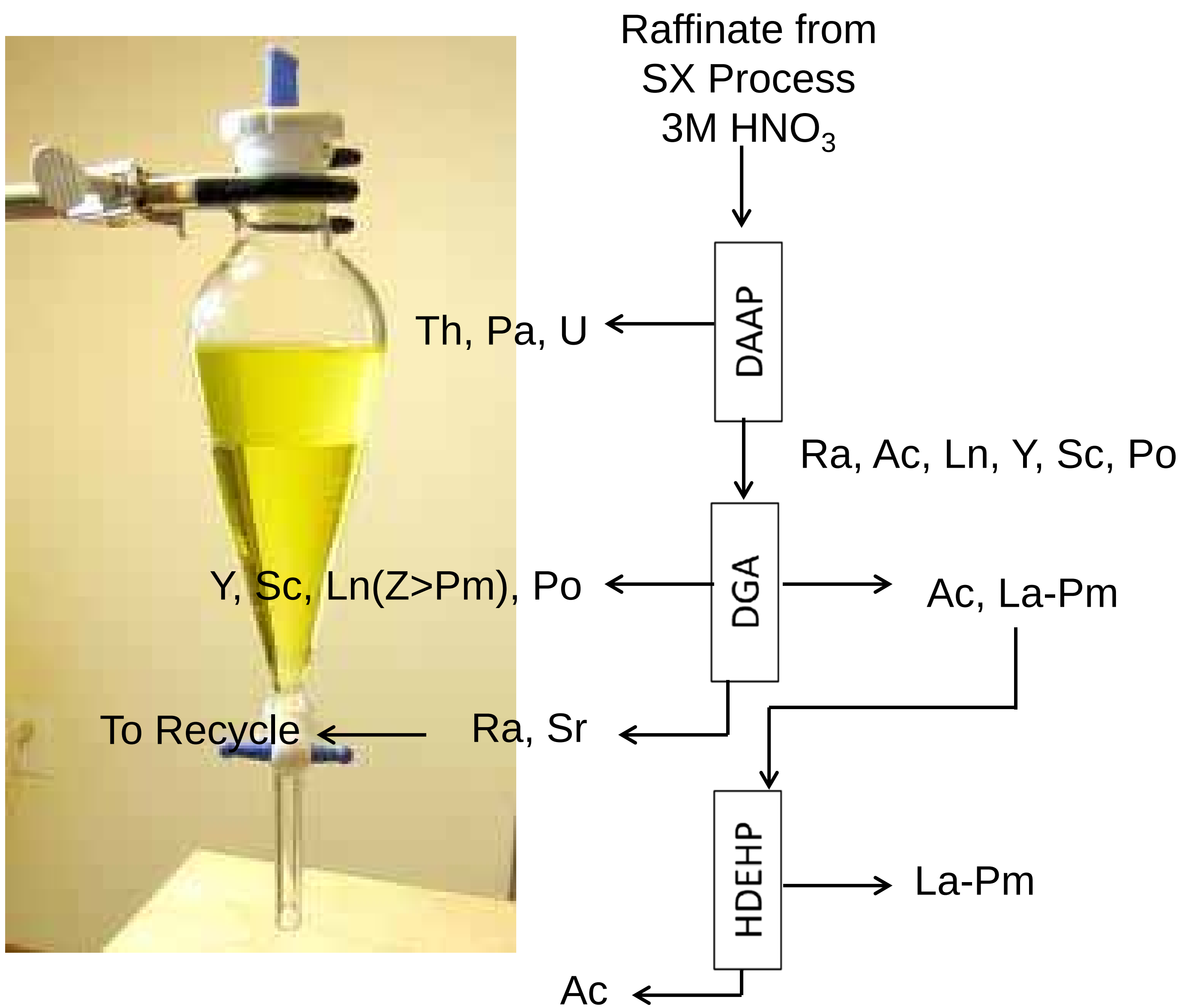
Ac-225 Production



35g Th Metal
(2.3 x 1.0 x 1.3 cm)



Dissolve Th
8M HNO_3 +
0.01M HF
Complex
Residual F^-
with Boric acid



Rare Earths?


Eu
Tb

MOLYCORP

CONCERN GROWS OVER RARE-EARTHS SUPPLY

Government tries to respond to U.S. vulnerability in these **CRITICAL MATERIALS**

DAVID J. HANSON, C&EN WASHINGTON

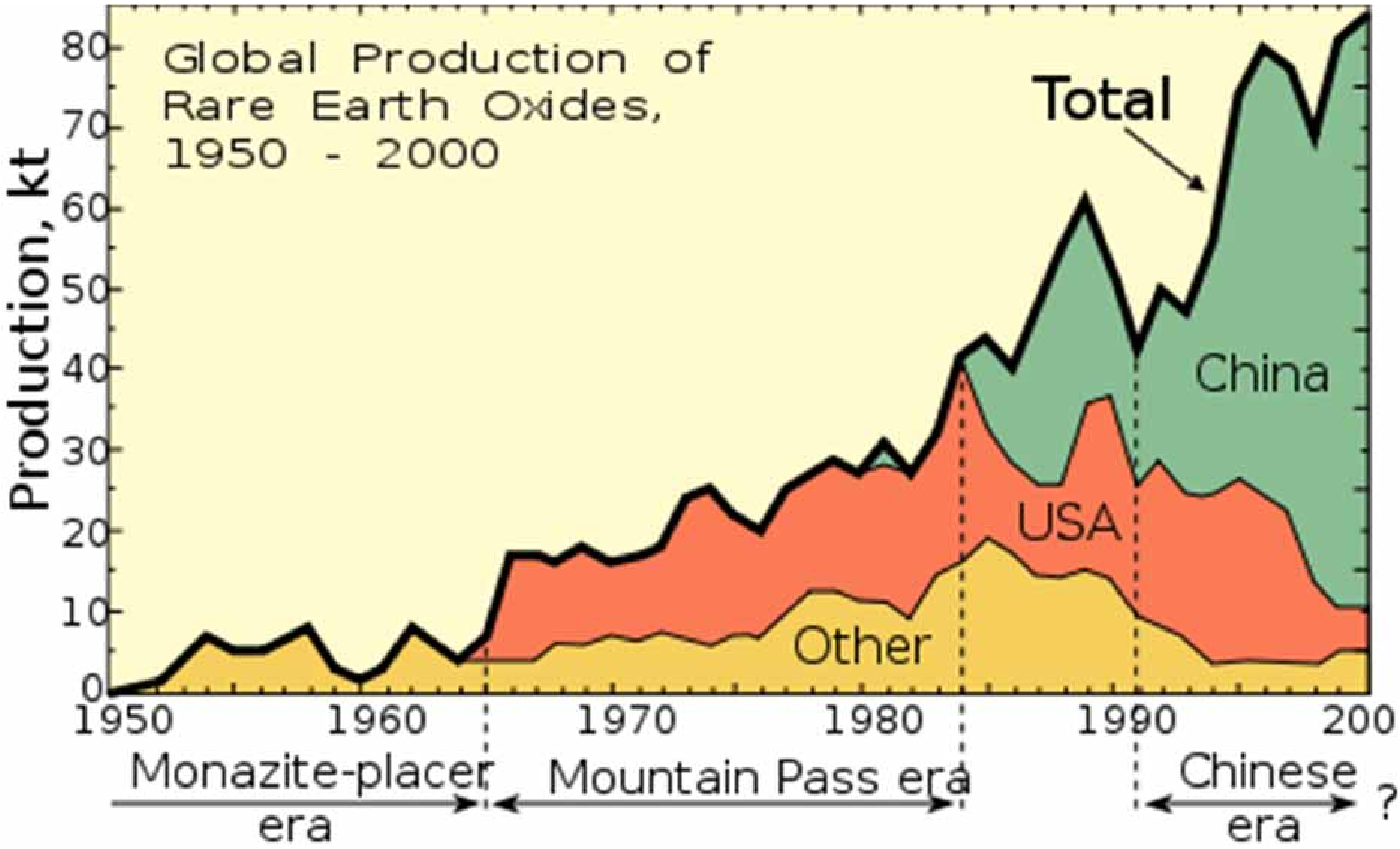
U.S. PRODUCTION Molycorp plans to restart production from its Mountain Pass, Calif., mine in 2012. It would be the only operating rare-earths mine in the U.S.

comprehensive bills focused on energy," says Jeffery A. Green, of J. A. Green & Co., a Washington, D.C., consulting company specializing in the rare-earths problem. "The spectrum runs from just studying the issues to actually getting out there to rev up production."

Congress is most concerned about the use of rare earths in national security and energy-efficiency technologies. According to the CRS report, DOD estimates the U.S. uses about 5% of the world's production of rare earths for defense purposes. For instance, the agency uses samarium cobalt magnets for disk drive motors on aircraft, tanks, and missile systems; in lasers for mine detection and various countermeasures; and in satellite communications and radar aboard ships and submarines. SmCo magnets are seen as ideal for such defense purposes because they retain their magnetic strength at elevated temperatures.

Gareth P. Hatch, founding principal of

Production



Global Production of
Rare Earth Oxides,
1950 - 2000
Production, kt
80
70
60
50
40
30
20
10
0
Total
China
USA
Other
1950
1960
1970
1980
1990
200
Monazite-placer
era
Mountain Pass era
Chinese
era
?

Production

World Mine Production and Reserves (2009 Data)		
Country	Production (Metric Ton)	Reserves (Metric Ton)
United States	insignificant	13,000,000
Australia	insignificant	5,400,000
Brazil	650	48,000
China	120,000	36,000,000
Commonwealth of Independent States	not available	19,000,000
India	2,700	3,100,000
Malaysia	380	30,000
Other countries	not available	22,000,000
World total (rounded)	124,000	99,000,000

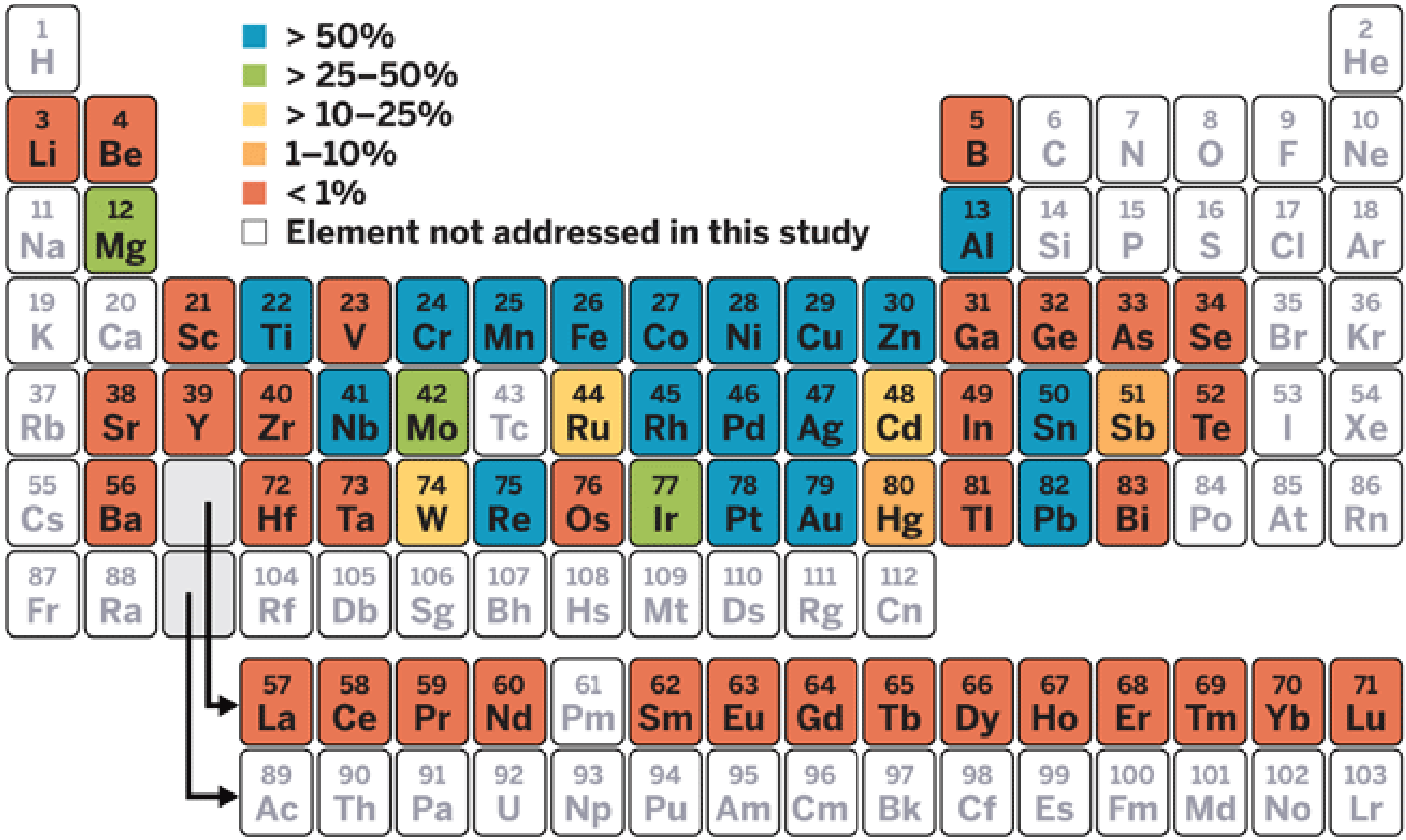
http://geology.com/articles/rare-earth-elements/

Metal	$/kg	Uses
La	15	Batteries (10 kg La in a Prius)
Ce	15	Catalytic Converter, Polishing
Pr	105	Alloys, Arc Lights, Welding Glasses
Nd	98	Magnets, Lasers
Sm	40	
Eu	**4000**	
Gd	210	
Tb	**2100**	
Dy	**1100**	
Ho	**1000**	
Er	275	
Tm	**4600-13000**	Lasers, Portable XRay Sources
Yb	**1000**	Atomic Clocks, Stress Gauges
Lu	**10000**	Few (Catalyst)
Y	68	Phosphors, Synthetic Garnets
Sc	**15000**	Alloys, Lamps, Dental Lasers
Au	45000	

DOE Critical Materials for Clean Energy

US DOE Critical Materials Strategy, December 2011.

REUSE STATS Global postconsumer recycling rates for many metals show lots of room for improvement.



SOURCE: UN Environment Program

C&E News, May 30, 2011 Volume 89, Number 22 p. 9
DOI:10.1021/CEN060211130455

Bastnäsite

$(Ce, La)CO_3F$

$(Y, Ce)CO_3F$

Table 2.3 Rare earth element distribution in bastnasite (w.r.t. 100% REO)

Rare earth	Bastnasite, Mountain Pass, California, U.S.	Bastnasite, Bayan Obo, Nei Monggol, China
La	33.2000	23.0000
Ce	49.1000	50.0000
Pr	4.3400	6.2000
Nd	12.0000	18.5000
Sm	0.7890	0.8000
Eu	0.1180	0.2000
Gd	0.1660	0.7000
Tb	0.0159	0.1000
Dy	0.0312	0.1000
Ho	0.0051	trace
Er	0.0035	trace
Tm	0.0009	trace
Yb	0.0006	trace
Lu	0.0001	trace
Y	0.0913	0.5000

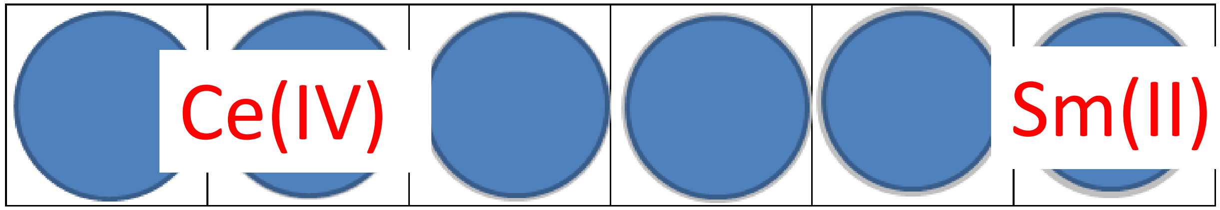
Monozite

monazite-Ce (Ce, La, Pr, Nd, Th, Y)PO_4 monazite-Nd (Nd, La, Ce, Pr)PO_4

monazite-La (La, Ce, Nd, Pr)PO_4 monazite-Sm (Sm, Gd, Ce, Th)PO_4

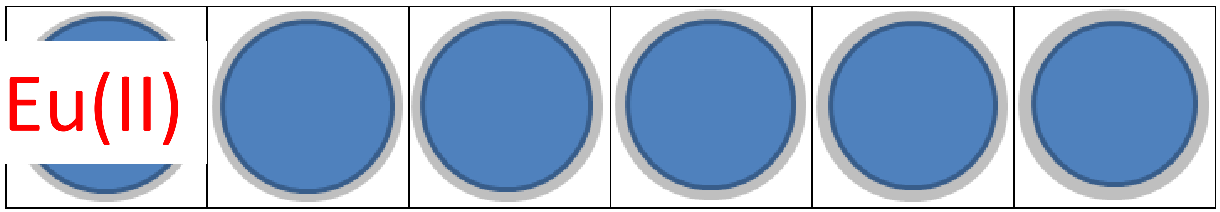
Table 2.4 Rare earth distribution in monazite from different locations

Rare earth	Australia, North Staradbroke Island, Queensland	Australia, Capel, Western Australia	Brazil, East coast	China, Nangang, Guang-dong	India	U.S., Green Cove Springs, Florida	U.S., Bear Valley, Idaho	Australia, Mount Weld
La	21.50	23.90	24.00	23.35	23.00	17.50	26.23	26.00
Ce	45.8	46.02	47.00	42.70	46.00	43.70	46.14	51.00
Pr	5.3	5.04	4.50	4.10	5.50	5.00	6.02	4.00
Nd	18.6	17.38	18.50	17.00	20.00	17.50	16.98	15.00
Sm	3.1	2.53	3.00	3.00	4.0	4.90	2.01	1.8
Eu	0.8	0.05	0.0550	0.10		0.16	1.54	0.4
Gd	1.8	1.49	1.00	2.03		6.60	0.77	1.0
Tb	0.29	0.04	0.1	0.70		0.26		0.1
Dy	0.64	0.69	0.35	0.80		0.90	Tb,Dy:0.31	0.2
Ho	0.12	0.05	0.035	0.12		0.11		0.1
Er	0.18	0.21	0.07	0.30		0.04		0.2
Tm	0.03	0.01	0.005	trace		0.03		trace
Yb	0.11	0.12	0.02	2.40		0.21		0.1
Lu	0.01	0.04		0.14		0.03	Ho-Lu:0.15	trace
Y	2.50	2.41	1.4	2.40	Eu-Y: 1.50	3.20	1.39	trace

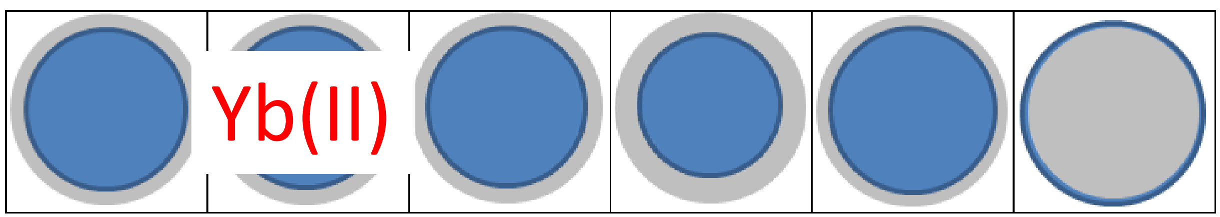


Ionic Radius (CN =8)	1.160	1.143	1.126	1.109	1.093	1.079
Element	**La**	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**
Z	57	58	59	60	61	62

(Am = 1.090)

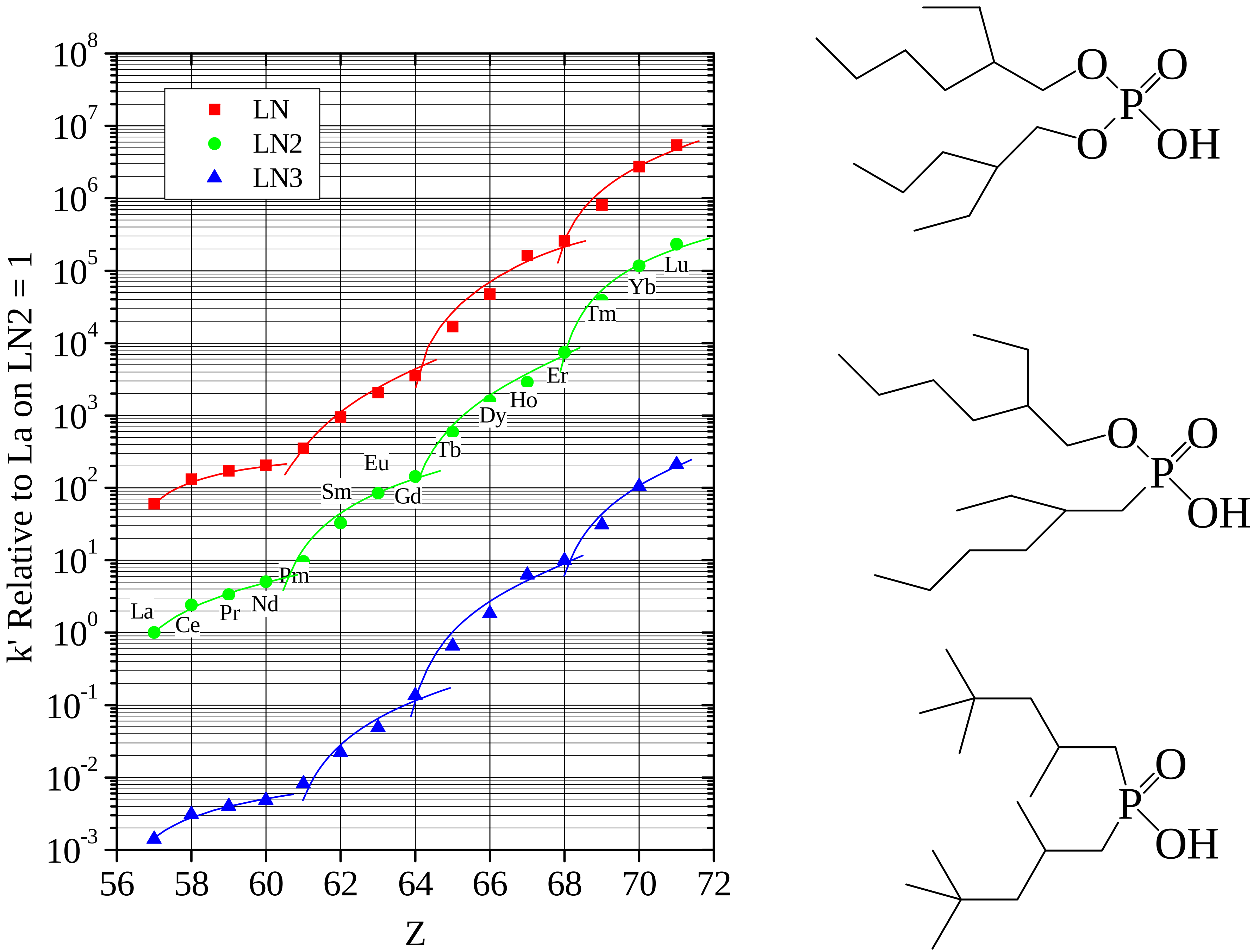


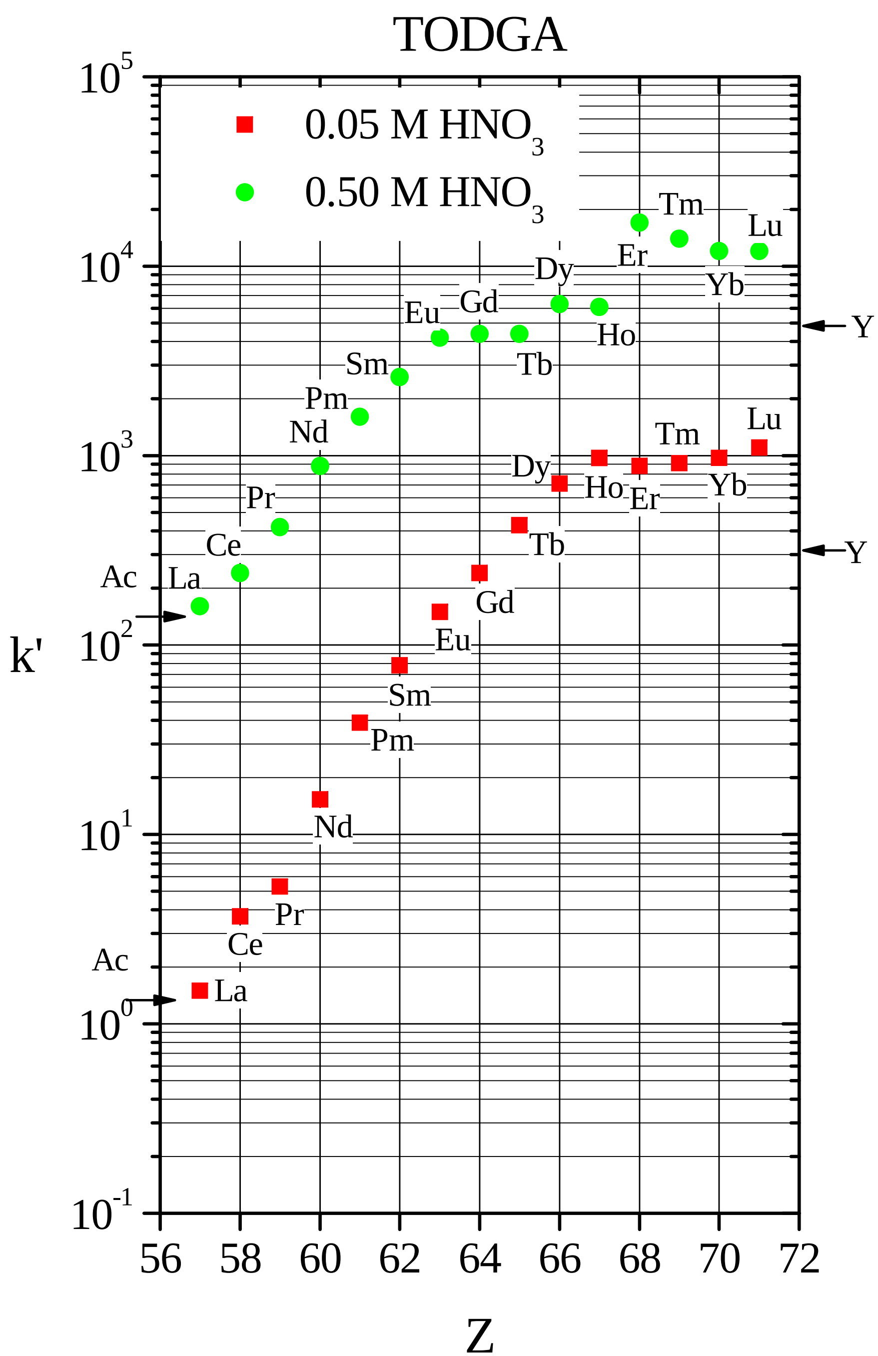
Ionic Radius (CN =8)	1.066	1.053	1.040	1.027	1.015	1.004
Element	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**
Z	63	64	65	66	67	68



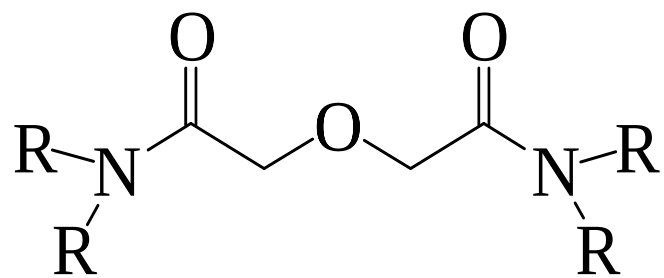
Ionic Radius (CN =8)	0.994	0.985	0.977	0.870	1.019	1.120
Element	**Tm**	**Yb**	**Lu**	**Sc**	**Y**	**Ac (CN=6)**
Z	69	70	71	21	39	89

La(6) = 1.032


LN
LN2
LN3
k' Relative to La on LN2 = 1
Z
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
10^-3
56
58
60
62
64
66
68
70
72
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
O
O
P
O
OH
O
O
P
OH
O
P
OH



TODGA
0.05 M HNO3
0.50 M HNO3
k'
Z
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Ac
Y



O
O
O
R
N
R
R
N
R

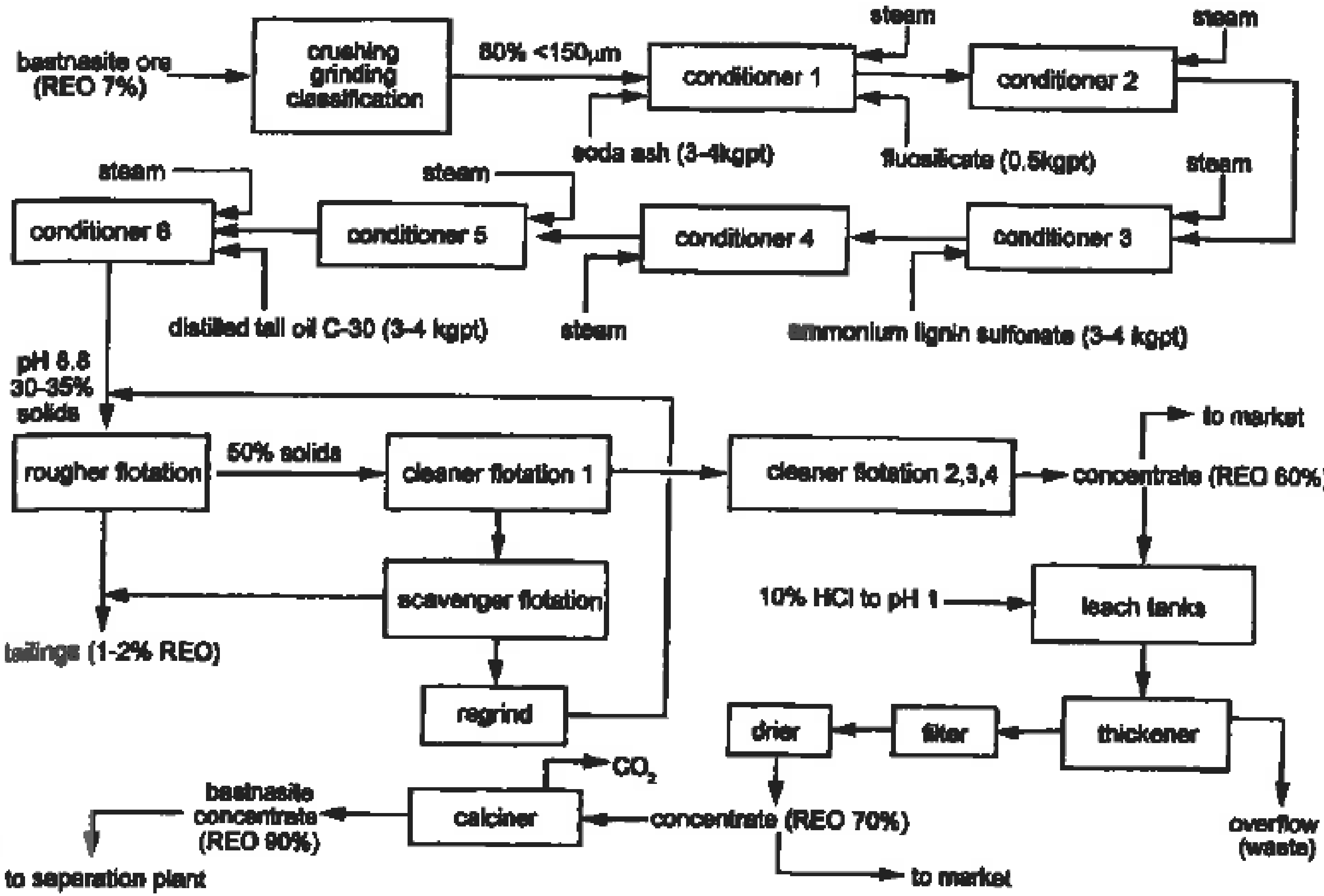


Figure 3.9 Simplified flowsheet for the recovery of bastnasite at the Molycorp plant (Aplan 1988).

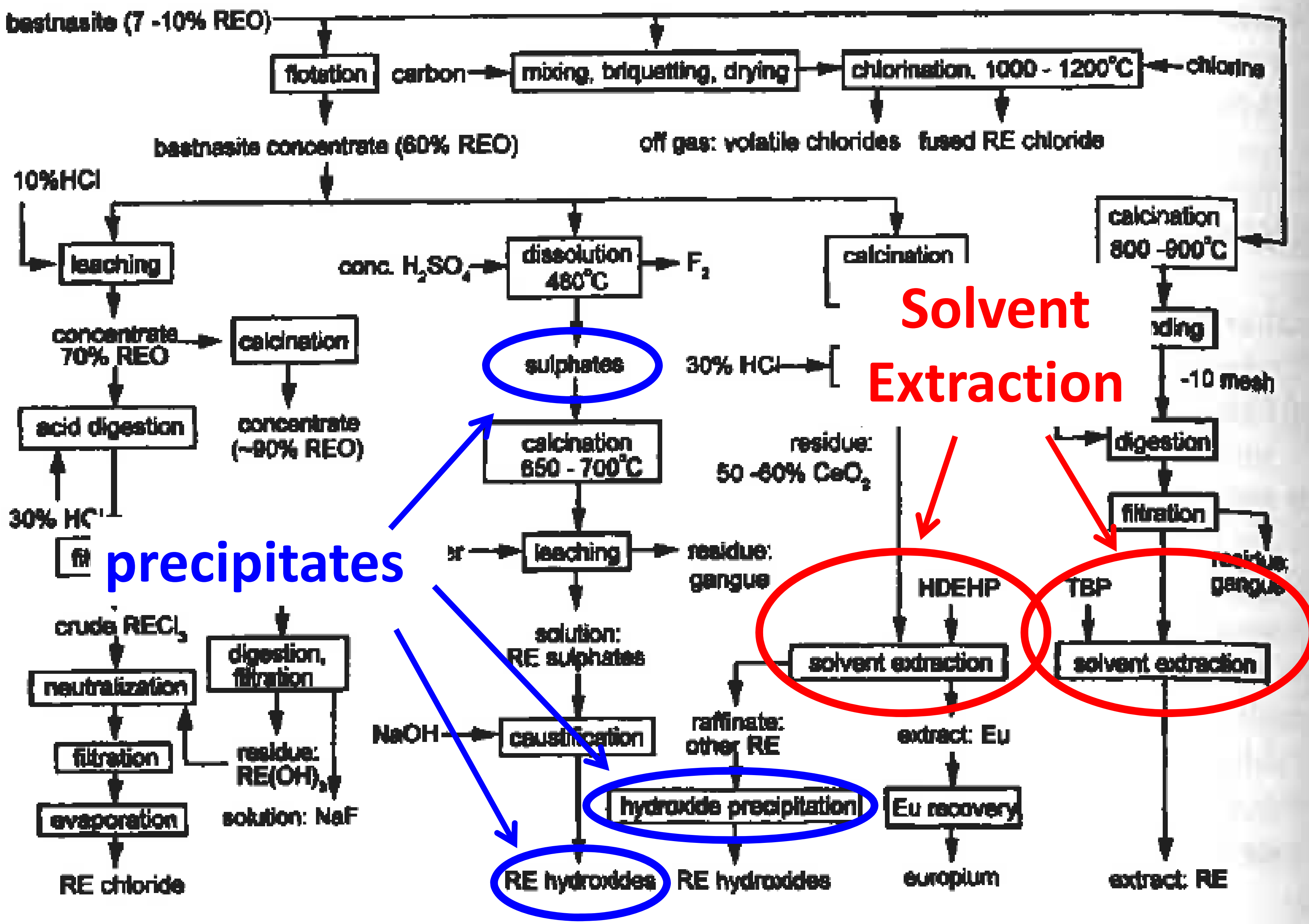
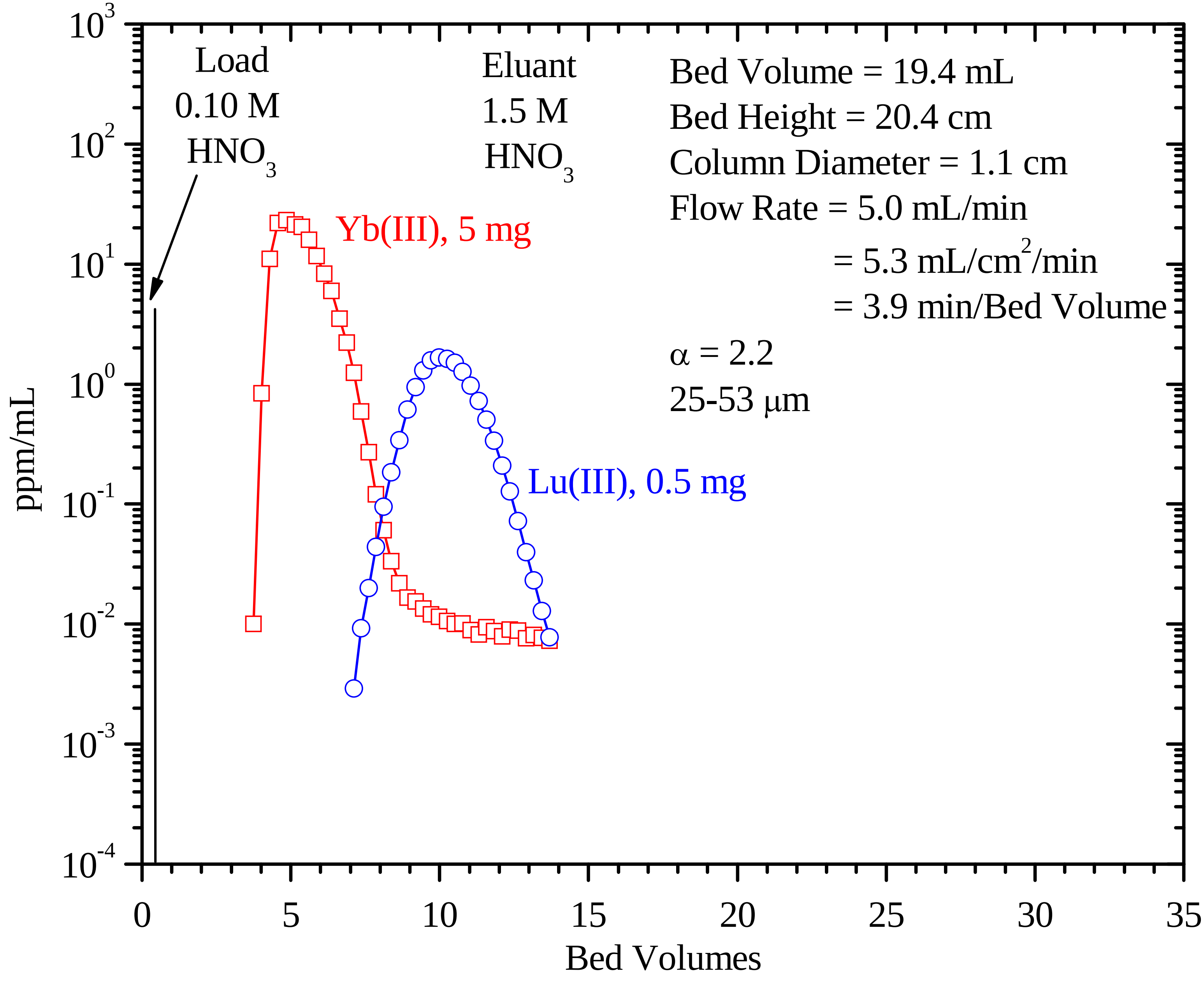
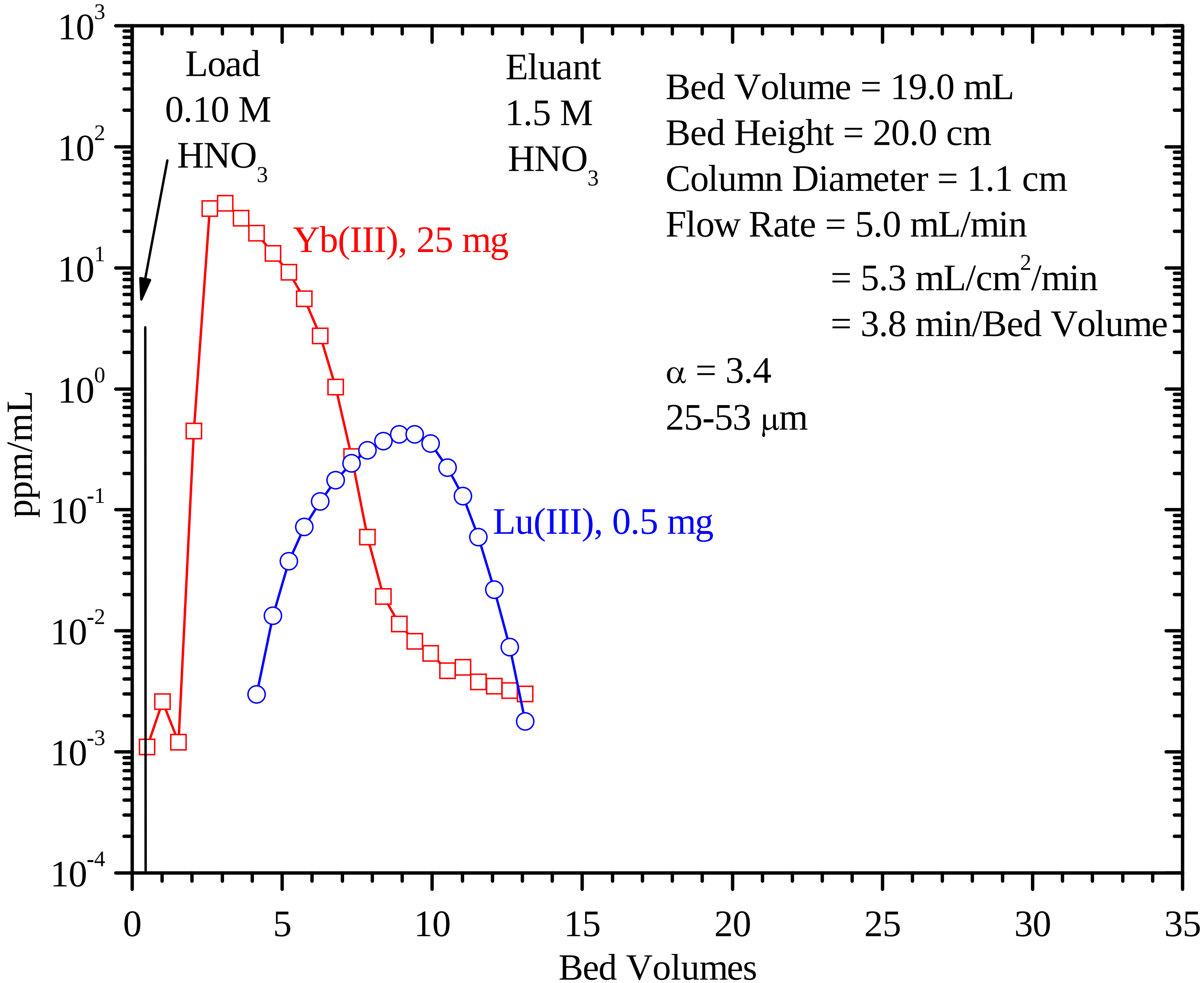


Figure 3.15 Chemical processing of bastnasite.

Lu/Yb Separation on LN2 Resin, 50°C, 5 mg Yb



Lu/Yb Separation on LN2 Resin, 50^{o}C, 25 mg Yb



Displacement Chromatography

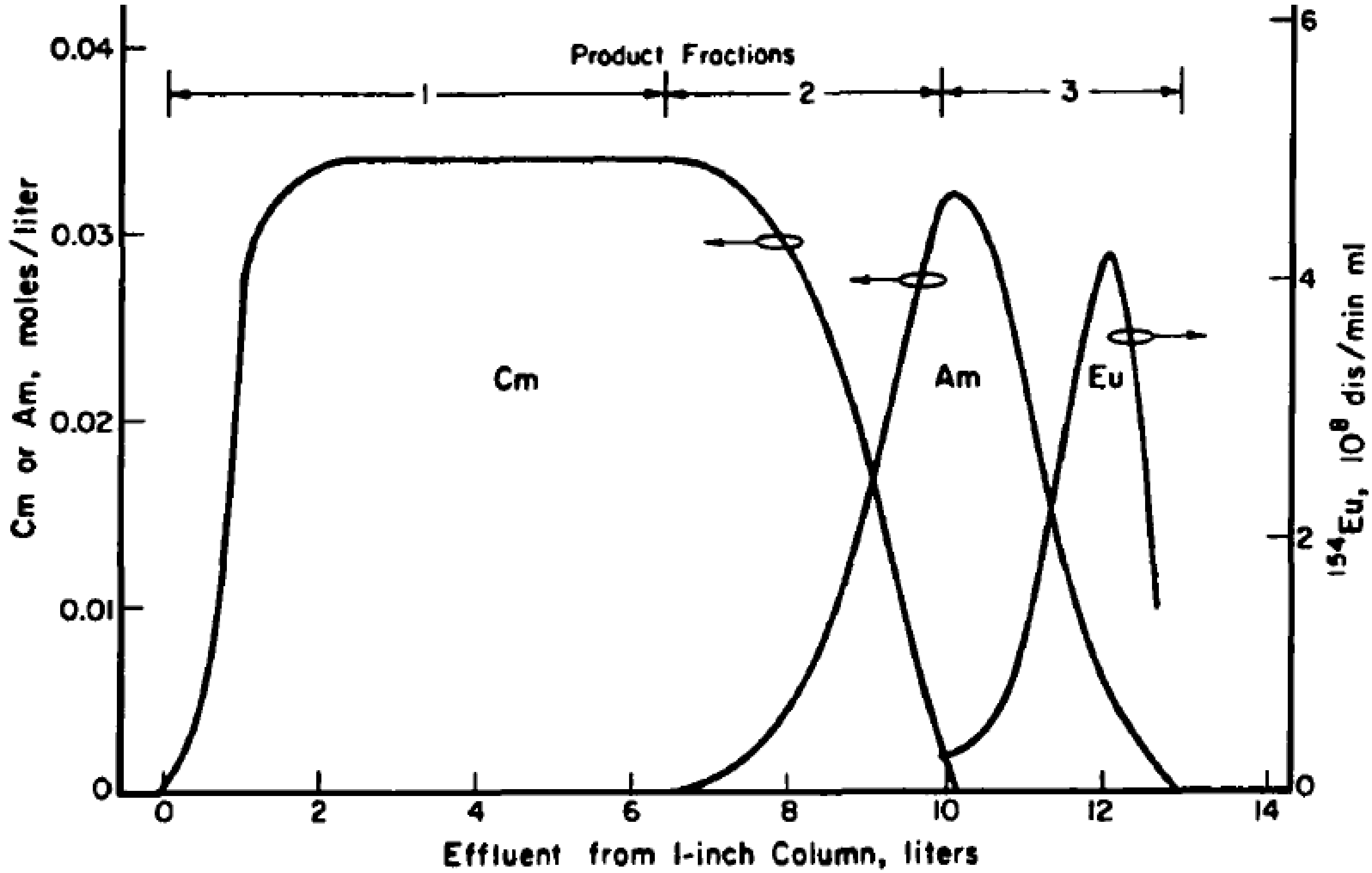


FIGURE 9

Typical Elution Diagram for Separation Using Displacement Development with DTPA in System Shown in Figure 8. Reprinted with permission from J. T. Lowe, W. H. Hale, Jr., and D. F. Hallman, Ind. Eng. Chem., Process Design Develop., 10, 131 (1971). Copyright by the American Chemical Society.

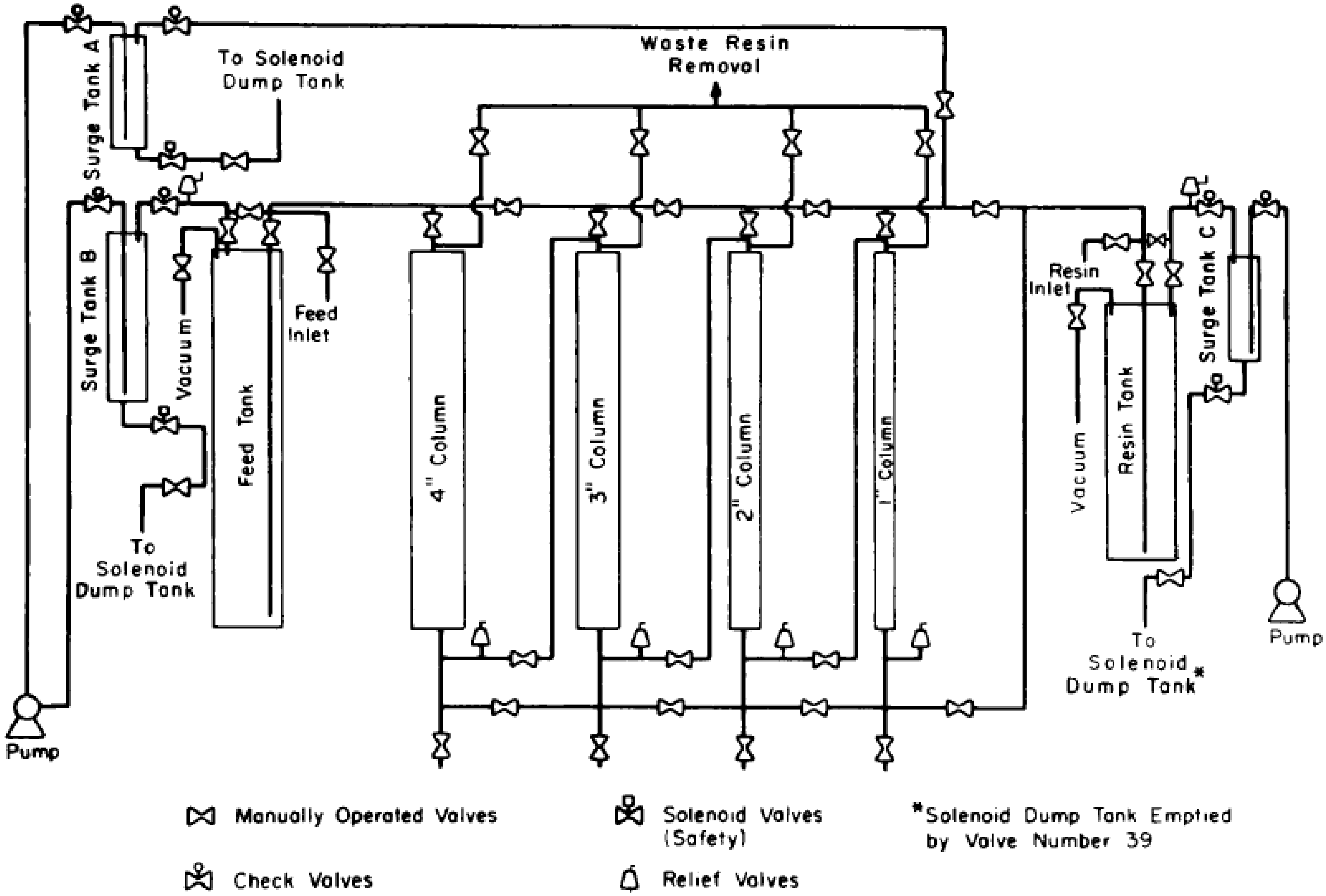


FIGURE 8. Flow Diagram for Displacement Development Separation of Actinides on the 100-g Scale. Reprinted with permission from J. T. Lowe, W. H. Hale, Jr., and D. F. Hallman, Ind. Eng. Chem., Process Design Develop., 10, 131 (1971). Copyright by the American Chemical Society.

Application of EXC to Large Scale Separations

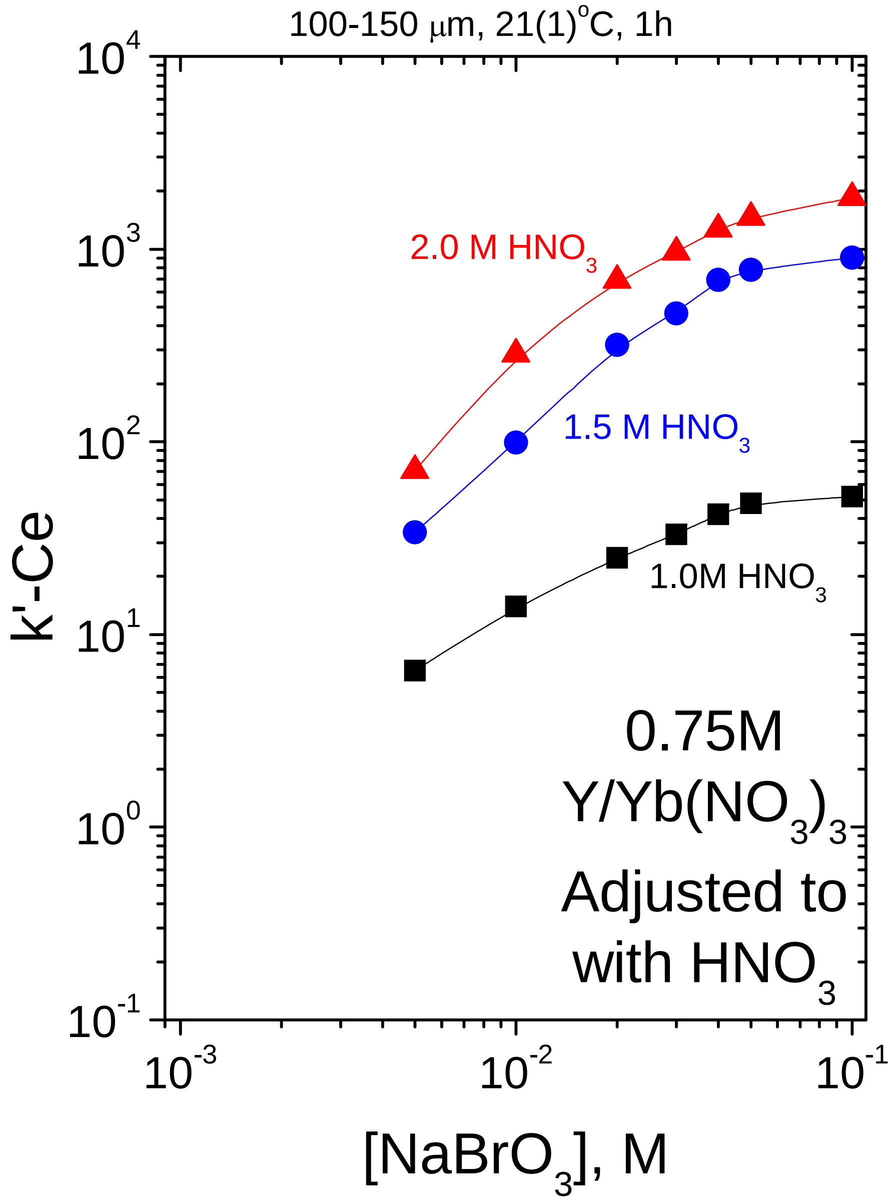
Limitation	Consequence(s)
High cost of resins	High Value Products
	Resin Stability
	Analytical Applications

Application of EXC to Large Scale Separations

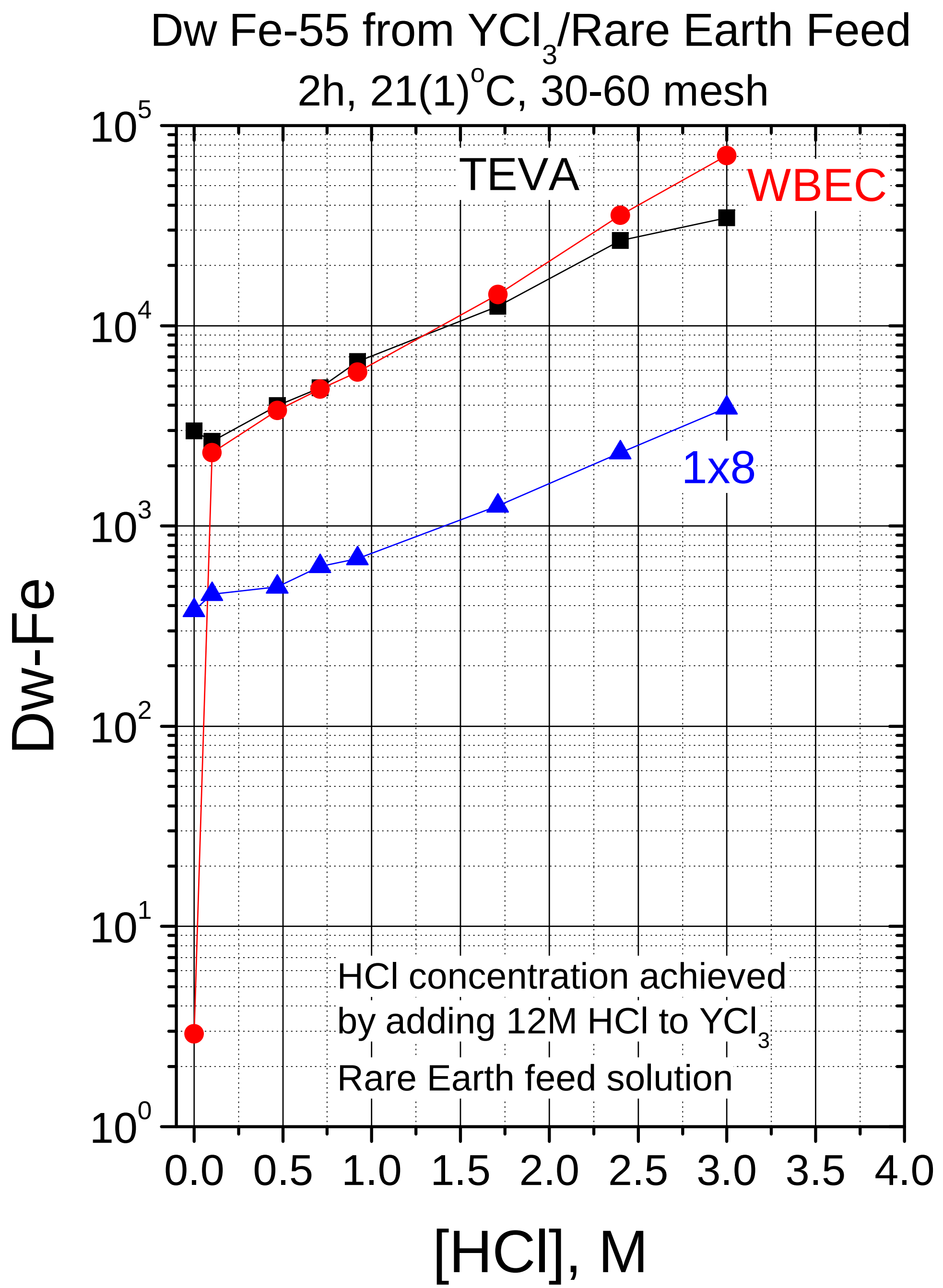
Limitation	Consequence(s)
Low Capacity	High Value Products
	Scavenge trace elements from large stream
	Add value to existing stream
	Enable better analytical results

Cerium Removal (analysis)

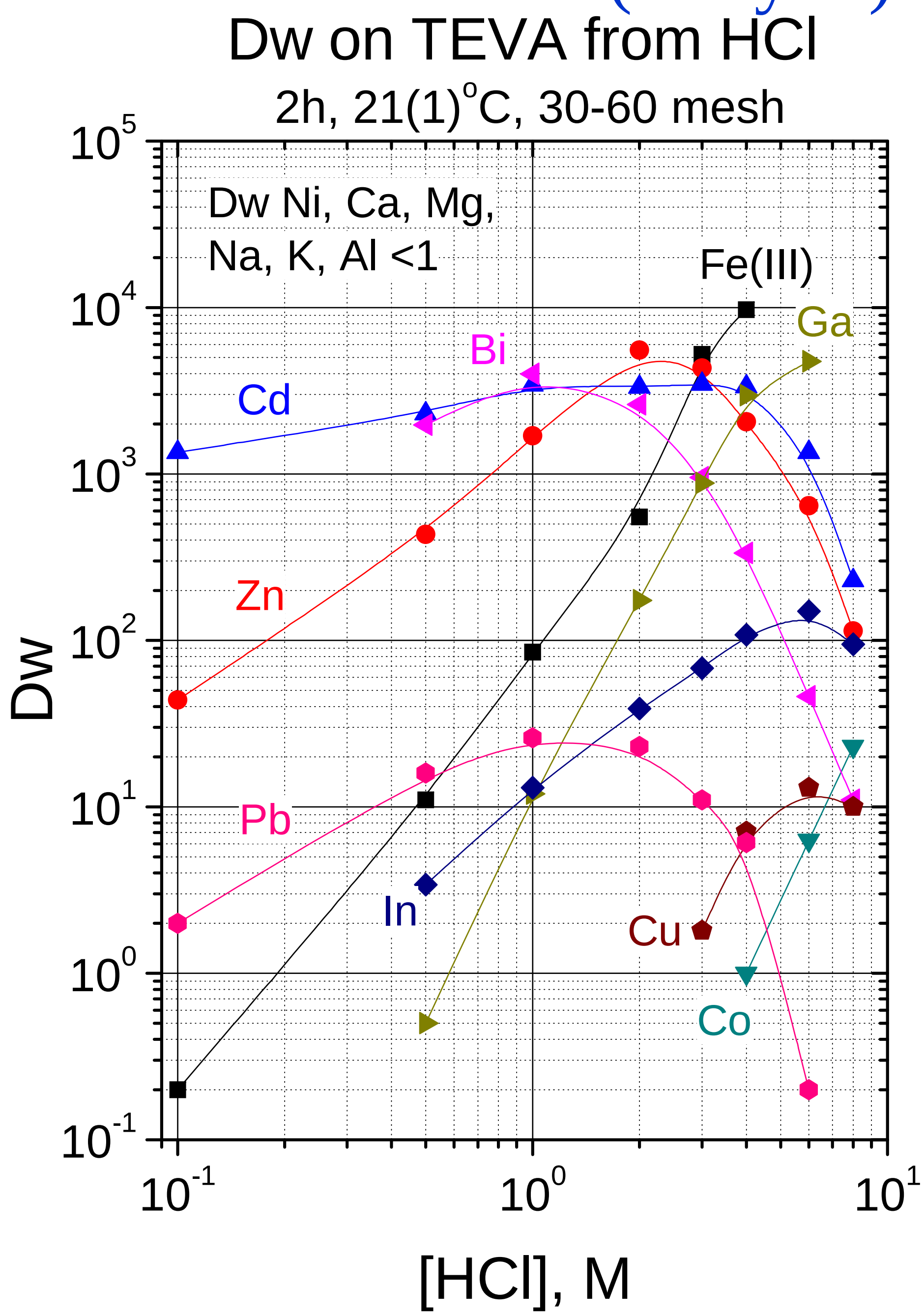
k' Ce-139 on UTEVA-3 vs $NaBrO_3$



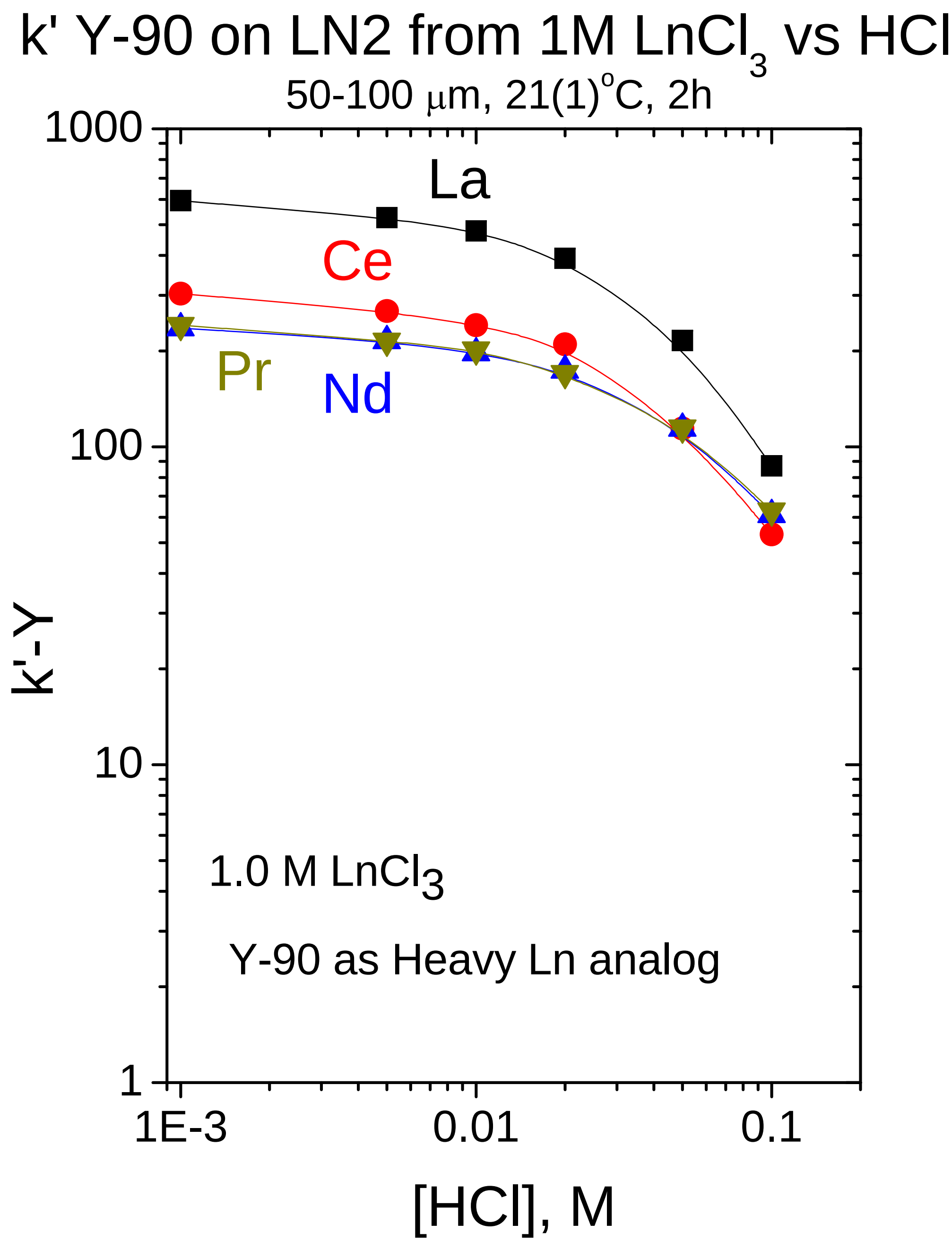
Iron Removal (analysis)



Iron Removal (analysis)



Heavy Lanthanide Separations (analysis)



Sc Separations (analysis)