Rare Earths Processing

from Mine to Metal

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Element[1]	Symbol	Atomic number	Atomic weight	Crustal abundance (part per million)
Light REEs				
Lanthanum	La	57	138.91	39
Cerium	Ce	58	140.12	66.5
Praseodymium	Pr	59	140.91	9.2
Neodymium	Nd	60	144.24	41.5
Samarium	Sm	62	150.36	7.05
Europium	Eu	63	151.96	2.0
Gadolinium	Gd	64	157.25	6.2
Heavy REEs				
Yttrium	Y	39	88.91	33
Terbium	Tb	65	158.92	1.2
Dysprosium	Dy	66	162.50	5.2
Holmium	Ho	67	164.93	1.3
Erbium	Er	68	167.26	3.5
Thulium	Tm	69	168.93	0.52
Ytterbium	Yb	70	173.04	3.2
Lutetium	Lu	71	174.97	0.8

[1]Promethium (Pm, atomic number=61) is not included in this list because it is extremely rare in nature.

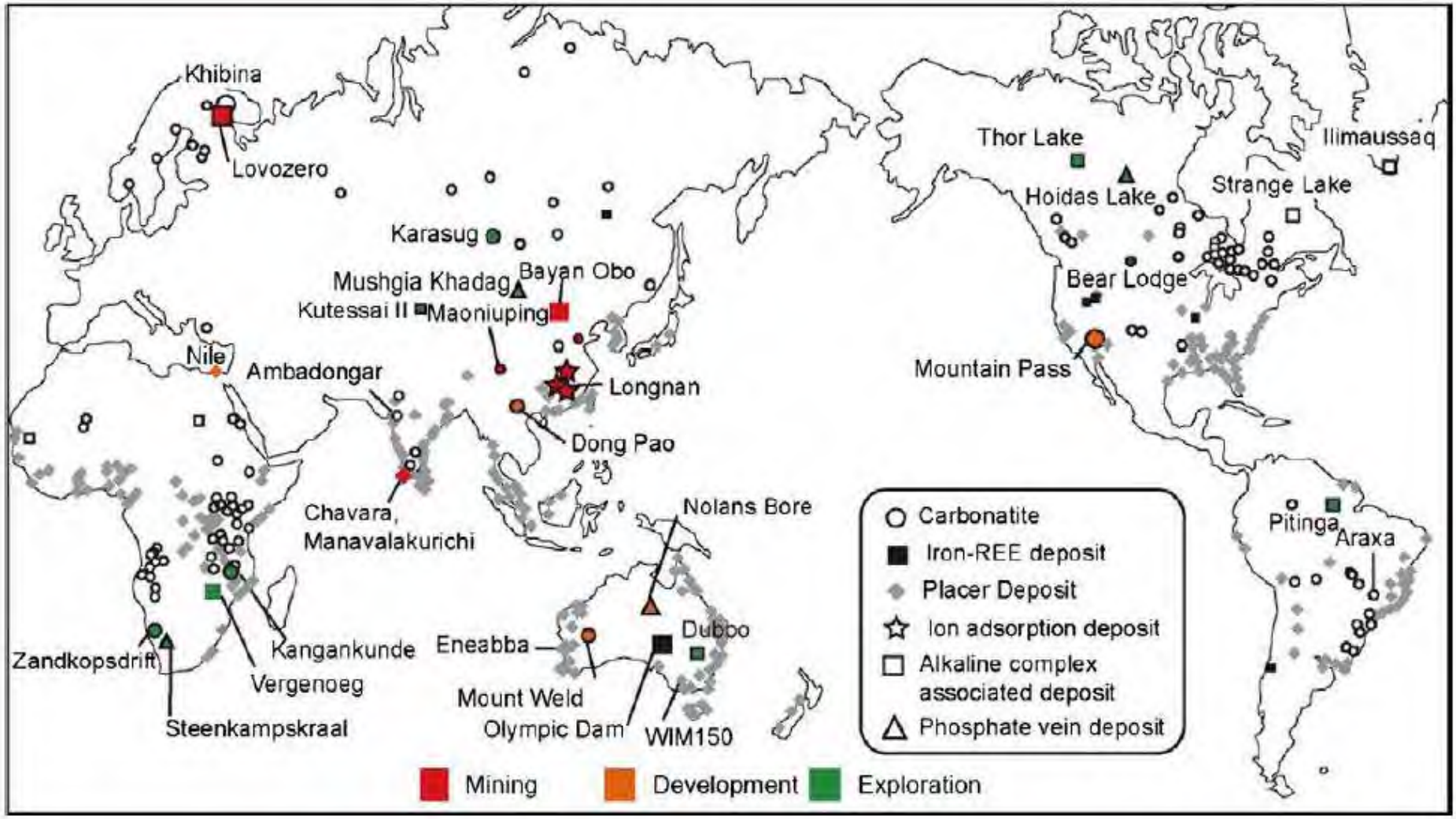


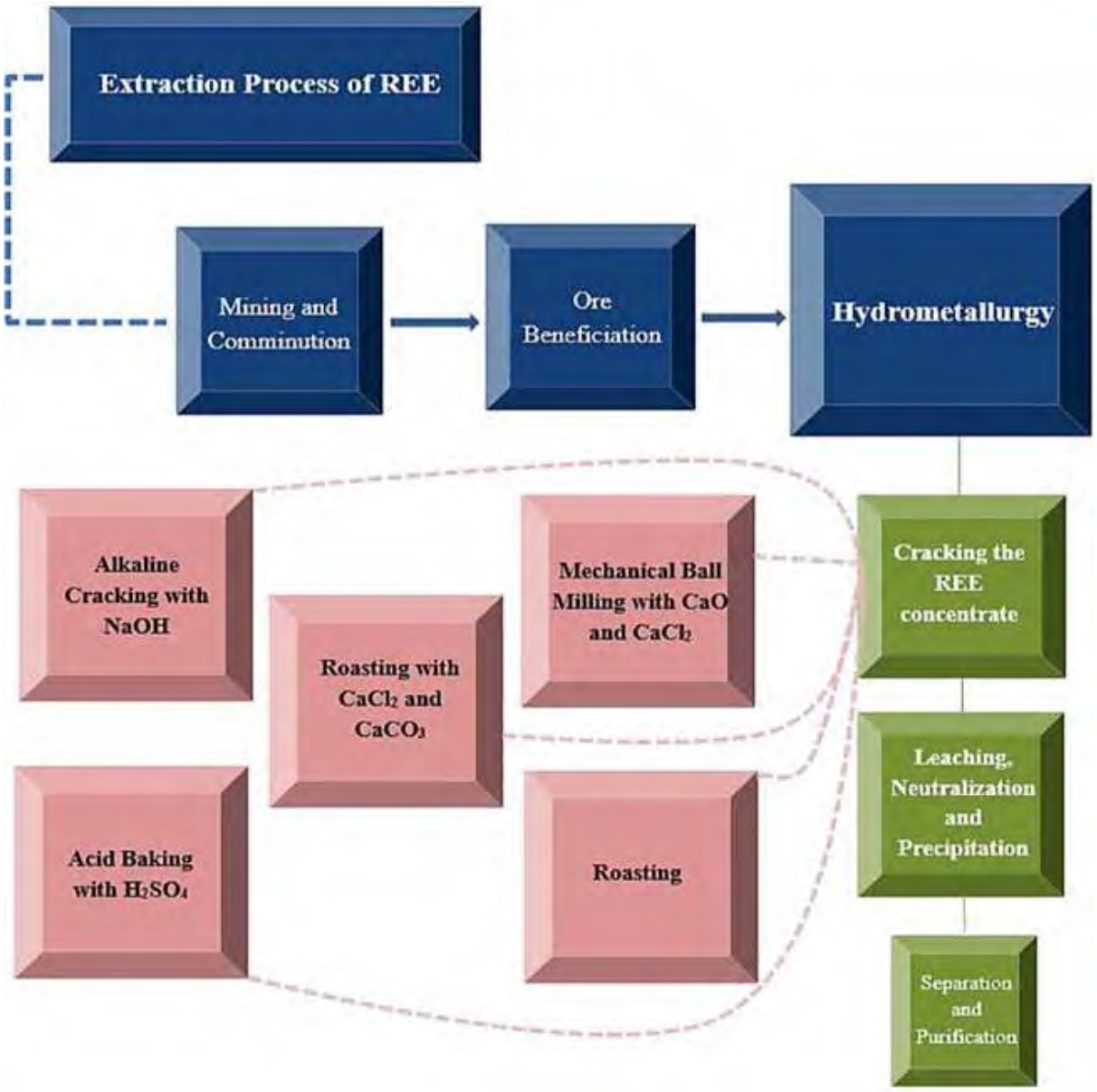
Fig. 10. Worldwide distribution of REE deposits, reserves and operating mines. Reproduced with permission from (Okuya, 2011).

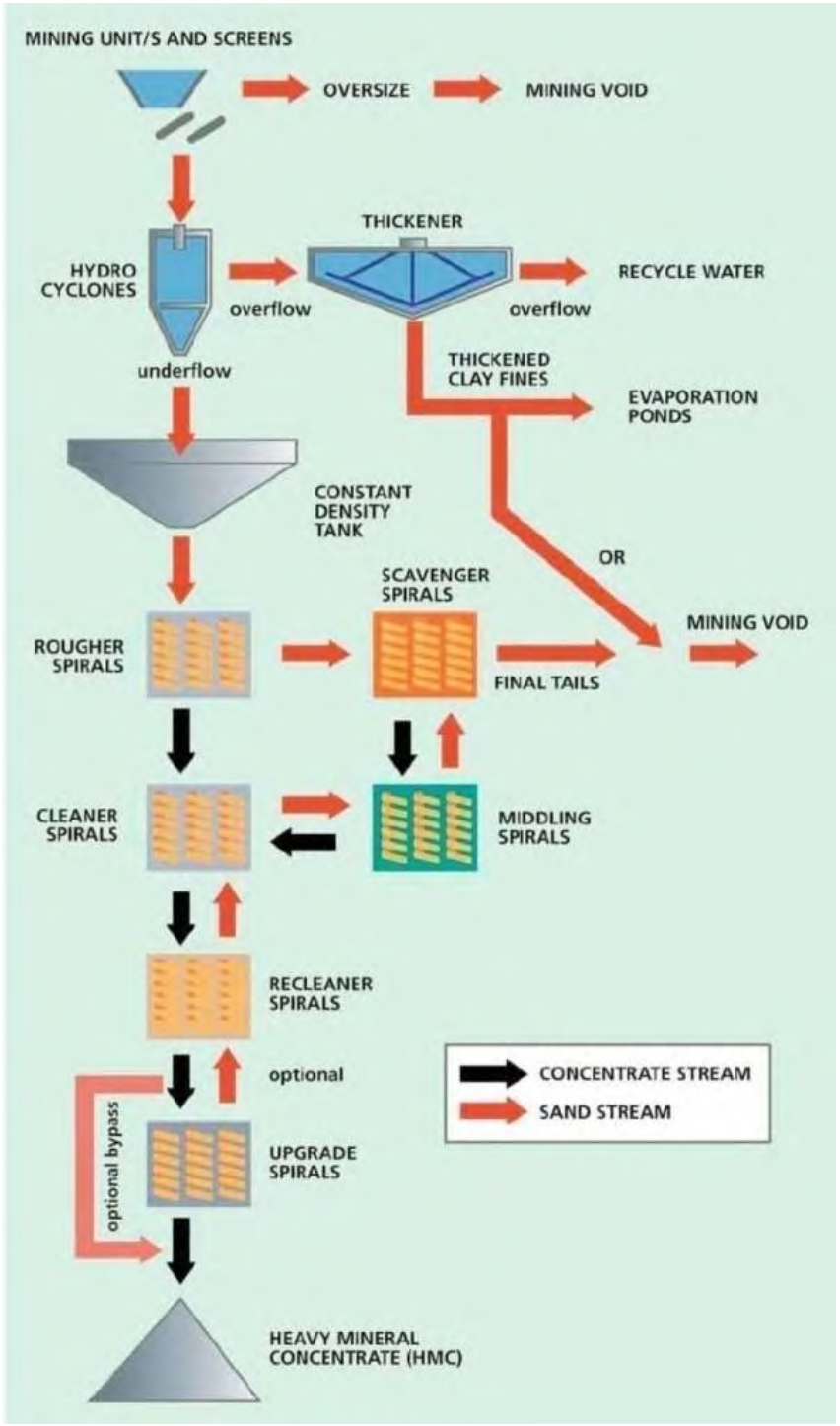
Table 7
REE Distributions of major rare earth mineral deposits. Adapted from (Chen, 2011; Long et al., 2010).

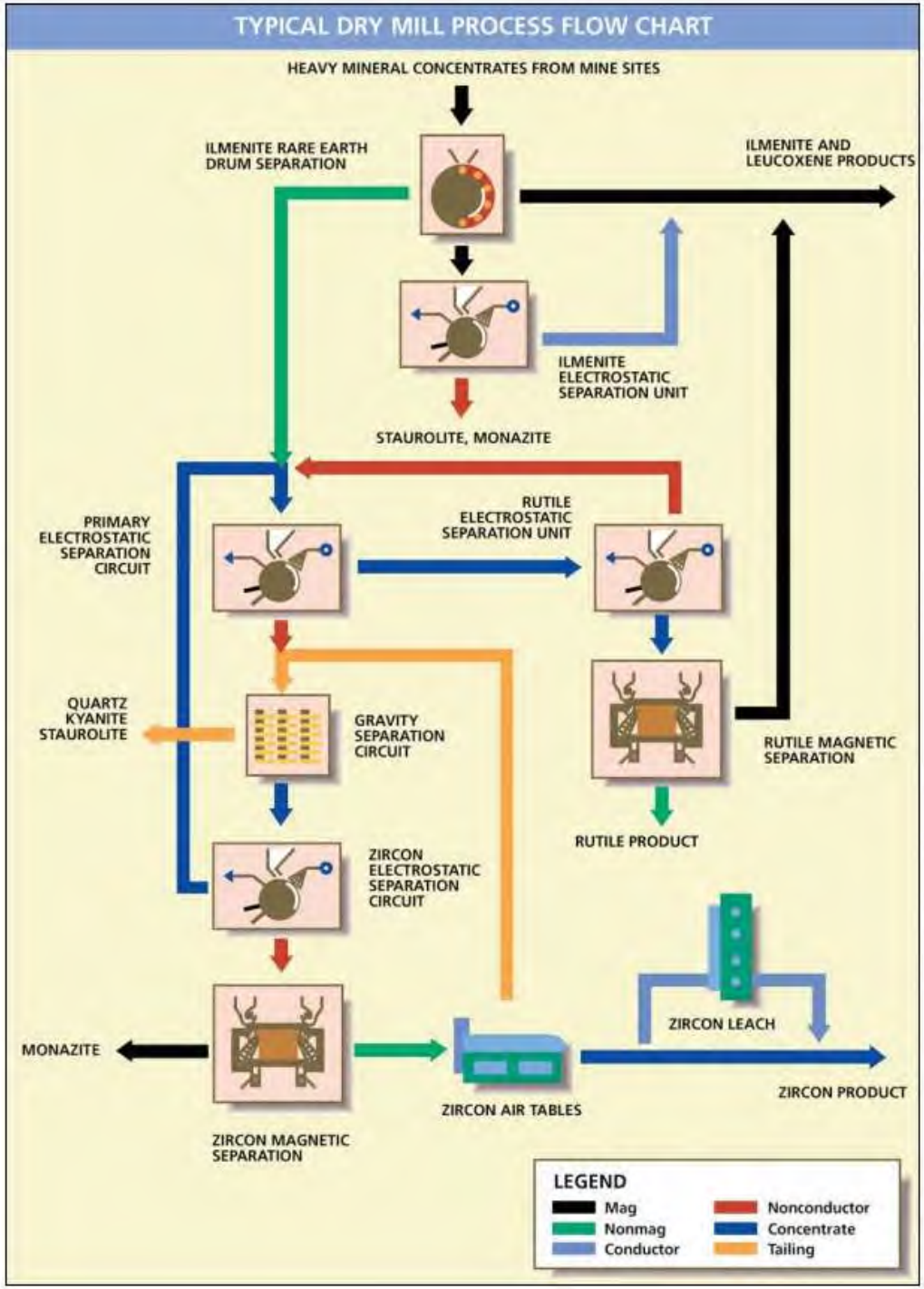
Element	Bastnäsite Mountain Pass, USA	Bastnäsite Bayan Obo, China	Monazite Green Cove Spring, USA	Xenotime Lehat, Malaysia	High Y REE clay Longnan, China	Low Y REE clay Xunwu, China	Loparite, Russia
La (%)	**33.8**	**23.0**	**17.5**	1.2	1.8	**43.3**	**25.0**
Ce (%)	**49.6**	**50.0**	**43.7**	**3.1**	0.4	2.4	**50.5**
Pr (%)	**4.1**	**6.2**	**5.0**	0.5	0.7	**7.1**	**5.0**
Nd (%)	**11.2**	**18.5**	**17.5**	1.6	**3.0**	**30.2**	**15.0**
Sm (%)	0.9	0.8	**4.9**	1.1	**2.8**	**3.9**	0.7
Eu (%)	0.1	0.2	0.2	Trace	0.1	**0.5**	0.1
Gd (%)	0.2	0.7	**6.0**	**3.5**	**6.9**	**4.2**	0.6
Tb (%)	–	0.1	0.3	0.9	**1.3**	Trace	Trace
Dy (%)	–	0.1	0.9	**8.3**	**7.5**	Trace	0.6
Ho (%)	–	Trace	0.1	**2.0**	**1.6**	Trace	0.7
Er (%)	–	Trace	Trace	**6.4**	**4.9**	Trace	0.8
Tm (%)	–	Trace	Trace	**1.1**	**0.7**	Trace	0.1
Yb (%)	–	Trace	0.1	**6.8**	**2.5**	0.3	0.2
Lu (%)	Trace	Trace	Trace	**1.0**	0.4	0.1	0.2
Y (%)	0.1	Trace	2.5	**61.0**	**65.0**	8.0	1.3

Bolded values indicate that a certain mineral deposit is a major source of the given element.

LREE


Extraction Process of REE
Mining and Comminution
Ore Beneficiation
Hydrometallurgy
Alkaline Cracking with NaOH
Roasting with $CaCl_2$ and $CaCO_3$
Mechanical Ball Milling with CaO and $CaCl_2$
Acid Baking with H_2SO_4
Roasting
Cracking the REE concentrate
Leaching, Neutralization and Precipitation
Separation and Purification


MINING UNIT/S AND SCREENS
OVERSIZE
MINING VOID
HYDRO CYCLONES
overflow
THICKENER
overflow
RECYCLE WATER
underflow
THICKENED CLAY FINES
EVAPORATION PONDS
CONSTANT DENSITY TANK
OR
SCAVENGER SPIRALS
MINING VOID
ROUGHER SPIRALS
FINAL TAILS
CLEANER SPIRALS
MIDDLING SPIRALS
RECLEANER SPIRALS
optional
optional bypass
UPGRADE SPIRALS
CONCENTRATE STREAM
SAND STREAM
HEAVY MINERAL CONCENTRATE (HMC)


TYPICAL DRY MILL PROCESS FLOW CHART
HEAVY MINERAL CONCENTRATES FROM MINE SITES
ILMENITE RARE EARTH DRUM SEPARATION
ILMENITE AND LEUCOXENE PRODUCTS
ILMENITE ELECTROSTATIC SEPARATION UNIT
STAUROLITE, MONAZITE
PRIMARY ELECTROSTATIC SEPARATION CIRCUIT
RUTILE ELECTROSTATIC SEPARATION UNIT
QUARTZ KYANITE STAUROLITE
GRAVITY SEPARATION CIRCUIT
RUTILE MAGNETIC SEPARATION
RUTILE PRODUCT
ZIRCON ELECTROSTATIC SEPARATION CIRCUIT
ZIRCON LEACH
MONAZITE
ZIRCON AIR TABLES
ZIRCON PRODUCT
ZIRCON MAGNETIC SEPARATION
LEGEND
Mag
Nonmag
Conductor
Nonconductor
Concentrate
Tailing

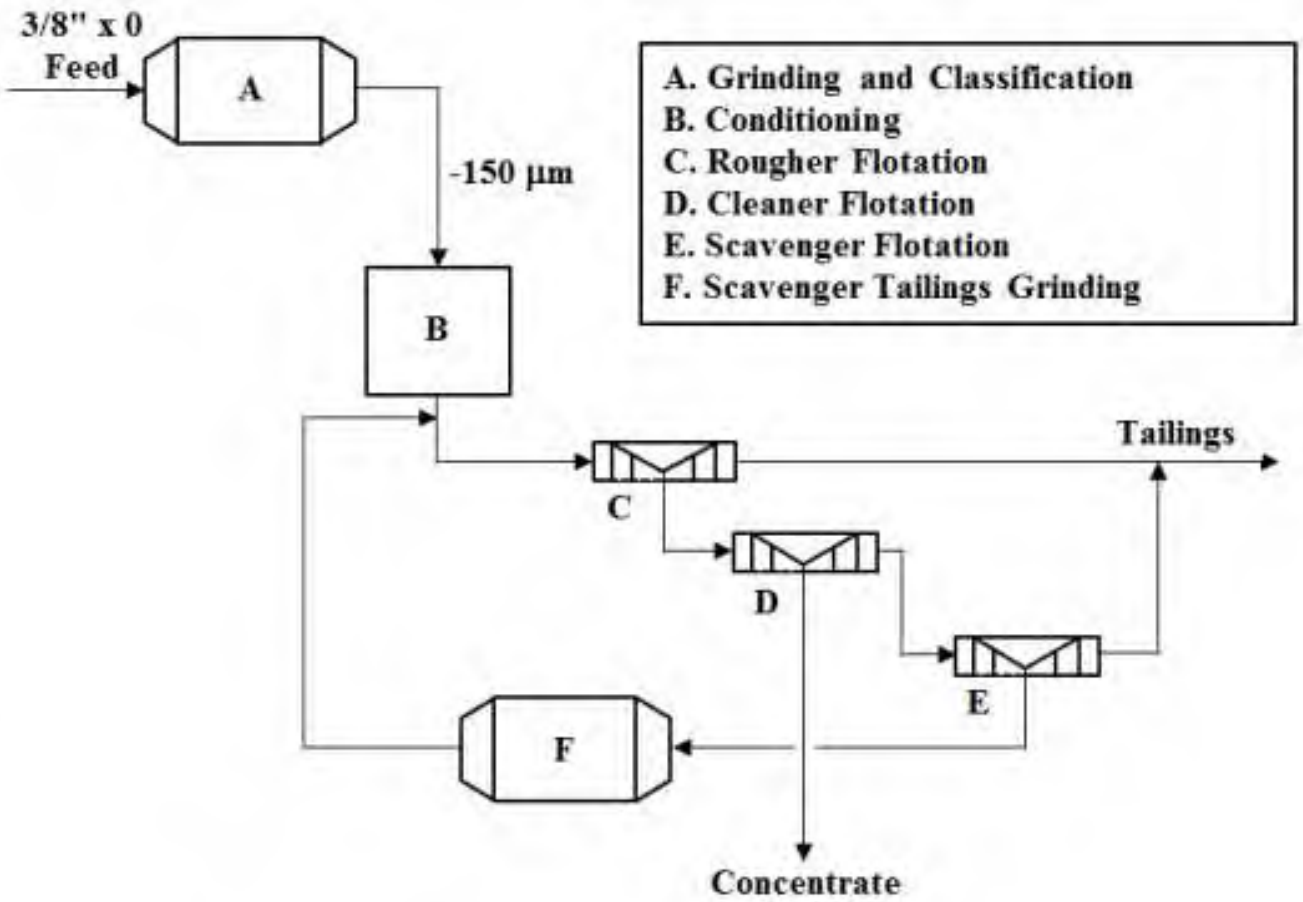


Figure 10: Mountain Pass Concentrator Flowsheet, from Aplan (1989)

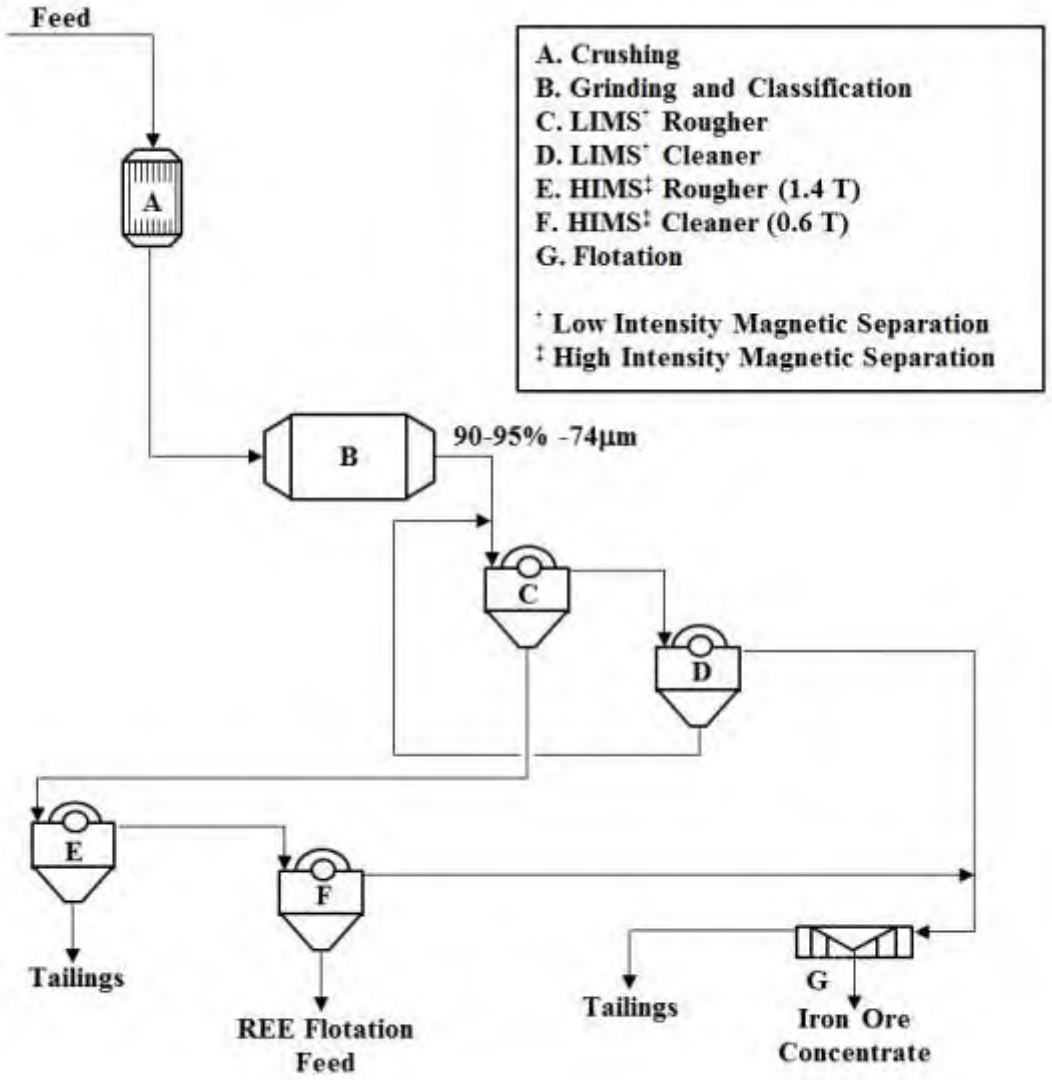


Figure 11: Bayan Obo Iron Ore Concentration Flowsheet from Li and Yang (2014)

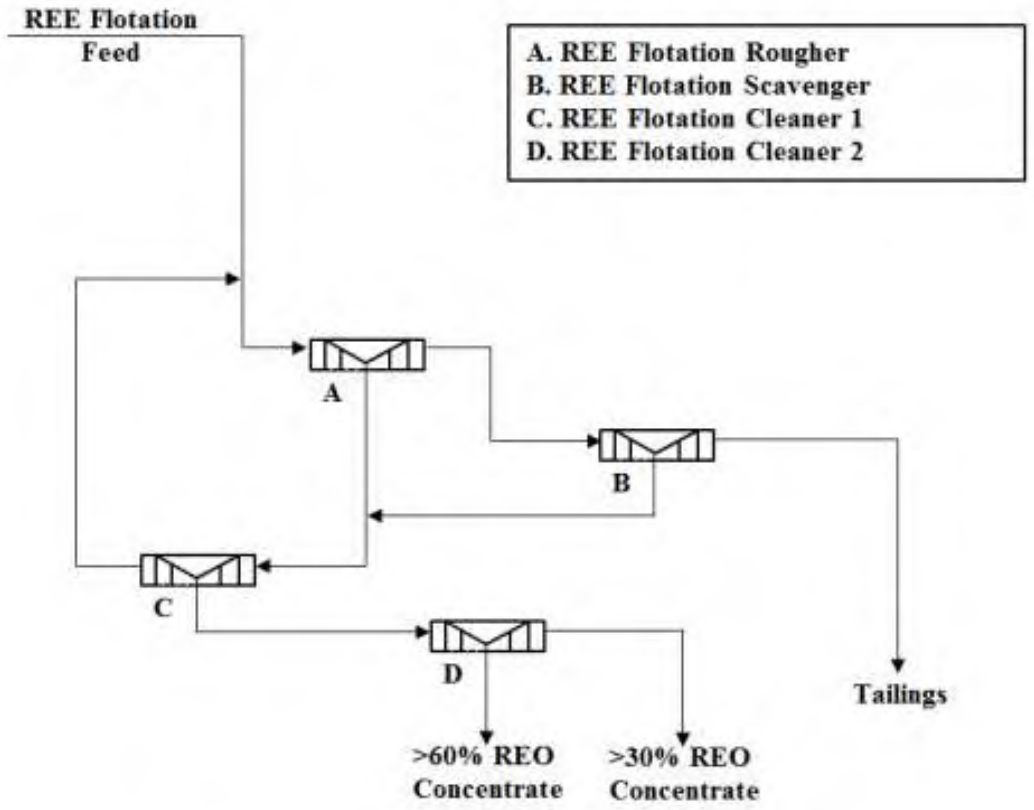
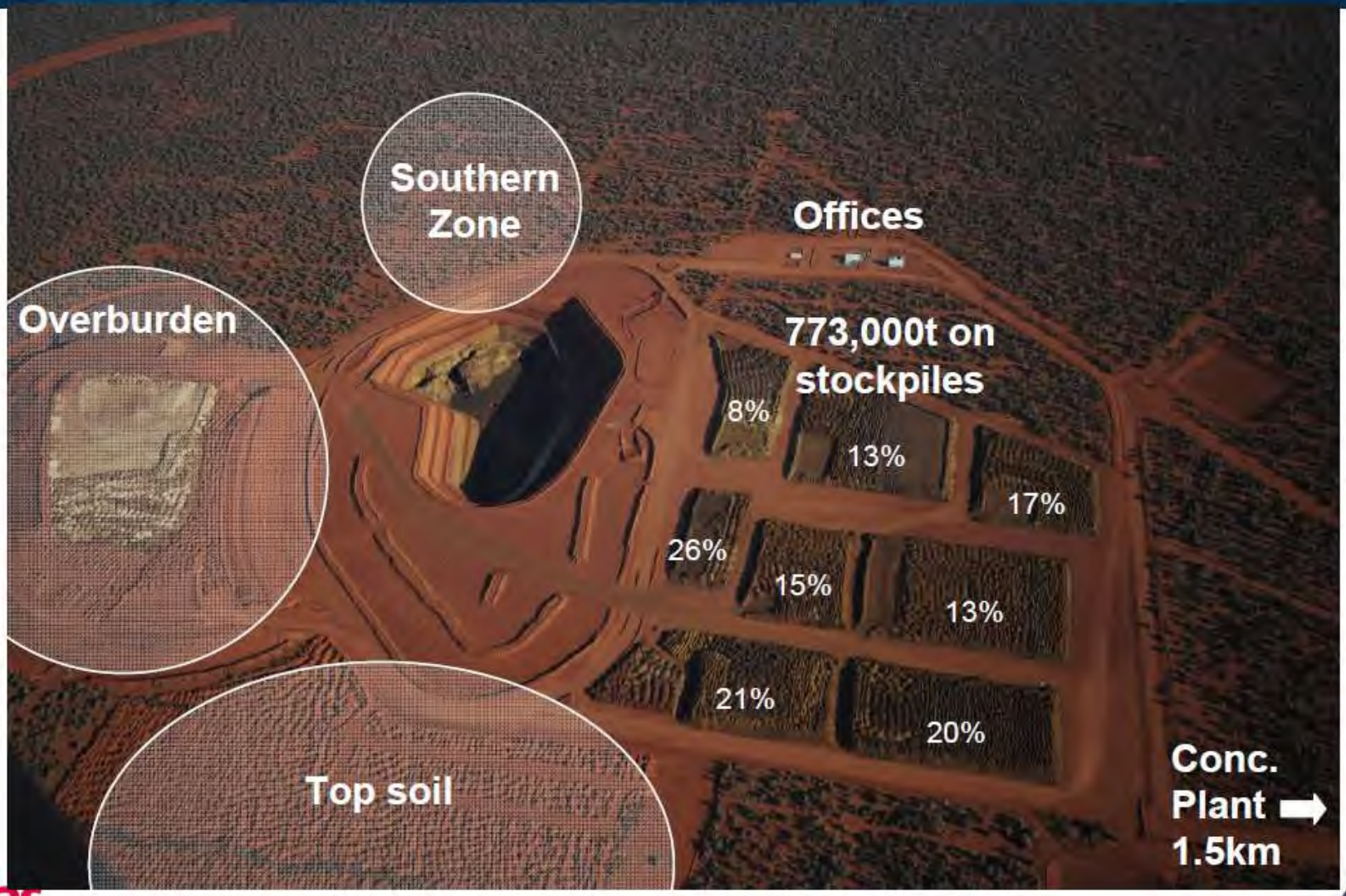
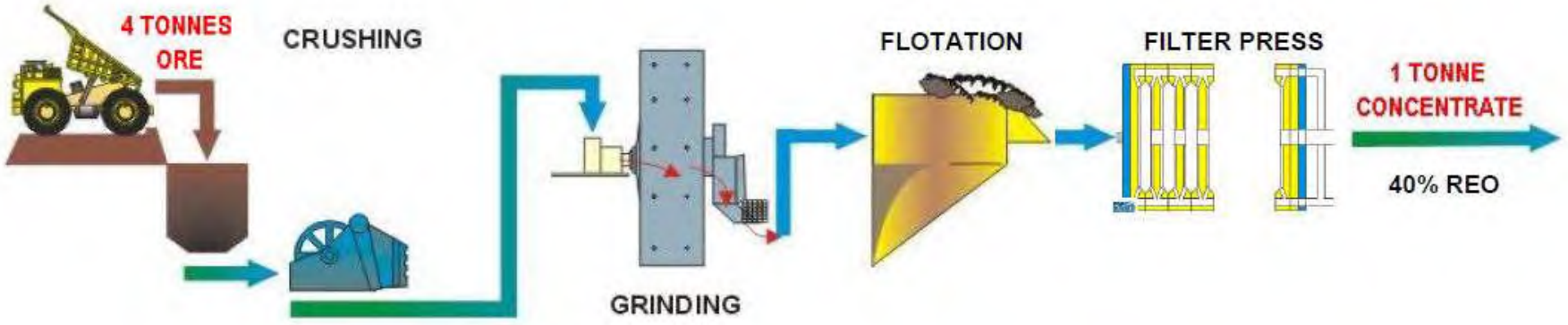


Figure 12: Bayan Obo Rare Earth Concentration Flowsheet, from Li and Yang (2014).

Mount Weld pit floor is currently 51m below surface, the mine plan pit floor is another 36m down



Schematic of Concentration Plant process at Mount Weld, which has been pilot plant tested



Abandoned plastic-lined wastewater pools in Longnan county. Such pools often contain high levels of the chemicals used to separate rare earth minerals from soil.
MICHAEL STANDAERT/YALE E360

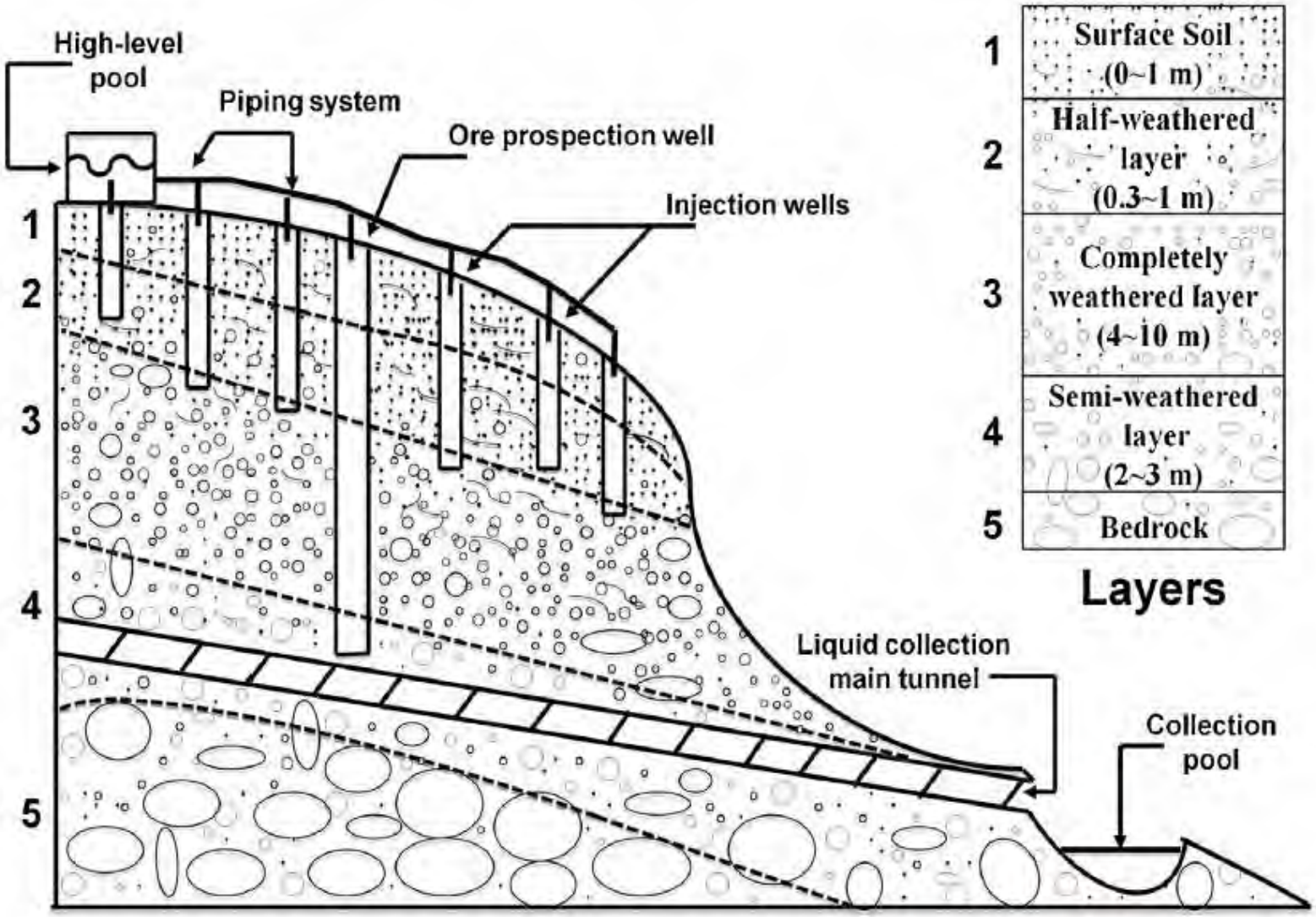


Fig. 1. Typical layers of mining site for ion adsorption clays (adapted from Zou, 2012).

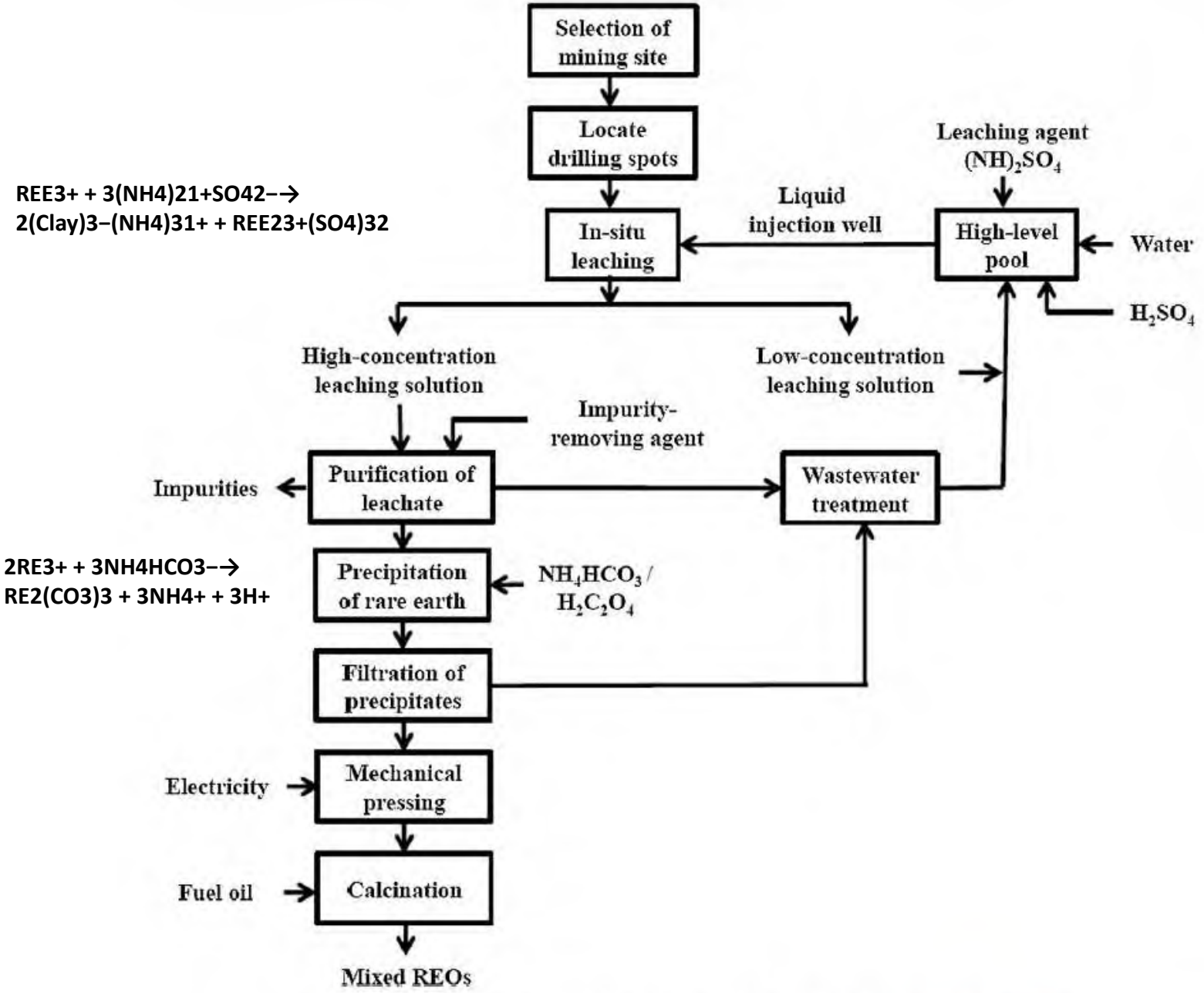


Fig. 2. Flow diagram of ion-adsorption process used in southern China (Luo et al., 2014).

TABLE 1. Total *REE* content of ion-adsorption clays from different geographical origins.

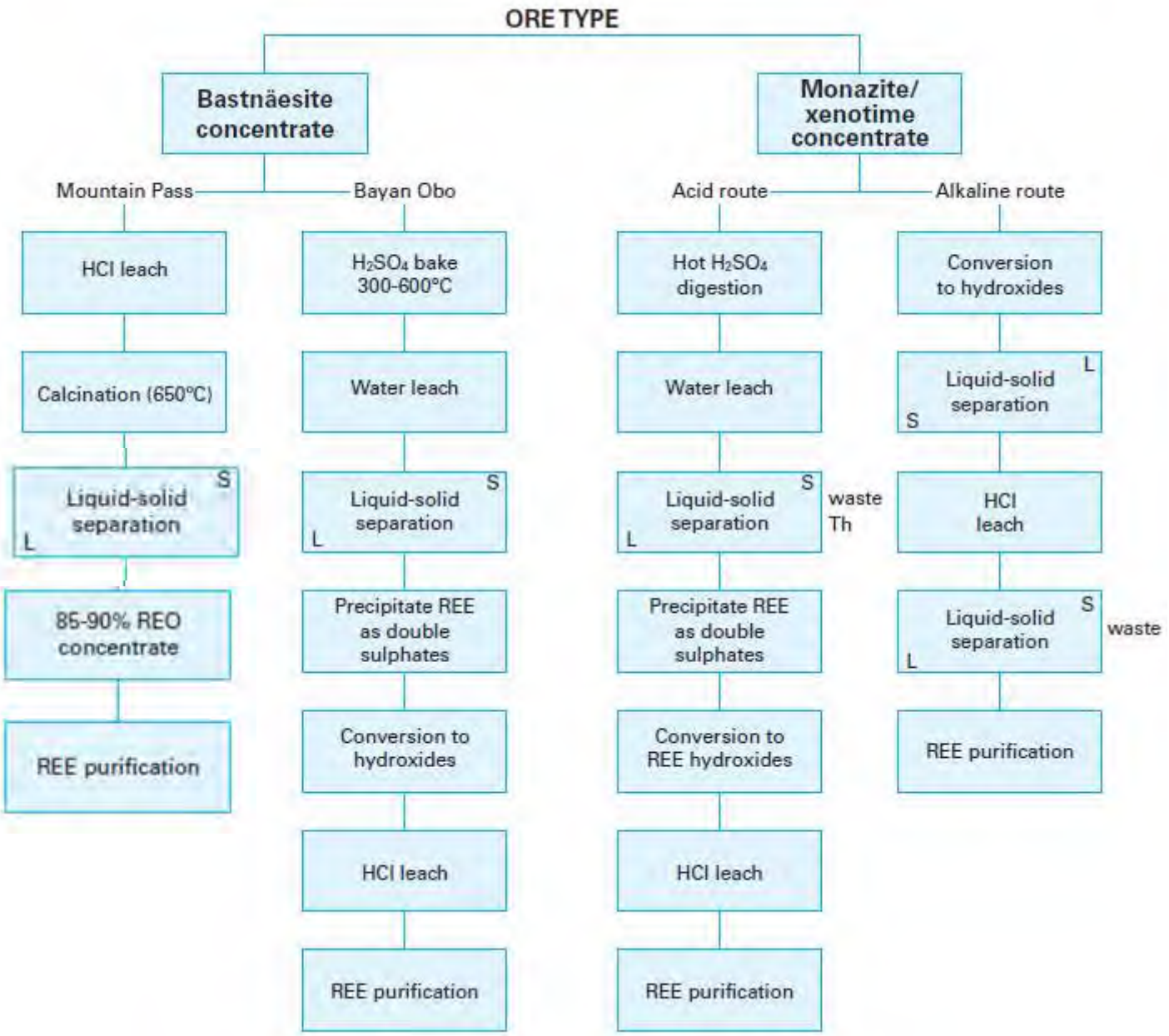
Origin	Africa					Asia		S. America
REE (ppm)	A1	A2	A3	A4	A5	B1	B2	C1
Y	290	140	180	120	100	1570	470	1200
La	1750	290	1790	460	250	70	980	450
Ce	260	170	220	450	280	60	200	120
Pr	280	70	270	120	40	30	190	100
Nd	1000	230	880	260	160	120	690	290
Sm	170	40	170	60	40	40	180	60
Eu	10	10	10	1.76	4.76	0.636	10	20
Gd	110	40	90	30	30	150	130	100
Tb	20	10	10	10	1.06	40	20	60
Dy	60	20	20	20	10	260	100	220
Ho	10	10	4.6	3.33	1.43	50	20	70
Er	20	10	150	120	10	380	250	210
Tm	2	0.869	0.685	0.0232	10	40	20	50
Yb	20	10	10	10	0	160	30	260
Lu	2.66	2.66	2.53	1.71	2.4	20	4.95	50
T*REE*	3990	1080	3800	1650	950	3000	3300	3260

LREE

TABLE 2. Final *REE* extraction levels, expressed as %E (leaching + washing).

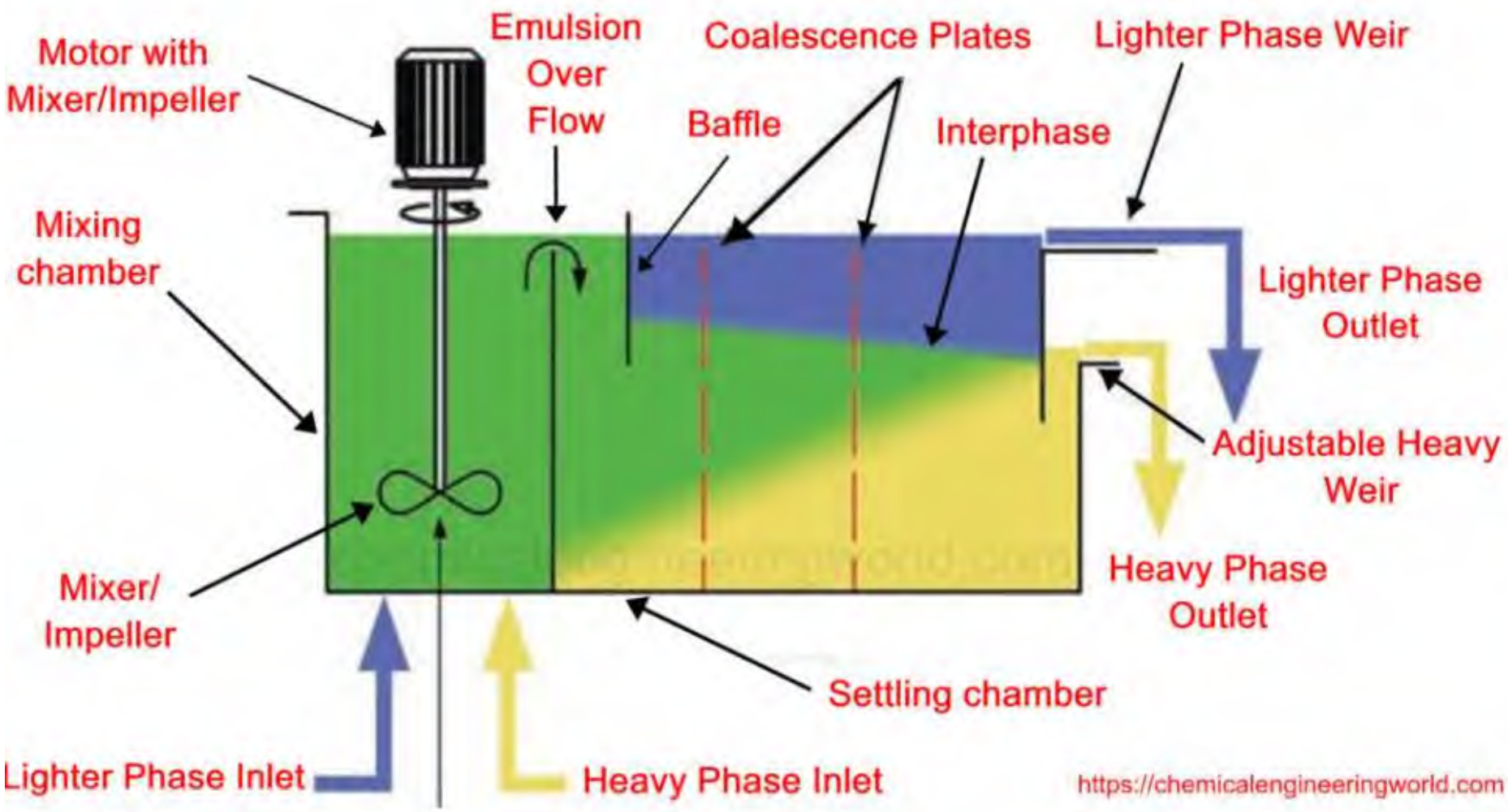
Origin	Africa					Asia		S. America
%E	A1	A2	A3	A4	A5	B1	B2	C1
Y	77.3	72.6	93.6	67.1	57.2	80.5	79.9	70.8
La	83.6	76.9	92.7	66.4	61.2	85.0	80.5	82.9
Ce	0.0	16.9	12.6	6.8	11.6	0.0	0.0	35.6
Pr	75.1	65.0	92.3	74.1	35.1	62.9	69.4	72.8
Nd	80.8	74.1	90.3	68.0	46.0	86.3	87.9	83.2
Sm	90.6	85.2	97.1	66.3	96.4	43.1	81.2	76.9
Eu	62.1	79.0	89.1	43.8	84.3	61.3	83.0	36.2
Gd	82.6	63.0	82.8	74.8	62.3	90.1	84.9	61.6
Tb	84.1	62.8	74.6	19.2	37.3	91.5	90.1	35.6
Dy	80.9	76.3	97.4	74.2	52.2	87.5	79.7	61.5
Ho	75.5	0.0	96.1	96.9	97.5	82.9	77.2	51.8
Er	86.8	73.5	80.2	63.0	44.7	75.2	91.5	53.0
Tm	53.4	79.4	30.0	23.1	7.0	57.9	26.8	47.0
Yb	73.2	64.0	17.6	16.0	25.4	77.9	73.2	61.9
Lu	52.3	34.9	33.7	31.7	12.2	78.5	67.5	51.5
T*REE*	76.6	64.0	76.7	57.1	42.6	80.3	82.1	68.7

LREE


ORE TYPE
Bastnäesite concentrate
Monazite/ xenotime concentrate
Mountain Pass
Bayan Obo
Acid route
Alkaline route
HCl leach
Calcination (650°C)
Liquid-solid separation
S
L
85-90% REO concentrate
REE purification
H_2SO_4 bake 300-600°C
Water leach
Liquid-solid separation
S
L
Precipitate REE as double sulphates
Conversion to hydroxides
HCl leach
REE purification
Hot H_2SO_4 digestion
Water leach
Liquid-solid separation
S
L
waste Th
Precipitate REE as double sulphates
Conversion to REE hydroxides
HCl leach
REE purification
Conversion to hydroxides
Liquid-solid separation
L
S
HCl leach
Liquid-solid separation
S
L
waste
REE purification

The rare-earth separation processes in use today were developed during and shortly after World War II at several U.S. Atomic Energy Commission (AEC) laboratories. Work on the ion-exchange process was carried out at the Oak Ridge National Laboratory (Oak Ridge, Tennessee) by Gerald E. Boyd and coworkers and at the Ames Laboratory (Ames, Iowa) by Frank Harold Spedding and coworkers. Both groups showed that the ion-exchange process would work at least on a small scale for separating rare earths. In the 1950s the Ames group showed that it was possible to separate kilograms of high-purity (>99.99 percent) individual rare-earth elements. This was the beginning of the modern rare-earth industry in which large quantities of high-purity rare-earth elements became available for electronic, magnetic, phosphor, and optical applications.

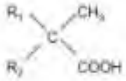
Donald F. Peppard and colleagues at the Argonne National Laboratory (near Chicago, Illinois) and Boyd Weaver and coworkers at Oak Ridge National Laboratory developed the liquid-liquid solvent extraction method for separating rare earths in the mid-1950s. This method is used by all rare-earth producers to separate mixtures into the individual elements with purities ranging from 95 to 99.9 percent. The ion-exchange process is much slower, but higher purities of more than 99.99999 percent (i.e., 5 nines or better) can be attained. For optical and phosphor-grade materials, where purities of 5 to 6 nines are required, the individual rare-earth element is initially purified by solvent extraction up to about 99.9 percent purity, and then it is further processed by ion exchange to reach the purity required for the given application.



Mixer-Settler Working Principle

Cation Exchangers

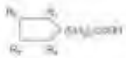
Carboxylic acids



Versatic acids:

$R_1 + R_2 = C_7$, Versatic 10;

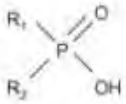
$R_1 + R_2 = C_6$–C_8, Versatic 911



Naphthenic acids:

R_1-R_4: varied alkyl groups

Phosphorous acids



Phosphoric acids:

$R_1 = R_2 = C_4H_9CH(C_2H_5)CH_2O$–, di-2-ethylhexylphosphoric acid (D2EHPA)

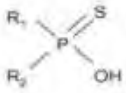
Phosphonic acids:

$R_1 = C_4H_9CH(C_2H_5)CH_2O$–, $R_2 = C_4H_9CH(C_2H_5)CH_2$–, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA, HEHEHP, P507, PC88A)

Phosphinic acids:

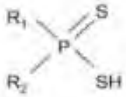
$R_1 = R_2 = C_4H_9CH(C_2H_5)CH_2$–, di-2-ethylhexylphosphinic acid (P229)

$R_1 = R_2 = CH_3(CH_2)_3CH_2CH(CH_3)CH_2$–, di-2,4,4-trimethylpentylphosphinic acid (Cyanex 272)



Monothiophosphorous acids

$R_1 = R_2 = CH_3(CH_2)_3CH_2CH(CH_3)CH_2$–, di-2,4,4-trimethylpentyl-monothiophosphinic acid (Cyanex 302)

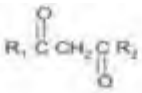


Dithiophosphorous acids

$R_1 = R_2 = CH_3(CH_2)_3CH_2CH(CH_3)CH_2$–, di-2,4,4-trimethylpentyl-dithiophosphinic acid (Cyanex 301)

Other Exchangers

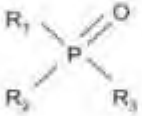
2, Chelating exchangers



β-diketones:

R_1 = R-C_6H_5, R_2 = $CH_3(CH_2)_5$–, R: unknown side alkyl, (LIX 54)

3, Solvating extractants



Phosphorous ester:

$R_1 = R_2 = R_3 = CH_2(CH_2)_2CH_2O$–, tri-n-butyl-phosphate (TBP)

$R_1 = R_2 = CH_2(CH_2)_2CH_2O$–, $R_3 = CH_2(CH_2)_2CH_2$–, dibutylbutylphosphonate (DBBP)

Phosphine oxides:

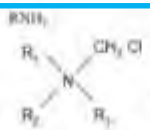
$R_1 = R_2 = R_3 = CH_2(CH_2)_6CH_2$–, tri-n-octylphosphine oxide (TOPO, Cyanex 921)

4, Anion exchanger

RNH_2

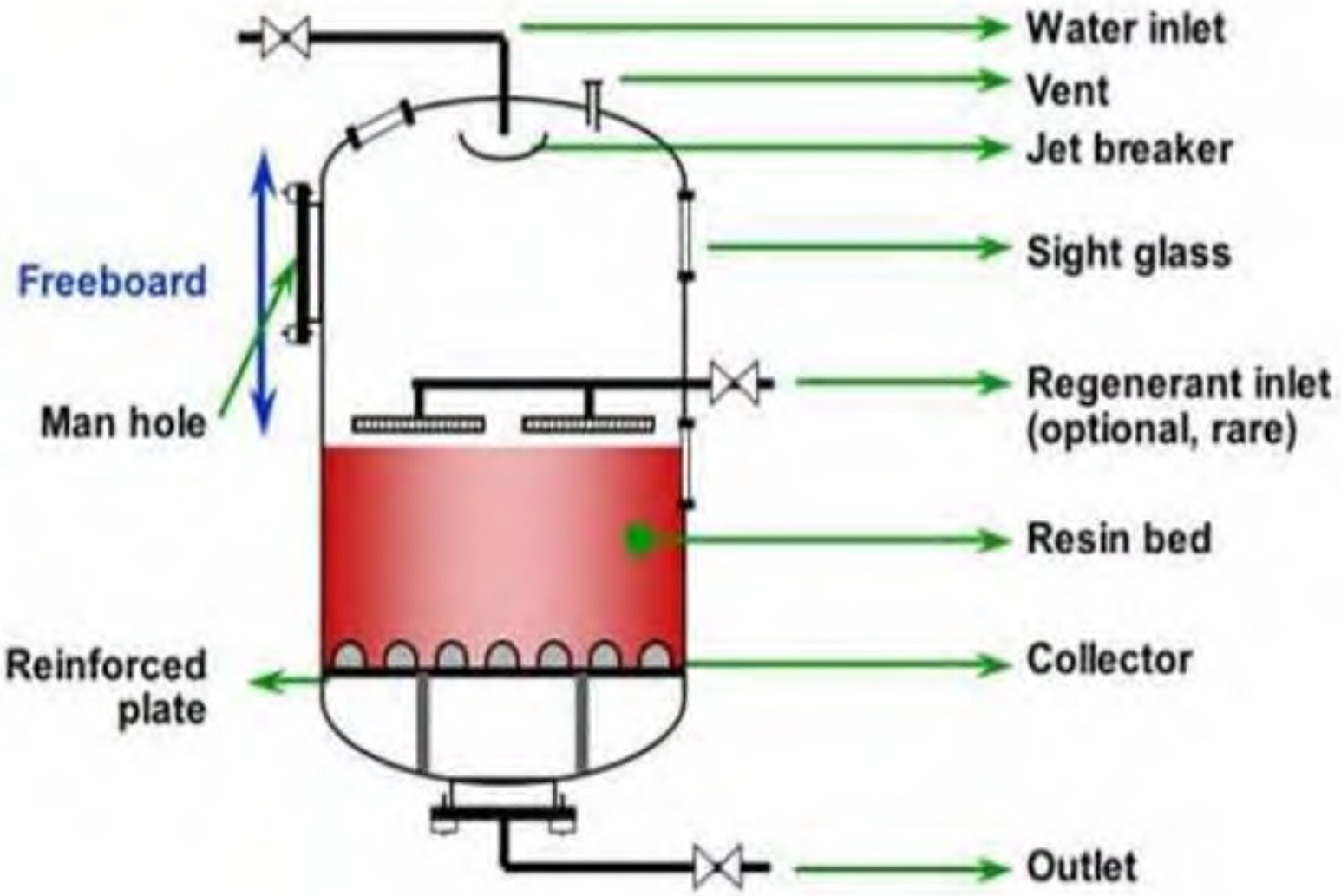
Primary amines

R = $(CH_3)_3C(CH)_2C(CH_3)_2)_4$ (Primene JMT, N1923)



Quaternary amines:

$R_1 = R_2 = R_3 = C_8$–C_{10} mixture (Aliquat 336, Adogen 464)



Ion exchange resin column

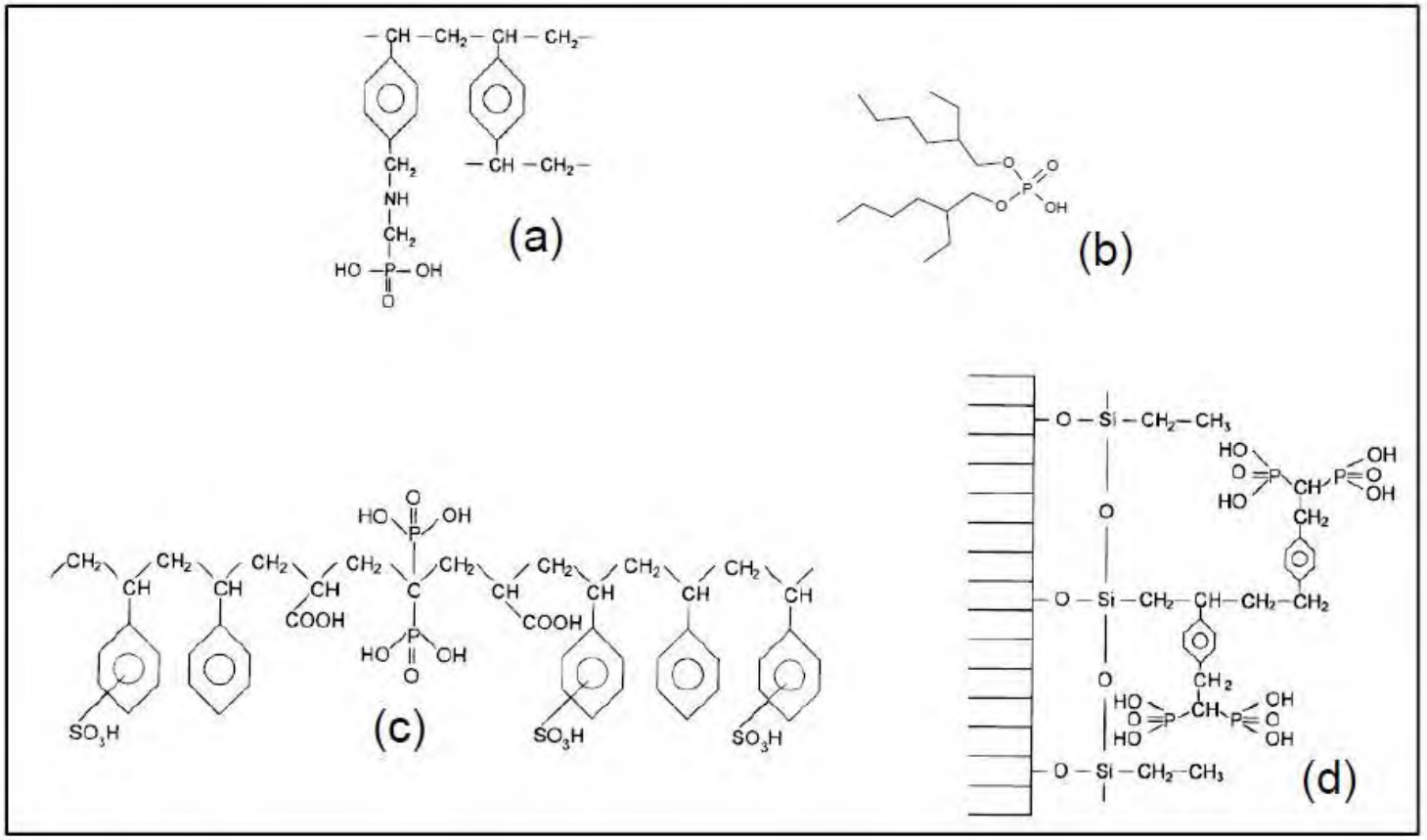


Figure 1. Chemical structure of functional groups present in various commercial resins potentially effective for extracting rare earth elements (REE) in a phosphoric medium. (**a**) Tulsion CH-93, Purolite S940, Amberlite IRC-747 and Lewatit TP-260, (**b**) Lewatit VP OC 1026, (**c**) Diphonix, (**d**) Actinide-CU (reproduced from [15], with permission of American Chemical Society, 1998).

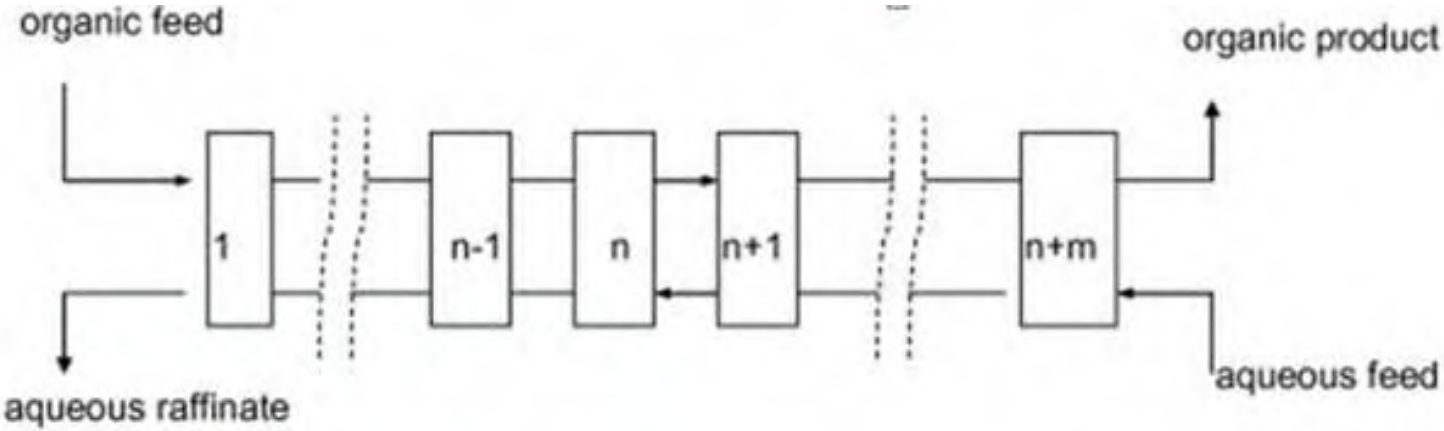


Fig. 3. Simplified countercurrent solvent extraction circuit.

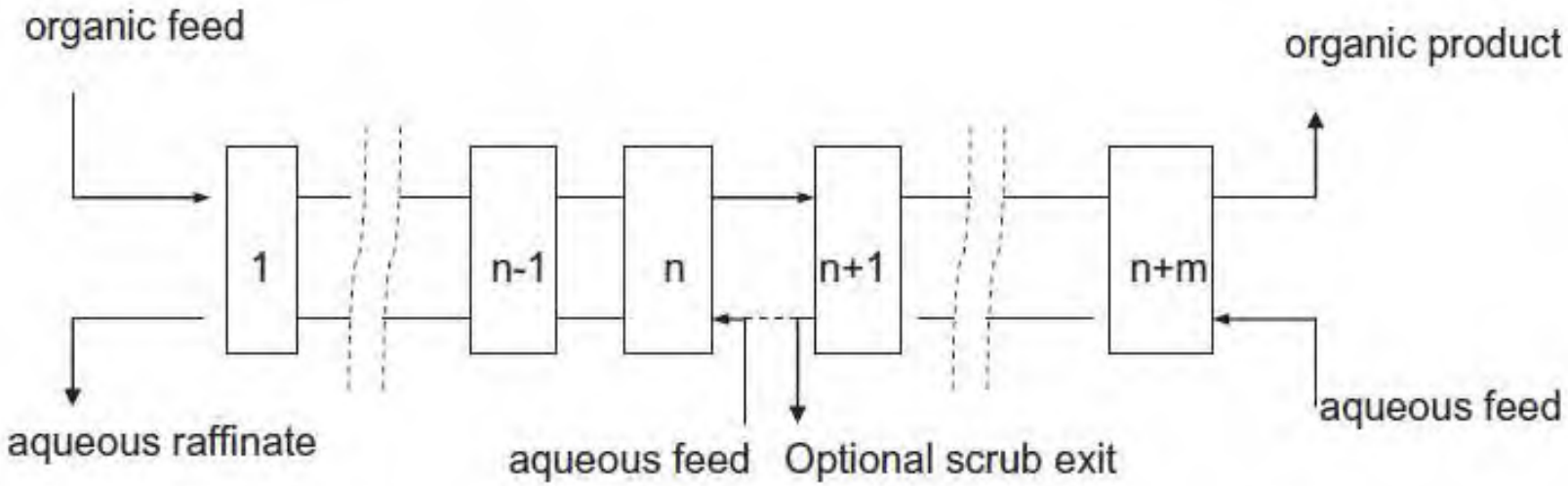


Fig. 4. Simplified configuration of countercurrent solvent extraction circuit with optional scrub exit.

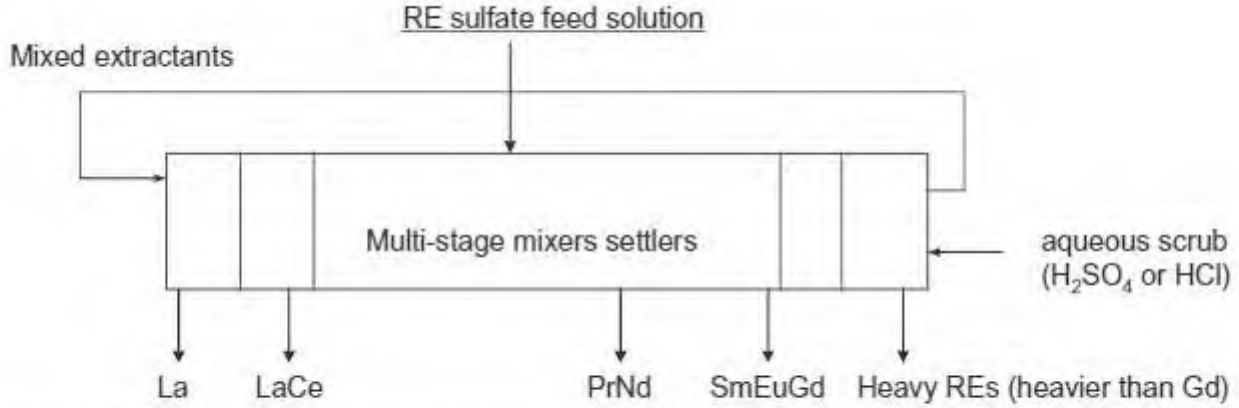


Fig. 14. Simplified configuration of countercurrent separation of rare earths to produce various rare earths products by solvent extraction.

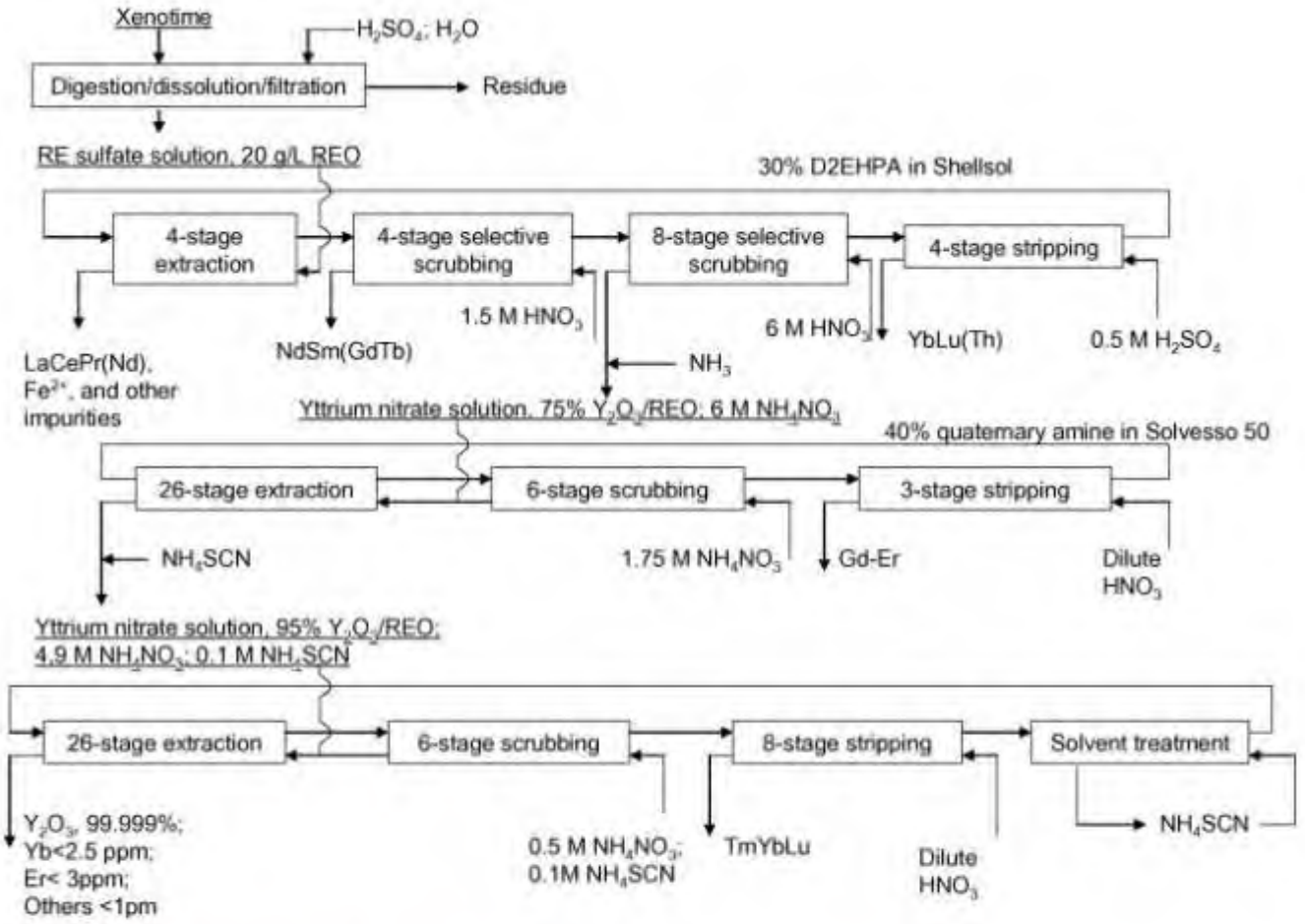


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Fig. 8. AS Megon process for high-purity yttrium oxide (after Gaudernack, 1973).

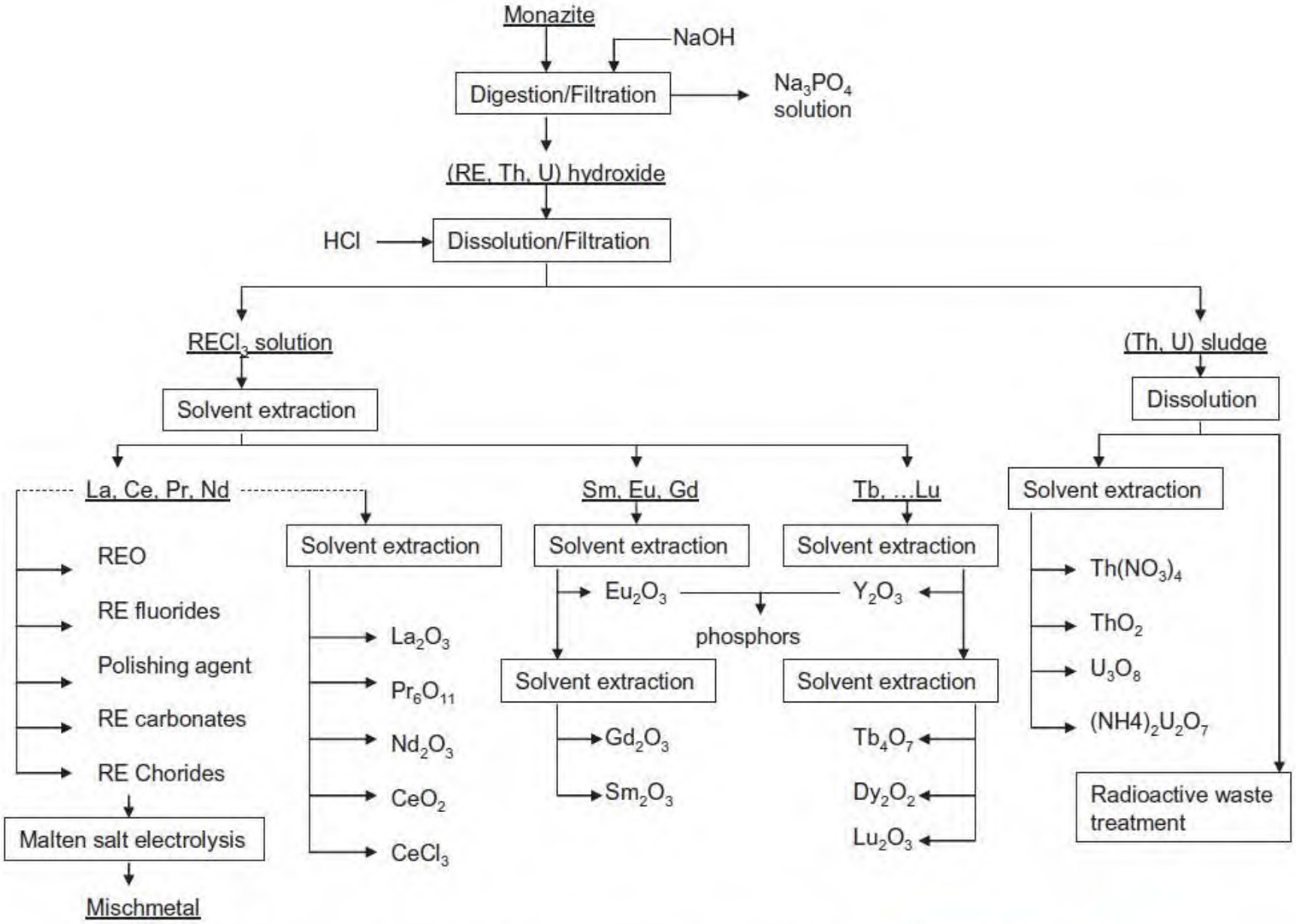


Fig. 10. Simplified flowsheet of the Shanghai Yue Long Chemical Plant (after Zhang et al., 1982).

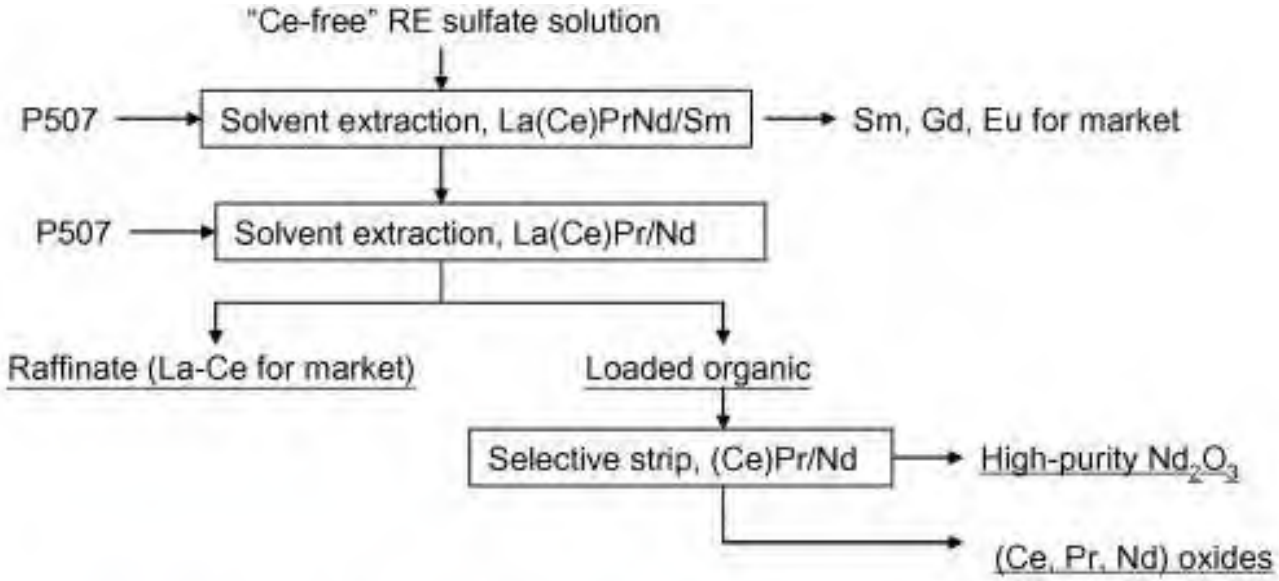
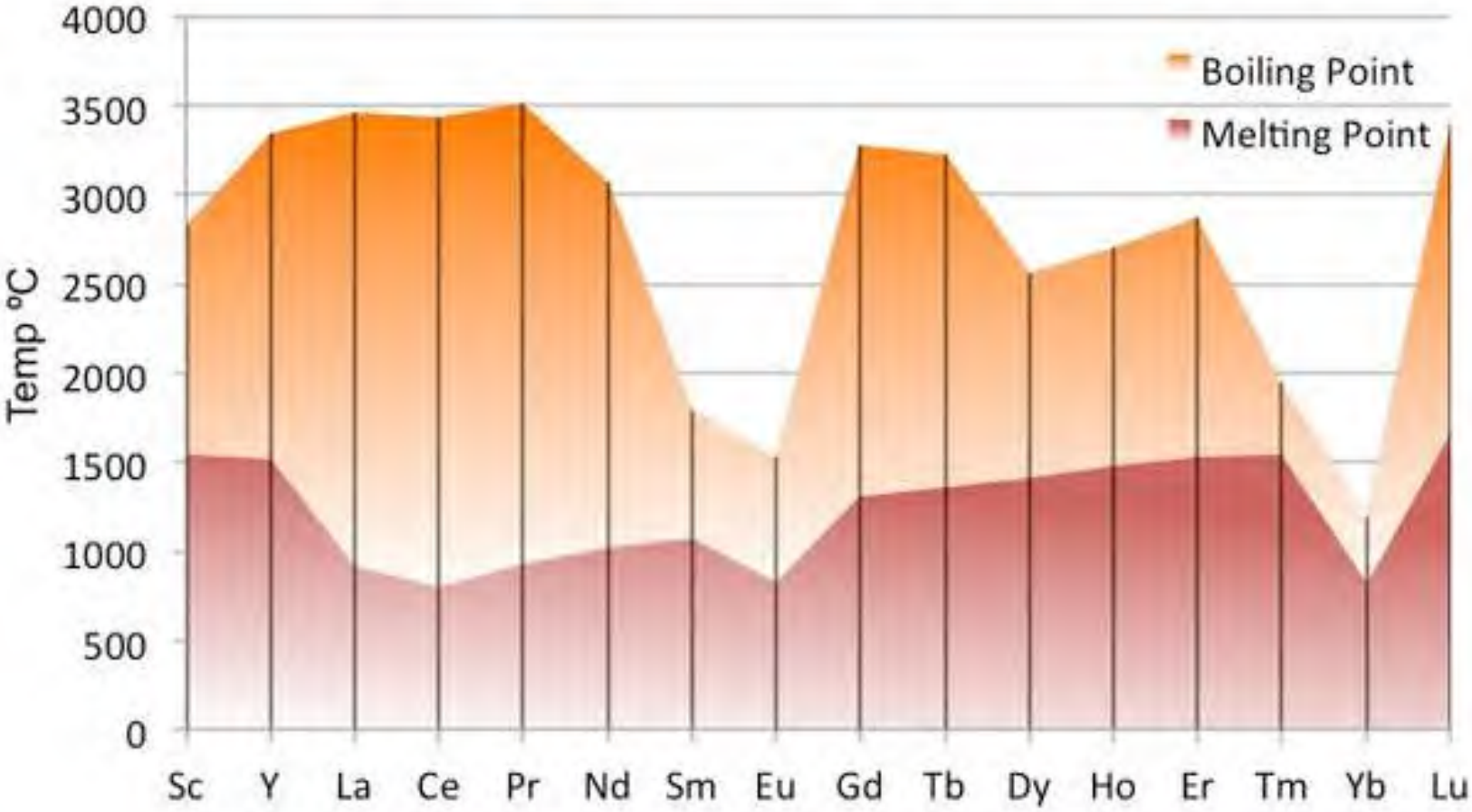
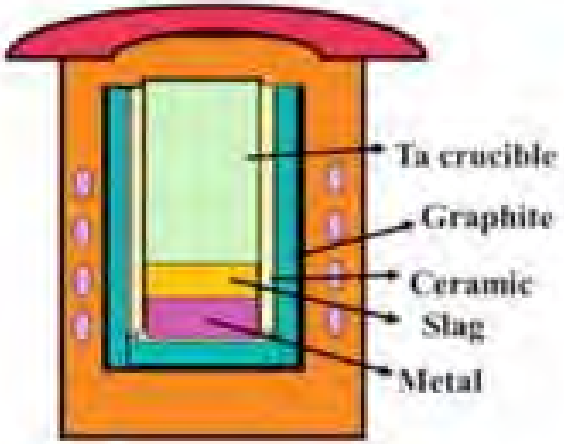


Fig. 13. Simplified flowsheet for solvent extraction process for producing low-cost permanent magnet feed (after Doyle et al., 2000).

REM – Melting & Boiling Points





- Vacuum induction furnace
- Ta crucible fabrication
- Loading the charge
- Lowest in impurity content
- RE metals :

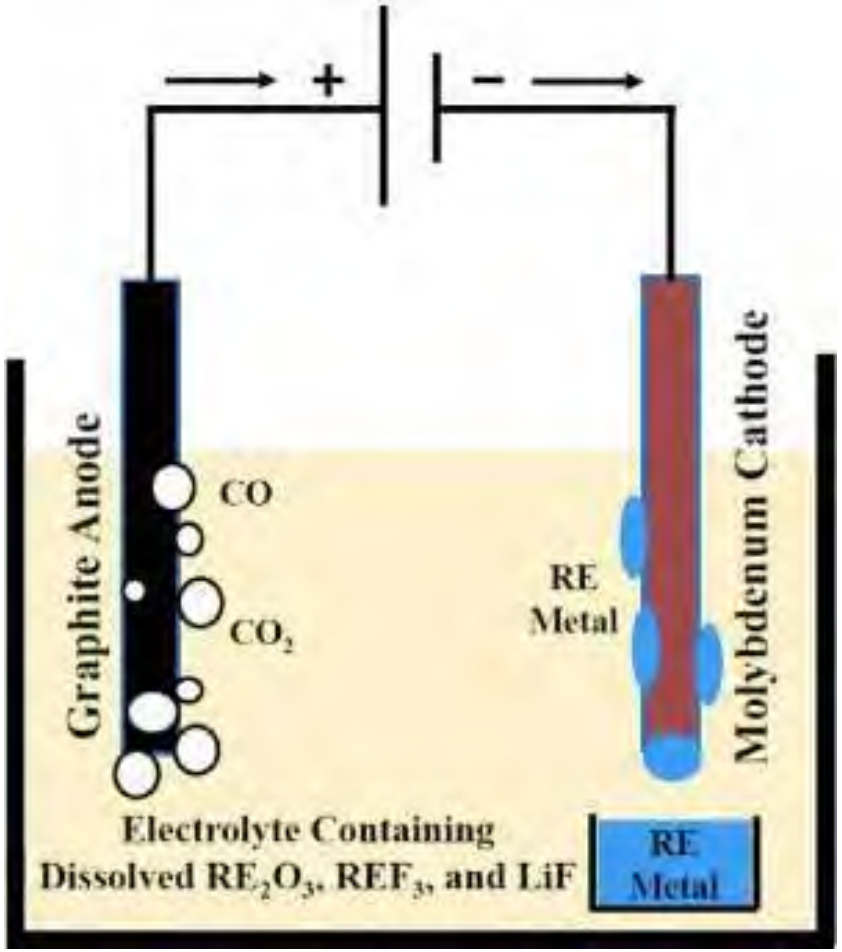
  Ce, Nd, La, Dy, Pr, Gd,

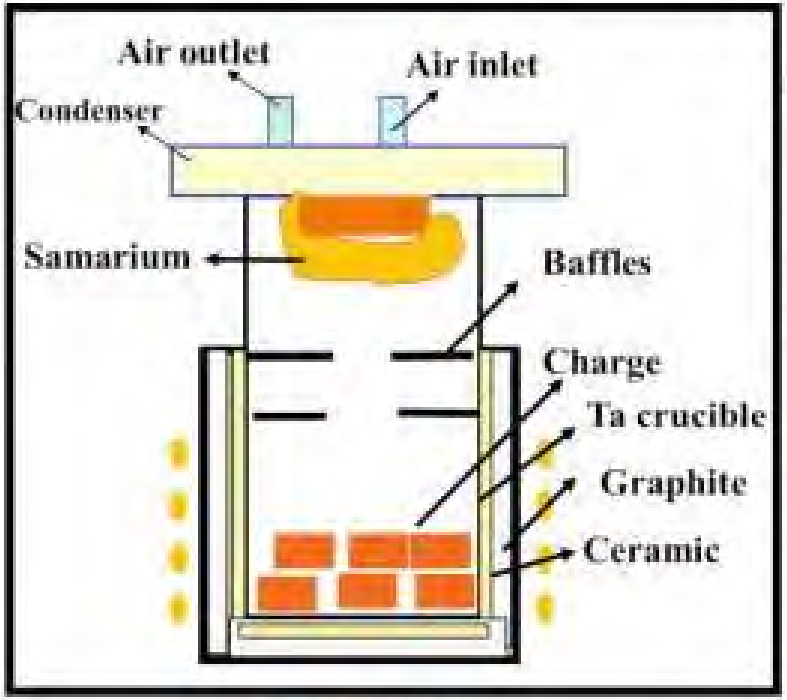
  Tb, Er, Ho, Y, Sc

1500 – 1600 °C

$2\ REF_3 + 3\ Ca \rightarrow 2\ RE + 3\ CaF_2$

$2\ RECl_3 + 3\ Ca \rightarrow 2\ RE + 3\ CaCl_2$


+
–
Graphite Anode
CO
CO_2
RE
Metal
Molybdenum Cathode
Electrolyte Containing
Dissolved RE_2O_3, REF_3, and LiF
RE
Metal



1200–1500 °C

$Sm_2O_3 + 2\ La \rightarrow 2\ Sm + La_2O_3$

Typical data for 1 Kg batch

Sublimation starts at 800 °C

Condenser temp. 500 °C

Rate – 3 g/h

Excess reductant : 15%

Vacuum level = 1 torr

Vapour pressure of Sm at 1000 °C

~ 4 mm Hg

•Similar process for Yb, Tm, Sm

REE production processes generally produce large amounts of waste. Values reported for the production of 1 tonne of REO in China are 60,000 m^3 of waste gases, 200 m^3 acidified water and 1.4 tonnes of radioactive waste (as most REE deposits contain uranium or thorium). The electricity needed for the energy intensive production processes comes with additional generation of waste and/or pollution (British Geological Survey, 2011), as does the production of the large amounts of chemicals required. (Schüler et al., 2011)

Possible air emissions from REE production include sulfur oxides, hydrogen chloride, hydrogen fluoride and dust, which may contain radioactive substances. Polluted water may contain radioactive substances, heavy metals, acids, fluorides and large amounts of ammonium. (Schüler et al., 2011) There are reports of emissions from REE facilities causing disease, poisoning, water pollution and destruction of farmlands. (British Geological Survey, 2011) For 1990s REE production in the US numerous types of waste produced in REE production processes were identified, including numerous types of solid waste, some of which contained lead or mercury, off-gases from several process steps (including particulates, acids, chlorine and carbon monoxide), waste solvents and processing solutions and possibly corrosive wastewater which could contain chromium, lead and ammonium. (US EPA - Office of Solid Waste, 1998)

Rare Earths are a group of elements with unique properties

Rare Earth Elements	Catalytic	Magnetic	Electrical	Chemical	Optical
▪ Lanthanum (La)	✓		✓	✓	✓
▪ Cerium (Ce)	✓		✓	✓	✓
▪ Praseodymium (Pr)		✓	✓	✓	✓
▪ Neodymium (Nd)	✓	✓	✓		✓
▪ Samarium (Sm)		✓			
▪ Europium (Eu)					✓
▪ Gadolinium (Gd)		✓			✓
▪ Terbium (Tb)		✓			✓
▪ Dysprosium (Dy)		✓			✓
▪ Holmium (Ho)					✓
▪ Erbium (Er)					✓
▪ Ytterbium (Yb)					✓
▪ Yttrium (Y)					✓

Applications use different Rare Earths, the supply distribution does not match demand distribution

Rare Earths Usage by Application

Application	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Other
• Magnets			23.4%	69.4%			2%	0.2%	5%		
• Battery Alloy	50%	33.4%	3.3%	10%	3.3%						
• Metallurgy ex batt	26%	52%	5.5%	16.5%							
• Auto catalysts	5%	90%	2%	3%							
• FCC	90%	10%									
• Polishing Powder	31.5%	65%	3.5%								
• Glass Additives	24%	68%	1%	3%						2%	4%
• Phosphors	8.5%	11%				4.9%	1.8%	4.6%		69.2%	
• Ceramics	17%	12%	6%	12%						53%	
• Others	19%	39%	4%	15%	2%		1%			19%	

Note: Percentages represent estimated average consumption distribution by application, actual distribution will vary from manufacturer to manufacturer