Hydrometallurgy A short overview of the history and a primer of solvent extraction

Part of the curriculum in hydrometallurgy Presented by PRICE Prepared by Dag Ø. Eriksen April 2020

Unless said differently: All pictures and figures are copyright Dag Øistein Eriksen

Use of metals - historically

- The first metals to be used were the ones which are easy to find or make in elemental form:
 - Gold
 - Silver
 - Copper and later bronze
- Bronze requires the alloying of two metals: copper and tin
 - Brass is copper and zinc
 - Both bronze and brass were impure with a lot of other components present (Al, Mn, As, ...)

Use of metals - historically

- Gold and silver may be found in elemental form in nature
 - They are soft and easy to form, but not useful as tools
- Copper and alloying metals may be reduced by carbon in fires: Cu₂S + C + 2O₂ = 2Cu + CO₂ + SO₂
- Bronze is harder than copper and can be used in tools

Pictures from The Natural Sapphire Company



Minoan gold jewelery



Egyptian bronze axes

Production of metals - historically

- The carboreduction route for making metals was used for > 4 000 years
- Hydrometallurgical routes were not needed before the industrial revolution (18th century)
 - Based on alchemy making gold, but founded the basis for chemistry: mineral acids, distillation, ...
 - Needs understanding of chemistry as separation is essential
 - Closely connected to understanding and knowledge of minerals, rocks and mining

Mining – short history

- St Joachimsthal, Ertzgebirge
 - Presently Jachymov, Czech Republic
- Rich siver mine which enabled Graf von Schlick, the owner, to mint Joachimsthaler
 - Later the name was Thaler which is the origin of Dollar and in Norway: Daler

(<1875)



- Georg Bauer, a German scholar, studied mining and founded mining as a field of science
 - As scholars did in the 16th century he took a latin name: Georgius Agricola



When the silver mine was depleted, uraniumsalt was mined (19th century). U-salts were used as yellow color in glass.

Pictures from Wikipedia

PRICE - April 2020

Mining – short history

- The mine in St Joachimsthal has also a more tragic story:
- It was the site where the «Miners decease» was first recognized.
- It was not understood before radon, Rn, was discovered
- The decease is Lung cancer

- In the waste from the mine Marie Sklodowska Curie separated first
- Polonium in July 1898, and
- Radium in December
 - 1898



Radiochemistry is an important part of hydrometallurgy



Teodora Retegan and Franz Schönhofer





Example of steps in modern mining

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



From Lynas Investors presentation – March 2010 PRICE - April 2020

Reason for crushing, grinding and milling

- Rocks consist of mixtures of minerals. A mineral is a (more or less) pure chemical compound
 E.g.: Eudialyte Group: Na₁₅Ca₆(Fe,Mn,Ln)₃Zr₃SiO(O,OH,H₂O)₃(Si₃O₉)₂(Si₉O₂₇)₂(OH,Cl,F)₂
- To access the interesting (valuable) mineral it is an advantage to mill down the rock so that the mineral grains are free, i.e. contain (almost) only one kind of mineral



PRICE - April 2020

Eudialyte

Beneficiation methods of ores

- Ores often contain only ca 1 % of the valuable metal, e.g. NiS, Cu₂S, REEs, CoS, Ta-, Nb-, Woxides,...
- A pre-concentration step reduces sizes of processing equipment and the consumption of acid/base. Allows higher flow of value through the system.

Beneficiation methods of ores

- First crushing, grinding, milling and sieving must be performed
- Flotation
 - Based on minerals different hydrofobicity
 - Uses surfactants like phosphonates
 - Foam is separated and filtered
 - Typically a particle size of 50 µm is employed
 - Milling consumes energy





PRICE - April 2020

Visit at a zinc & lead mine in Poland



Visit at a zinc-lead mine in Poland





PRICE - April 2020

Beneficiation methods of ores

- Gravitational separations
 - Uses differences in density of minerals or rock materials
 - Usually in aqueous slurries
- Magnetic separation
 - Many minerals possess magnetic properties
 - Usually slurries are used





Pictures from Wikipedia

A short history of radiochemistry

- 1898: Marie and Pierre Curie discovered Po and Ra by chemical separations of dissolved uranium ore
 - 1903 M. Curie has produced ca 100 mg pure Ra by fractional crystallisation
- 1923: de Hevesy uses ²¹²Pb as a tracer to follow the absorption in the roots, stems and leaves of the broad bean
- 1938: Otto Hahn proves fission of uranium as Ba is separated from irradiated uranium solution
- 1940: First transurane produced: Np by McMillan and Abelson
- Nuclear power requires separation of fission products
 - Requires methods remotely operated and with selective chemistry

The cycle of nuclear energy



Figure ref.: DOI: 10.13140/RG.2.2.16166.78407

Figure from Wikipedia

Thermal fission yields – ²³⁵U



Thermal fission yields – ²³⁵U and ²³⁹Pu



Fission yields of ²³³U and ²³⁵U



There are almost no differences in waste handling of fission products for ²³³U and ²³⁵U PRICE - April 2020

Radiochemistry has contributed to the development of hydrometallurgy

The need for safe, remote handling of the laborious separations required in the nuclear sector boosted innovation in:

- Solvent extraction:
 - Continuous, counter current process enabled large quantities to be processed
 - Contactors like mixer-settlers were developed
- Ion exchange to perform difficult purifications by chromatography

Nuclear chemistry has contributed to the development of hydrometallurgy

- Most ores contain traces of radioactive materials, i.e. U- and Th-oxides
- Handling of radioactivity is therefore essential as radioactive isotopes may be concentrated during the separation process
- Knowledge of radioactivity, radiation protection and dose assessment is important contribution to hydrometallurgical process development

Hydrometallurgy and nuclear chemistry

Nuclear (radio-)chemistry offers special methods useful in hydrometallurgy:

- Use of radioactive tracers, i.e. radioactive isotopes of the elements studied
 - Particularly important in liquid-liquid extraction
- Neutron activation can be used on all phases: solid, aqueous-, organic phases (and gas)
- AKUFVE-method very efficient in measuring extraction kinetics
- Many "hydrometallurgical" elements have suitable isotopes for use as tracers
 - In addition, e.g. Eu(III) can be used as tracer for Am(III), and Nd³⁺ has equal ionic radius as Am³⁺

The natural radioactive series



 $\overset{235}{92}U \xrightarrow{\alpha,7\ 10^8y} \overset{231}{90}Th \xrightarrow{\beta,25,6h} \overset{231}{91}Pa \xrightarrow{\alpha,3,3\ 10^4y} \overset{227}{89}Ac \xrightarrow{\beta,22y} \overset{227}{90}Th \xrightarrow{\alpha,18,7d} \overset{223}{88}Ra \xrightarrow{\alpha,11,4d} \overset{219}{86}Rn \xrightarrow{\alpha,3,9s} \overset{215}{84}Po \xrightarrow{\alpha,1,8ms} \overset{211}{212}Pb \xrightarrow{\beta,36,1m} \overset{211}{83}Bi \xrightarrow{\alpha,2,15m} \overset{207}{81}Tl \xrightarrow{\beta,4,8m} \overset{207}{82}Pb$

 ${}^{232}_{90}Th \xrightarrow{\alpha,1,4\ 10^{10}y}{88}Ra \xrightarrow{\beta,5,7y}{88}Ra \xrightarrow{\beta,6,7y}{89}Ac \xrightarrow{\beta,6,13h}{90}Th \xrightarrow{\alpha,1,9y}{88}Ra \xrightarrow{\alpha,3,64d}{220}Rn \xrightarrow{\alpha,55,6s}{84}Po \xrightarrow{\alpha,0,15s}{212}Pb \xrightarrow{\beta,10,6h}{212}Bi \xrightarrow{\beta,60,6m}{212}Pb \xrightarrow{\alpha,0,3\mu s}{82}Pb and {}^{212}_{83}Bi \xrightarrow{\alpha,60,6m}{208}Tl \xrightarrow{\beta,3,05m}{208}Pb$

Challenges connected to thorium

"Thorium problem" impedes supply of REs

- Dilemma: Ores rich in desired HREE tend to be high in Th content, frustrating access to such ores
- Radioactive materials add cost to processing due to regulations related to health and environment
- Thorium has almost no market, so any recovered Th becomes a waste that is expensive to dispose of
- Hopes for a Th nuclear fuel cycle creating a large new market for Th in the future are ill-founded
- · Therefore there is no revenue to offset the added cost
- Technical solution is to avoid concentrating Th or embrace otimism and find new applications for Th

gulatory solution could be government Th stockpile

DZP Process "NORM"





NORM Management

The process does not produce a mineral concentrate and does not concentrate the uranium and thorium.

These waste products are neutralised with limestone and dispersed in the residue storage facilities at less concentration than in the primary deposit.

All wastes are contained within the project site.

The deportment and concentration of "daughter products" (radionuclides) within the process streams is an important consideration. Currently being audited by ANSTO.

Elements to be recovered through hydrometallurgical methods

Group → ↓ Period	• 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 0	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			└──┦															
Lanthanides				57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides				89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The rare earth containing mineral eudialyte

- Theoretical stoichiometric formula: Na₁₅Ca₆(Fe,Mn,Ln)₃Zr₃SiO(O,OH,H₂O)₃(Si₃O₉)₂(Si₉O₂₇)₂(OH,F)₂
- Dissolvable in dilute acid
- Gives Na⁺ and F⁻ in solution
- Gives also silicate/silicic acid and ferrous ions



Think holistic!



Think holistic!



From a visit at a tin mine in South Africa



Waste deposit



Dried out tailings dam



Separation chemistry

- Imperative to have a change in phase
 - Solid to liquid or gas
 - Liquid to solid
 - Liquid to liquid
 - Gas to solid or liquid
 - Liquid to gas and back
- Membranes can be viewed as phase separators



Types of Separation chemistry

Leaching:

- Alkaline
- Acid based
- Other: chlorination, baking, calcining, ...

Phase separations:

- solid phase liquid,
- liquid gas,
- solid –gas,
- liquid liquid,
- distillation, ...

Chemical means:

- Precipitation, crystallisation
- Ion-exchange, IX
- Solvent Extraction (Liquid Liquid Extraction, LLX or SX)
- Membranes
- Mixing of methodes: impreg.resin, SLM, ...
- Ionic liquids

Basic theory E.g.: Solvent Extraction – SX or LLX

- Basic SX
 - Acidic, alkaline and solvating extractants
 - Saponification
 - D-, %E-, K-values
 - Solvents and solvabilities
 - Complexes
 - Lewis' acid-base concept (HSAB)
 - Salting out effects
 - Solubility curves
 - Kinetics extraction and strip

• Cation exchanging extractant:

 $M^{n+}(aq) + nHA(org) \leftrightarrow nH^{+}(aq) + MA_{n}(org)$ $K = \frac{[\overline{MA_{n}}][H^{+}]^{n}}{[M^{n+}][\overline{HA}]^{n}}$ $D = \frac{[\overline{MA_{n}}]}{[M^{n+}]}$

 $\log K = \log \frac{[\overline{MA_n}]}{[M^{n+1}]} + n \log[H^+] - n \log[\overline{HA}]$

 $\log K = \log D + n \log [H^+] - n \log [\overline{HA}] \Rightarrow$

 $logD = nlog[\overline{HA}] + pK + npH$ (linear in log-log plot) $log = log_{10}$, pK = - logK, pH = - log[H⁺]

Basic theory E.g.: Solvent Extraction – SX or LLX

Anion exchanging extractant:

$$MX_{y}^{n-}(aq) + nACl(org) \leftrightarrow nCl^{-}(aq) + MX_{y}A_{n}(org)$$

$$K = \frac{\left[\overline{MX_{y}A_{n}}\right][Cl^{-}]^{n}}{\left[MX_{y}^{n-}\right][\overline{ACl}]^{n}}$$

$$D = \frac{\left[\overline{MX_{y}A_{n}}\right]}{\left[MX_{y}^{n-}\right]}$$

 $\log K = \log \frac{[MX_y A_n]}{[MX_y^{n-}]} + n \log[Cl^-] - n \log[\overline{ACl}]$

 $\log \mathsf{K} = \log \mathsf{D} + n \log[\mathsf{Cl}^-] - n \log[\overline{ACl}] \Rightarrow$

 $logD = nlog[\overline{ACl}] + pK - nlog[Cl⁻]$ (linear in log-log plot)

Solvating extractant:

 $MX_n(aq) + pA(org) \leftrightarrow MX_nA_p(org)$ $K = \frac{\left[MX_{n}A_{p}^{-}\right]}{\left[MX_{n}\right]\left[\bar{A}\right]^{p}}$ $D = \frac{\left[M\overline{X_{n}}\overline{A_{p}}\right]}{\left[M\overline{X_{n}}\right]}$ $\log K = \log \frac{\left[\overline{MX_nA_p}\right]}{\left[MX_n\right]} - p \log[\overline{A}]$ $\log K = \log D - p \log[\overline{A}] \Rightarrow$ $\log D = p \log[A] - pK$ (linear in log-log plot)

Extractants - examples

- Cation exchangers
 - Di-2-ethylhexylphosphoric acid: HDEHP or D2EHPA
 - 2-ethylhexyl-(2-ethylhexyl) phosphonic acid: PC88A,
 Cyanex 272, longuest 801, ..

- Solvating extractants
 - Tri-octylphosphine oxide, TOPO
 - Tri-butylphosphate, TBP





Parts of the extractant is hydrophobic while one part is hydrophilic

PRICE - April 2020

Cation exchangers

- Copper extraction is a major field in SX. Extractants are usually oxime derivatives
- Versatic acid is carboxylic acid R-COOH
- Today there are also commercially available extractants like R₂POOH, R₂POSH, R₂PS(SH). Cytec is the main producer
- The acidity of the functional groups vary as: R₂PSSH < R₂POSH < R₂POOH < (RO)RPOOH < (RO)₂POOH < (RO)₂POP(OH)(RO)₂
- HDEHP forms dimers in aliphatic solvents: H(DEHP)₂, making the capacity only half, but the acidity is larger than for the monomer
- The solubility of HDEHP can reach about 1 M

Extraction with HDEHP and PC88A of Eu and Y Data from MEGON





n = - 3

Extraction of Y and Eu Data from MEGON



Extraction of Ce(III) and Ca Data from MEGON



n = - 3

n = - 2

Extraction with 1M PC88A in Shellsol D-70



Summary: Extraction depends on

- pK_a of extractant
- Solvent aliphatic or aromatic
- Concentration of extractant
- Acid concentration

Traditional selective extractants for copper

- Oxime compounds have proven to be selective and stable compounds for recovery of Cu²⁺
- They only work for pH > 1, which makes them unusable for extraction from strong acids
- Well proven technology for Cu-extraction at industrial conditions



http://www.mining-solutions.basf.com/ev/internet/mining-solutions/en/download-center/redbook/index

Examples of extractions of REE with pure TBP

- TBP is a liquid at STP
- Chemically very stable
- REE can form complexes with nitrate

E. Hesford, E.E. Jackson, and H.A.C McKay "TRI-n-BUTYL PHOSPHATE AS AN EXTRACTING AGENT FOR INORGANIC NITRATES – VI" J. Inorg. Nucl. Chem. Vol.9, 279-289 (1959) D. Scargill, K. Alcock, J.M. Fletcher, E. Hesford, and H.A.C. McKay "TRI-n-BUTYL PHOSPHATE AS AN EXTRACTING AGENT FOR INORGANIC NITRATES – II" J. Inorg. Nucl. Chem. Vol.4, 304-314 (1957)





Anion extractants - examples

- Majority of anion extractants are amines
- Employed are:
 - Primary amines: RNH₂
 - (Secondary: R₂NH)
 - Ternary amines: R₃N
 - Quarternary amines:
 R₃R'NCl,
 R' may be smaller than
 the other organic groups

- Primary to ternary amines must be activated:
 R₃N: + HCl = R₃NH⁺ Cl⁻
- For large complexes quarternary amines may suffer from steric effects

Examples of use of amines

- Comparison of extraction of Th, Lu, La and Zr fra sulphuric acid environment, M(SO₄)_p^(n-2p), Mⁿ⁺
- JM-T: primary amine, LA-1: secondary amine, TiOA: tertiary amine (tri-isooctylamine)





Can we foresee which extractant will bind to which solute?

- The best theory is the Hard-Soft Acid Base theory – HSAB
- Based on Lewis acid-base theory
- Hard acids require hard bases and soft acids require soft bases
- Examples:

Fe³⁺ is strongly extracted by HDEHP Cd²⁺ needs R₂PS(SH)

In SX, Phase separation is imperative

Phase separation methods available:

- Gravitational
 - Electrostatic
- Centrifuges
- One continuous phase Electrodynamic contactor

Challenges with phase separations:

- Crud-formation, i.e. third phase or formation of solids at the interface between the liquid phases
- Modifiers may be used to enhance phase separation. Often an alcohol that replaces co-extracted water
- Interfacial tension and formation of micelles may make phases dissolved in each other

Advantages and disadvantages of Liquid-liquid (solvent) extraction

Advantages:

- True continuous process
- Can be run counter-currently
- Washing and scrubbing is easy
- Accepts fines and large flows
- Can be stopped and restarted without changes in equilibrium

Disadvantages:

- Every physical stage is less than a theoretical plate => Many stages may be needed
- Settlers contain a large volume of the product. Increases investment cost.
- Organic liquids will have some evaporation and dissolution
- Organic liquids may have some negative environmental impact

Mixer-settlers







Counter current liquid-liquid extraction

In solvent extraction the key parameters to control are:

- Flow rates
- Concentrations, i.e. pH, extractant, feed solutes etc.
 - Evaporation of diluent
- Densities of loaded and barren phases
- Stirring speed
- Presence of silicic acid, extractant's "poisons"



An example of copper extraction

- PLS = Pregnant Leach
 Solution
- Pregnant strip solution will accumulate Cu



http://www.mining-solutions.basf.com/ev/internet/mining-solutions/en/download-center/redbook/index

Part of the former MCI-MEGON's Y-plant



Another example of mixer-settlers

