The "toolbox" of a Hydrometallurgist...

Processes available to purify metal-containing aqueous solutions:

- Chemical precipitation (oxides, hydroxides, carbonates, sulphides etc.)
- Crystallisation (metal salts)
- Electrochemical precipitation (cementation, H2-reduction)
- Electrodeposition
- Liquid-liquid Extraction (organic solvents)
- Ion Exchange (resins)
- Ultra Filtration/RO
- And others...

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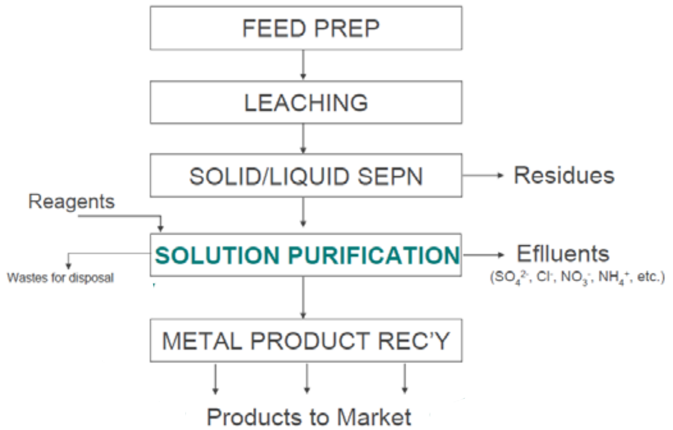
Generic flowsheet for a hydrometallurgical process

Purification Processes in the Context of Metal Recovery



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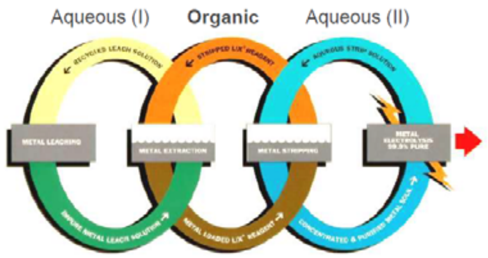
In this lecture – Liquid-liquid extraction, or Solvent eXtraction (SX) will be discussed

Solvent Extraction (SX) - the organic is the convenient "shuttle bus" between two aqueous solutions



The SX liquid organic phase:

(i) **extractant** -- the organic chemical reagent reacting with the metal species from the aqueous solution to form a metal-extractant complex which is preferentially distributed to the organic phase

(ii) **modifier** -- another organic chemical, which improves the solubility of the extractant and/or the metal-extractant complex in the organic diluent, and may also improve the phase separation properties of the SX system

(iii) **diluent** -- dissolves the extractant (and the modifier) as well as the metal-extractant complex, and provides the required physico-chemical properties of the SX system

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Solvent extraction in Hydrometallurgy
We begin in the laboratory...

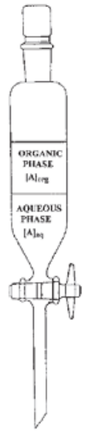

Fig. 1.1 A schematic representation of solvent extraction (liquid-liquid distribution). A solute A is distributed between the upper layer, for example an organic solvent, and the lower layer, an aqueous phase.

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Solvent extraction in Hydrometallurgy

Requirements for the organic phase

The extractant should:

- have very low solubility in the aqueous phase
- have good chemical stability and be resistant to oxidation
- not form stable emulsions with the aqueous phase
- have high solubility in aliphatic and aromatic diluents
- be non-flammable (high flash point) and non-volatile (low evaporative losses)
- have low toxicity
- have reasonable cost (and be preferably available from more than one supplier)

... in addition to the process requirements such as having:

- the required metal selectivity
- high loading capacity
- fast loading and stripping kinetics

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Solvent extraction in Hydrometallurgy

Requirements for the organic phase

The diluent should:

- provide the solvency for the extractant, the modifier, and the extracted metal species
- have very low solubility in the aqueous phase
- have good chemical stability and be resistant to oxidation
- not form stable emulsions with the aqueous phase
- have high flash point and low volatility
- low viscosity and low specific gravity
- low toxicity (and smell)
- non-corrosive
- low cost and readily available (at the plant location)

The organic modifier should also:

- improve the phase-separation and/or the solubility of the metal-extractant complex

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Solvent extraction in Hydrometallurgy

Requirements for the organic phase

A modifier can improve the solubility of the metal-extractant complex and prevent third-phase formation

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Solvent extraction in Hydrometallurgy
Classes of organic ligands

Extractants are normally divided into three different classes of ligands

Cationic extractants:
Type of exchange required: Simple cations or cationic complexes of metal ions (net charge > 0)
Examples: Cu(2+), Fe(3+), UO2(2+) etc.

Anionic extractants:
Type of exchange required: Anionic complexes of metal ions (net charge < 0)
Examples: CuCl3(2-), PdCl4(2-), FeCl4(-), PtCl6(2-), ReO4(-), WxOy(z-) etc.

Solvating extractants:
Type of exchange required: Neutral complexes of metal ions (net charge = 0)
Examples: HFeCl4, H2PtCl6, UO2SO4, H3AsO4 etc.

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Solvent extraction in Hydrometallurgy
Cation exchange

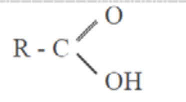
Solvent Extraction of Metals from Aqueous Solutions

Cation Exchange -- reaction and reagents

In its simplest form ... $Me^{n+} + n\,\overline{HR} \Leftrightarrow \overline{MeR_n} + nH^+$

With additional coordination $Me^{n+} + (n+s)\,\overline{HR} \Leftrightarrow \overline{MeR_n \cdot sHR} + nH^+$

- The extractant is an organic acid HR (reagent capable of exchanging H⁺)
- equilibrium reaction, pH dependent
- metal extraction usually requires some form of pH control
- metal stripping from the organic requires acid (H⁺)



carboxylic acid; R is alkyl group, e.g., C_nH_{2n+1}

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Solvent extraction in Hydrometallurgy
Anion exchange

Solvent Extraction of Metals from Aqueous Solutions

Anion Exchange (ion-pair formation) - reaction and reagents

Acid extraction: $\overline{R_3N} + HX \Leftrightarrow \overline{R_3NH^+ \cdot X^-}$

Metal extraction: $(m-n)\overline{R_3NH^+ \cdot X^-} + MeX_m^{(m-n)-} \Leftrightarrow \overline{(R_3NH^+)_{m-n} \cdot MeX_m^{(m-n)-}} + (m-n)X^-$

Metal complexation (anionic complexes formation):

$$Me^{n+} + mX^- \Leftrightarrow MeX_m^{(m-n)-}$$

where HX is an inorganic acid, such as HCl

- The extractant is an organic base (capable of extracting acid to form an amine salt and then of exchanging anionic species)
- equilibrium reaction
- the reaction is acid (HX) <u>and</u> X^- ion dependent *(all three reactions interdependent)*
- *Example:*
  $R_3N_{org} + HCl \Leftrightarrow R_3NH^+Cl^-_{org}$ $2R_3NH^+Cl^-_{org} + CoCl_4^{2-} \Leftrightarrow (R_3NH^+)_2CoCl_4^{2-}{}_{org} + 2Cl^-$

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Solvent extraction in Hydrometallurgy
Advantages and disadvantages

Metal Solvent Extraction and Ion-Exchange

Advantages

(i) Very pure and concentrated metal solutions can be produced by both SX and IX

(ii) The organic phase, or the resin, is regenerated and repeatedly used

(iii) Ability to recover trace amounts of metals (IX) in concentrated form

(iv) Generally operate at, or close to, ambient temperatures

(v) Continuous processes, can be readily automated

Limitations

i) SX: the organic solvents (diluents, modifiers, extractants) are flammable liquids

ii) SX: some solvents are toxic; all have certain (although very low) solibility in aqueous solutions

iii) as organic compounds, most extractants, diluents, and resins, are prone to oxidation

iv) the aqueous solution must be free of solids

v) limits for the feed concentration of target metal(s), particularly for IX (low intensity mass-transfer)

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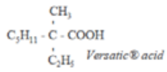
Solvent extraction in Hydrometallurgy
Cation-exchange extractants

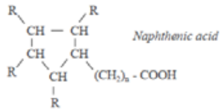
Solvent Extraction of Metals from Aqueous Solutions

Cation-exchange extractants

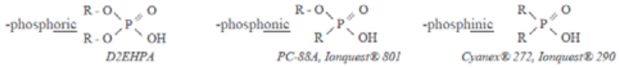
Acid extractants -- examples:

- Carboxylic acids



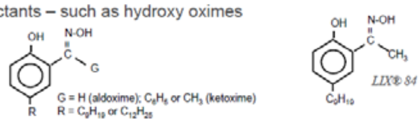


- Organophosphorus acids



- Thio-substituted organophosphorus acids

Chelating extractants – such as hydroxy oximes (LIX®, Acorga®)



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Solvent extraction in Hydrometallurgy
Anion-exchange extractants

Solvent Extraction of Metals from Aqueous Solutions

Anion-exchange extractants -- organic amines

- **Primary amines** $R-NH_2$
- **Secondary amines** R_2NH (e.g., R is $CH_3(CH_2)_{12}-$)
- **Tertiary amines** R_3N (e.g., R is $CH_3(CH_2)_7-$ or $CH_3-CH(CH_3)-(CH_2)_5-$)
  Tri-iso-octyl amine (Alamine® 308); tri-n-octyl / decyl amine (Alamine® 336)
- **Quaternary amines** $R_3N^+-CH_3Cl^-$ (e.g., R is $CH_3(CH_2)_9-$)

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Solvent extraction in Hydrometallurgy
Solvating extractants

Solvent Extraction of Metals from Aqueous Solutions

Solvating extractants

- Organophosphoric esters $(RO)_3$ P=O **(e.g., TBP $(C_4H_9O)_3P=O$, tri-butyl phosphate)**
- Phosphine oxides R_3 P=O **(e.g., TOPO $(C_8H_{17})_3P=O$, tri-octyl phosphine oxide)**
- Phosphine sulfides R_3 P=S **(e.g., Cyanex® 471 $(CH_3\text{-}CH(CH_3)\text{-}CH_2)_3P=S$, tri iso-butyl phosphine sulfide)**
- Ketones R-CO-R' **(e.g., MIBK $CH_3\text{-}CO\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$, methyl iso-butyl ketone)**
- Ethers R-O-R' **(e.g., DBC $CH_3\text{-}(CH_2)_3\text{-}O\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_3\text{-}CH_3$, dibutyl carbitol)**

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Solvent extraction in Hydrometallurgy
Presentation of experimental data

Equilibrium constant K: KMe

Example rx. cation exchanger: Me(n+) + nHR(org) = MeRn(org) + nH(+)

KMe = ([MeRn(org)] x [H(+)]^n) / ([M2(n+)] x [HR(org)]^n), assume act.coeffs ~ 1

Distribution coefficient D: DMe = [Me(org)] / [Me(aq)]

%-extracted: Percent of initial metal content in aq.feed solution transferred into the organic phase
(Assume data produced in experiments with O/A-ratio = 1/1 & single metal salt solutions with low concentrations of the metal of interest.)

Selectivity coefficient S: example S(Co-Ni) = DCo / DNi

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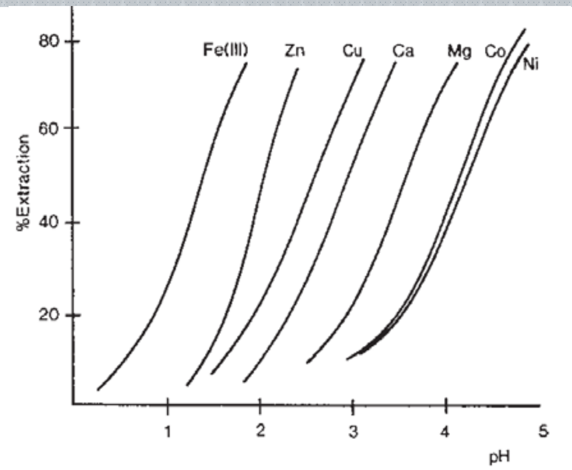
Solvent extraction in Hydrometallurgy
Example 1: D2EHPA in SO4-media



Extraction of metals from sulfate media by DEHPA.

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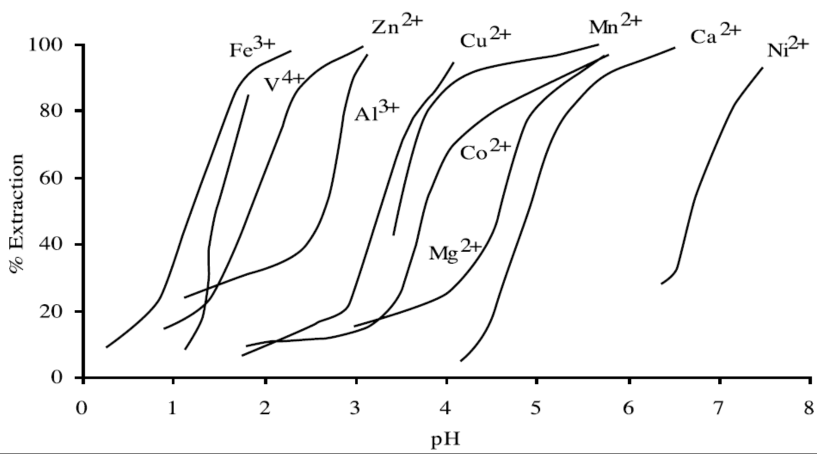
Solvent extraction in Hydrometallurgy
Example 2: Cyanex 272 in SO4-media

- Extraction of Metals by CYANEX 272 Extractant from Sulfate Solutions



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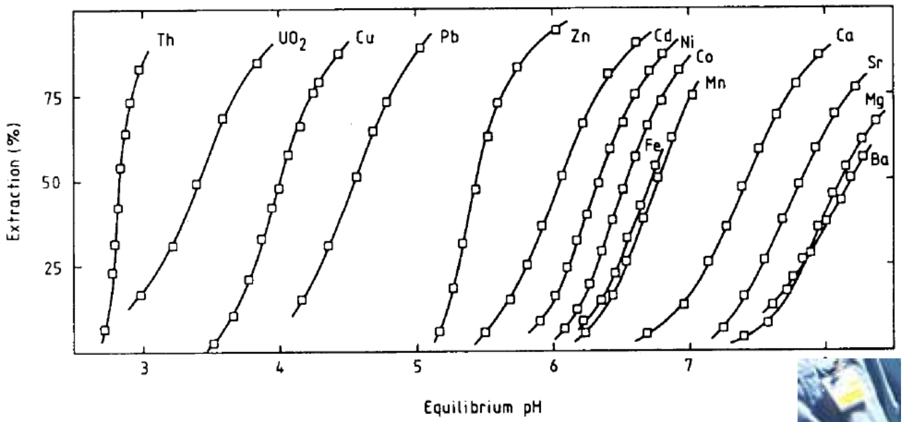
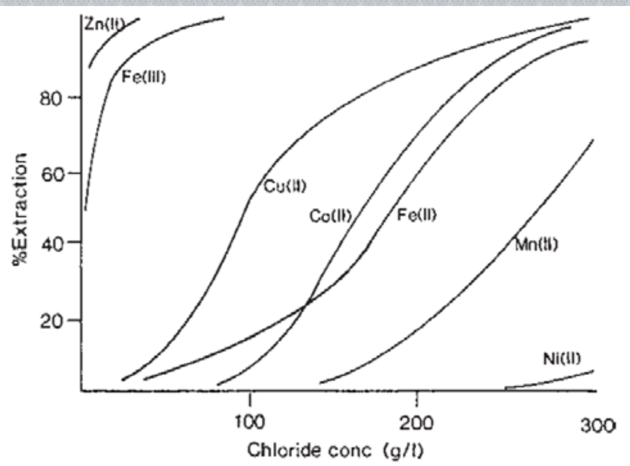
Solvent extraction in Hydrometallurgy
Example 3: Versatic 10 in SO4-media



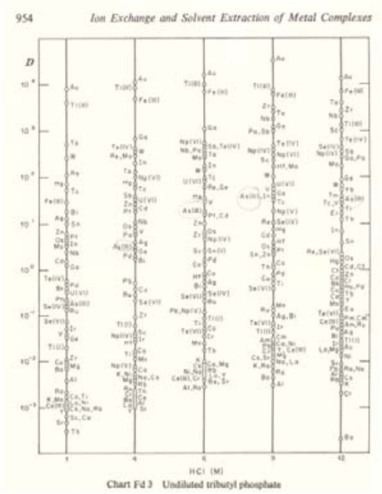
Preston, J.S., Solvent Extraction of Metals by Carboxylic Acids, *Hydrometallurgy*, 1985, 14

Solvent extraction in Hydrometallurgy
Example 4: Tertiary amines in Cl-media



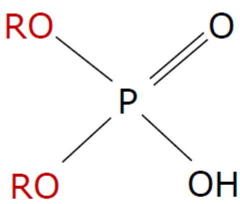
Extraction of metal chlorocomplexes by amines.

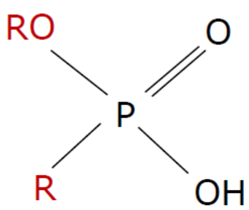
Solvent extraction in Hydrometallurgy
Example 5: TBP in Cl-media

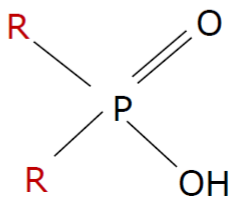


Fra Markus og Kertes:
Ion Exchange and Solvent Extraction of Metal complexes (1969),
D-coeffs in TBP (100%) in HCl-media, 1-12 mol/l HCl, logaritmic scale (0.001 – 10 000)

Solvent extraction in Hydrometallurgy
Example 6: Development of Co-extractants

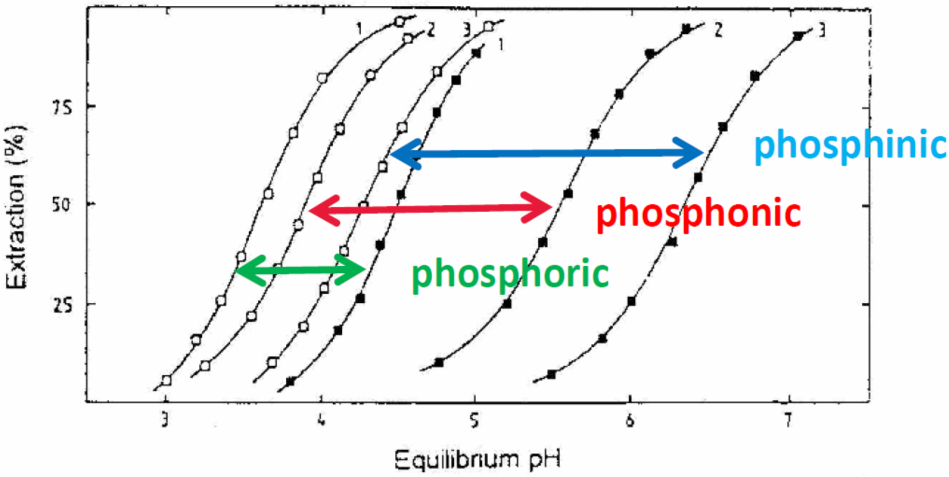






Phosphoric	phosphonic	phosphinic
D2EHPA	Ionquest801 PC-88A P507	CYANEX 272 Ionquest 290 LIX 272

Solvent extraction in Hydrometallurgy
Example 6: continued...



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Solvent extraction in Hydrometallurgy
Example 6: continued...

Development of separation coefficient S(Co-Ni)

		Co:Ni
D2EHPA	RBMR, South Africa	**10**
PC-88A	Nippon Mining, Japan	**300**
P507	Jinguan Nickel, China	**300**
CYANEX 272	40% of world Co	**7000**

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Solvent extraction in Hydrometallurgy
Description of the complete SX-process

Extraction, Scrubbing and Stripping

Extraction

- Unhindered extraction of one or more metals (extractant available for all)
- Metal-metal displacements – i.e., a more strongly extracted metal can displace a more weakly extracted metal(s) – leading to an improved overall selectivity
- Presence of a 'buffer' metal with medium extractability can enhance the separation of a metal pair (M1 > M(b) > M2 – the extraction of M(b) will suppress the extraction of the least extractable M2) – e.g., Mg plays this role for enhancing Co/Ni selectivity with Cyanex® 272

Scrubbing

- Metal-loaded organic phase is contacted with an aqueous solution of a preferentially extractable metal so that it will displace less extractable metals from the loaded organic – e.g., contacting Co/Ni loaded organic with Co solution to displace Ni (e.g., with Cyanex® 272)
- Washing vs scrubbing

Stripping

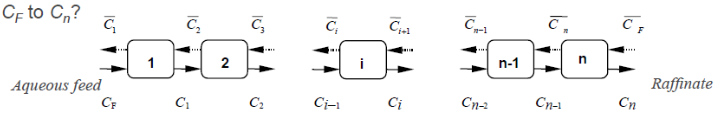
- Metal-loaded organic phase is contacted with strip aqueous solution to transfer the extracted metals into that aqueous solution

Regeneration: Remove minors accumulating, regenerate extractant molecule

Solvent extraction in Hydrometallurgy
Equilibrium isotherms, McCabe-Thiele

Metal Isotherms, Operating Line and McCabe/Thiele diagrams

How many stages are needed to decrease the metal concentration in the aqueous from C_F to C_n?



The extraction (or stripping) **isotherm** represents in graphical format (a numerical equation can be "fitted") the changes in the metal distribution coefficient over a wide range of metal concentrations in the aqueous and the organic phases, for constant other conditions (e.g., temperature, pH, total extractant (&modifier), counter-ion, etc., concentrations).

The **operating line** reflects the mass-balance for the extraction circuit (a straight line with a slope equal to the A/O ratio: V_{aq}/V_{org}):

$$\overline{C}_1 = \overline{C}_F + \frac{V}{\overline{V}}(C_F - C_n)$$

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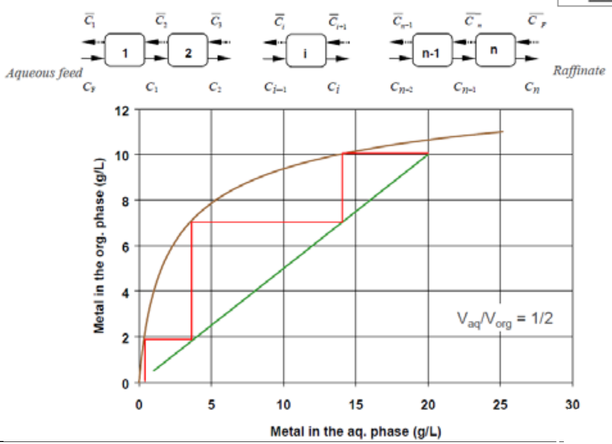
Solvent extraction in Hydrometallurgy
McCabe-Thiele method, the ideal case

The McCabe-Thiele diagrams: the **ideal** case

Metal Isotherms, Operating Line and McCabe/Thiele



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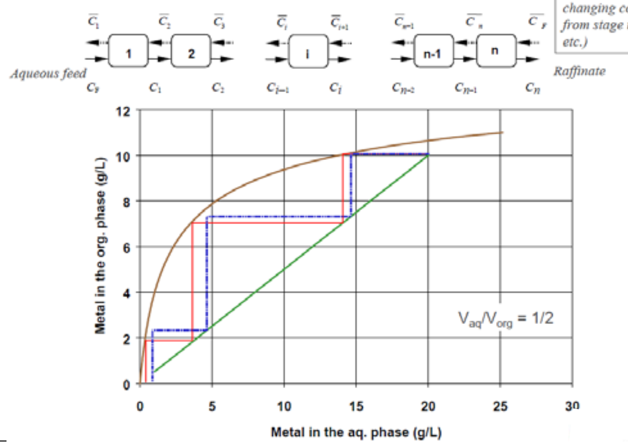
Solvent extraction in Hydrometallurgy
McCabe-Thiele method, the real case

The McCabe-Thiele diagrams: the **real** case *(stage efficiency, changing conditions from stage to stage, etc.)*

Metal Isotherms, Operating Line and McCabe/Thiele



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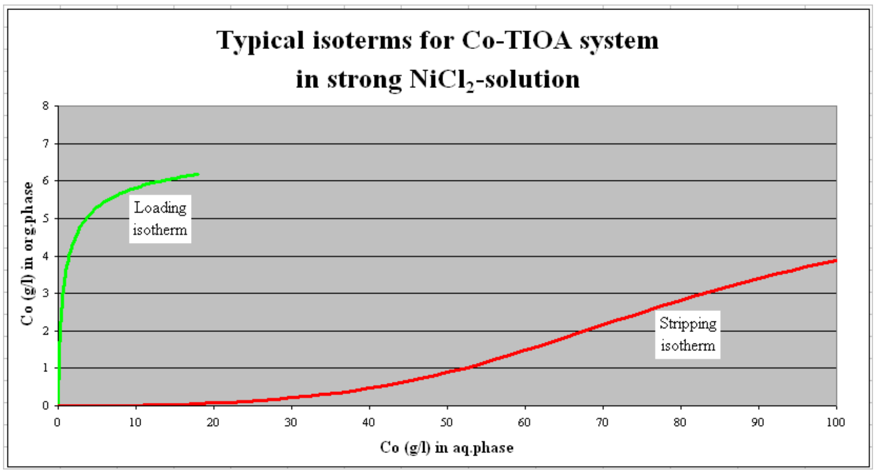
Solvent extraction in Hydrometallurgy

Loading and stripping isotherms for Nikkelverk Co-SX



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Solvent extraction in Hydrometallurgy

Equipment for SX-processes in HM

Solvent Extraction Contacting Equipment

- All current Ni/Co SX operations use mixer-settlers of the same types as in copper SX
- Advantages: relatively simple to operate and recover from upset conditions; easier for crud removal; able to handle large (e.g., 1,000 m^3/h and higher) aqueous feed flows (more than one mixer per M/S); suitable for systems requiring longer residence time; easier process control; "easier to comprehend"
- Limitations: one stage per M/S; capital intensive; require large footprint and extensive piping; combined pumping and mixing functions of the mixer impeller, often leading to overmixing; relatively difficult phase-continuity control; internal phase recycle may be required to maintain O/A~1 in the mixer; difficult to seal (when needed)
- High-rate units are often used to reduce footprint and organic inventory, and improve maintenability
- Three prominent designs -- from Technip (Krebs), Bateman and Outotec
- Over the last ~10 years, Bateman Solvent Extraction (Israel) has been the leader in developing and implementing pulsed columns technology for large scale hydrometallurgical applications (Uranium SX at Olympic Dam, Goro Nickel and others).

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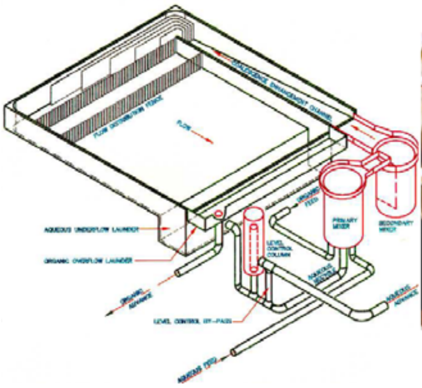
Solvent extraction in Hydrometallurgy
Equipment: Bateman reverse flow M-S

Contacting Equipment – Bateman RFMS

- The Reverse Flow Mixer Settler (RFMS) offers improved separation through the use of the coalescence enhancement channel and the turning vanes; linear flowrates of both phases is maintained the same and without sudden changes in flow direction to minimize turbulence

BATEMAN SETTLER™
BATEMAN U.S. PATENT NO. 5558780



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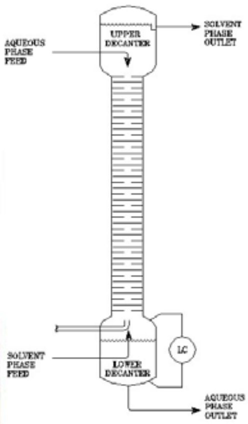
Solvent extraction in Hydrometallurgy
Equipment: Bateman pulse column

Contacting Equipment – Bateman Pulsed Columns

- Disc/donut pulsed columns with no internal moving parts has been used in the nuclear industry (i.e., in France)
- Bateman has successfully developed further and implemented the technology to the large scale hydrometallurgical refining (extraction columns at Olympic Dam for Uranium SX)



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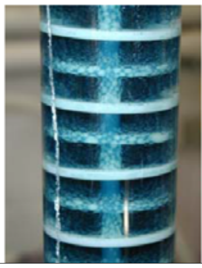
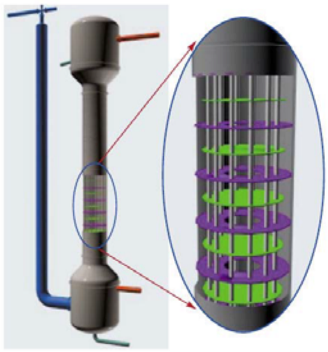
Solvent extraction in Hydrometallurgy
Equipment: More on Bateman pulse column

Contacting Equipment – Bateman Pulsed Columns

- Energy for mixing provided by compressed air via an external leg; usually, constant frequency, variable amplitude
- Maintaining dispersed phase hold-up is a key parameter to ensure residence time requirements
- Organic/liquid interface controlled in upper (for aqueous-continuous) or lower (for organic-continuous) decanter





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Solvent extraction in Hydrometallurgy
Equipment: More on Bateman pulse column

Contacting Equipment – Bateman Pulsed Columns for Goro Nickel

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Solvent extraction in Hydrometallurgy
Application of SX: Development stages

Solvent Extraction Process Development

Objective?	
Literature & contacts	metal solution chemistry, extractant/diluent selection; focus on potential fatal flaws
Bench scale tests (synthetic or actual solution)	extraction equilibria and kinetics; phase-separation; solubility/TOC in aqueous; identify # of stages and key process parameters
Continuous tests	Confirm bench scale results; confirm circuit configuration; phase-continuity; means of control; crud
Mini-plant integrated	Confirm with more realistic process solution; crud, silica, other surprises; organic stability; circuit operability and control
Pilot plant	Operate with real solution; process control and ability to handle upsets; organic stability, organic loss and removal from aqueous streams, cross-contamination, VOC control, accumulation of impurities; crud (and silica) handling
Comm Plant design	

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Solvent extraction in Hydrometallurgy
SX in Ni-Co industry

Solvent Extraction for Ni/Co Purification

There are three important nickel solution media:

Chloride from Cl_2 and/or HCl leaching of Ni matte or intermediates

- Kristiansand, Le Havre, Niihama, Hoboken Refineries
  +Norilsk Monchegorsk (Russia) and VALE Goro (New Caledonia)

Ammoniacal, NH_3-$(NH_4)_2CO_3$, from leaching of roast reduced laterites

- Yabulu, Tocantins, Punta Gorda, Cawse (Ni/Co ppte)

Sulphate from oxidative or H_2SO_4 leaching of sulphide concentrates, mattes, precipitates or laterite ores.

- Harjavalta, Rustenberg, Bulong, Minara (Murrin-Murrin)
  +VALE Long Harbour (Canada), Goro and Sherritt Ambatovy (Madagaskar)

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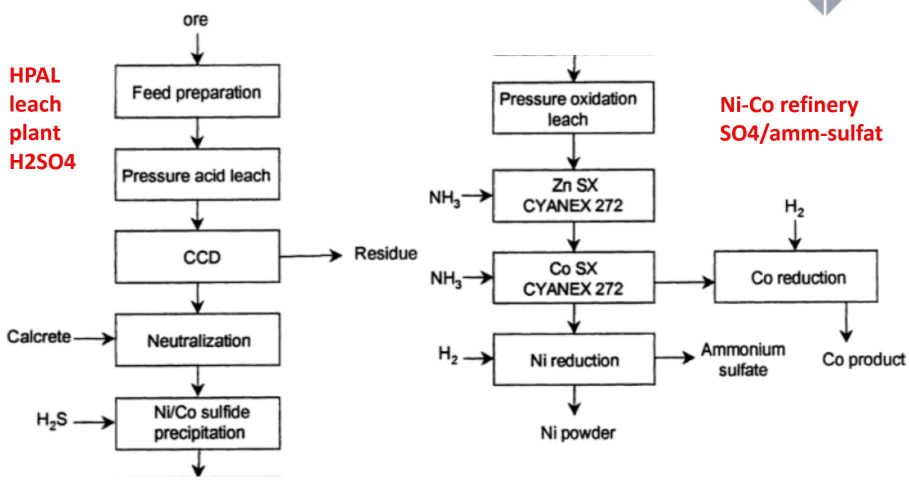
Solvent extraction in Hydrometallurgy

"Murrin Murrin": 45 000 T/a Ni HPAL Laterite operations



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Solvent extraction in Hydrometallurgy

Glecore "Murrin Murrin" operations, Australia

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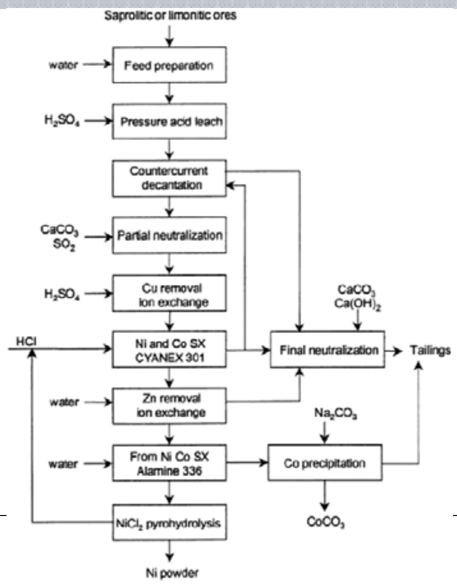
Solvent extraction in Hydrometallurgy

VALE Goro: 50 000 T/a Ni laterite HPAL with Cl-based refinery



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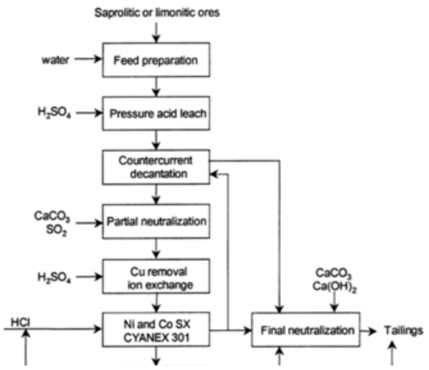
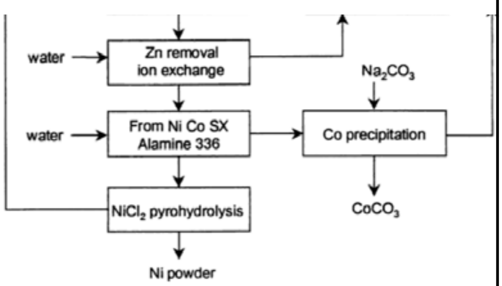
Solvent extraction in Hydrometallurgy

VALE Goro: Flowsheet

HPAL leach plant H2SO4



Ni-Co refinery Cl/HCl



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Solvent extraction in Hydrometallurgy

VALE Goro operations in New Caledonia

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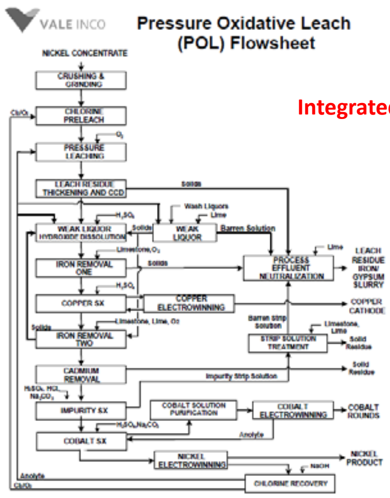
Solvent extraction in Hydrometallurgy

VALE Long Harbour: 50 000 T/a Ni S-concentrate leach-SX-EW



Integrated SO4/Cl circuit

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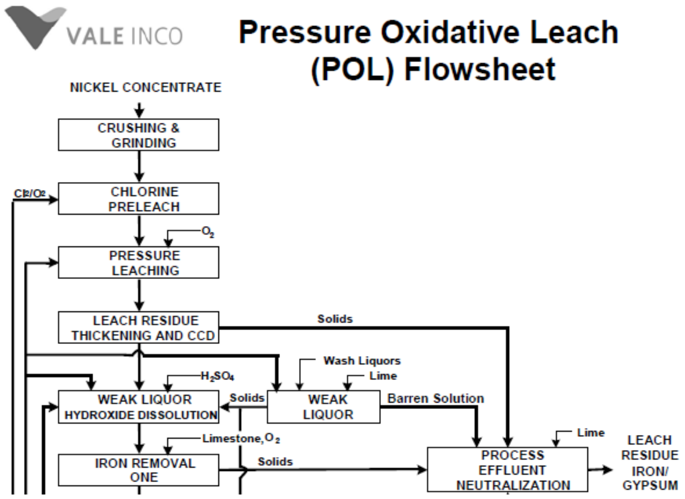
Solvent extraction in Hydrometallurgy

VALE Long Harbour: Flowsheet first part



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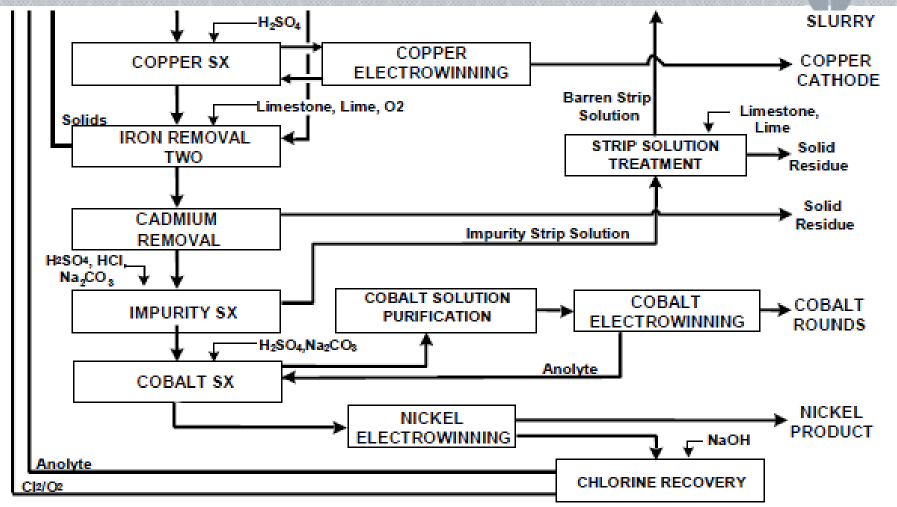
Solvent extraction in Hydrometallurgy

VALE Long Harbour: flowsheet second part



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Solvent extraction in Hydrometallurgy

VALE Long Harbour operations in New Foundland, Canada

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Solvent extraction in Hydrometallurgy

Queensland Nickel: 32 000 T/a Ni Caron plant (NH3) with Ni-SX

Integrated NH3/(NH4)2CO3 circuit

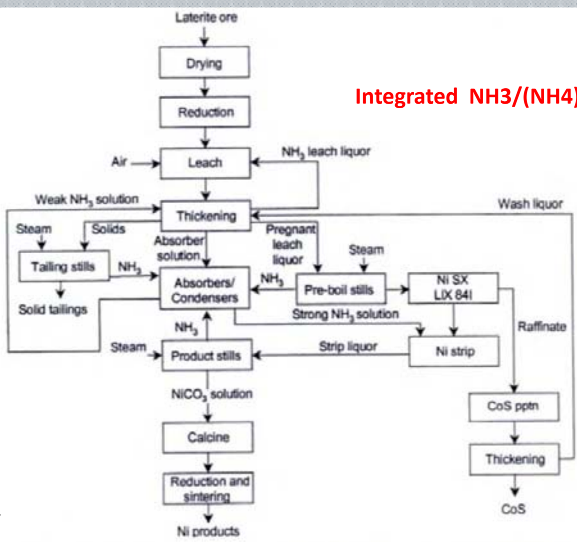

Figure 10 Flow sheet of the Queensland Nickel Industries' process. (From Ref. 53.)

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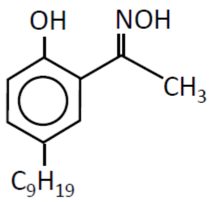
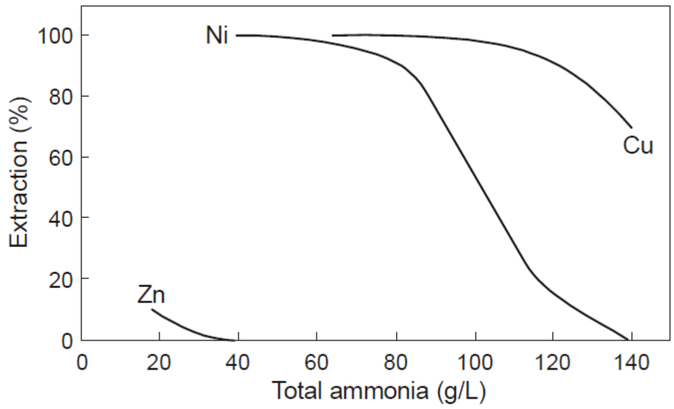
Solvent extraction in Hydrometallurgy
Eq. Isotherm for extractant LIX87QN



LIX 84-I



Queensland Nickel use a slightly modified LIX 84-I for its Ni-SX, named LIX87QN

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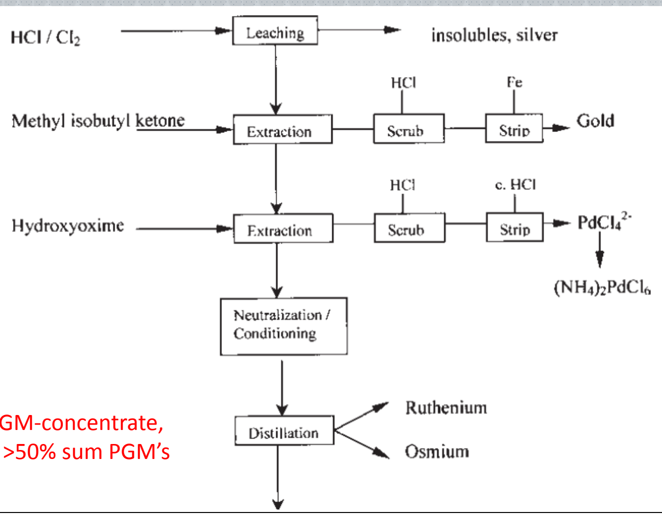
Solvent extraction in Hydrometallurgy

Anglo Platinum: ~2 mill oz/a Pt-refinery at Rustenburg, S.Africa
First part



Feed: PGM-concentrate,
Usually >50% sum PGM's

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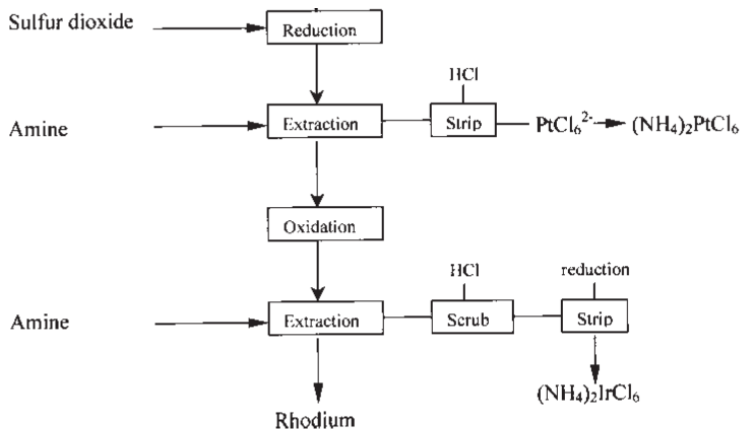
Solvent extraction in Hydrometallurgy

Anglo Platinum: ~2 mill oz/a Pt-refinery at Rustenburg, S.Africa
Second part



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Solvent extraction in Hydrometallurgy
Application in some key industries

Solvent extraction in the mining industry is a mature technology

Metal	Global market primary metal	% using SX
Cu	20 mill T/a	20%
Co	100 000 T/a	50%
U	50 000 T/a	80%

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