특별강연

HYDROMETALLURGICAL RECYCLING OF INDUSTRIAL WASTES: ROLE OF SOLVENT EXTRACTION IN THE SEPARATION AND RECOVERY OF METALS

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Why Do We Need to Recycle Waste ....?

Industrialization has improved the man's life easy , exciting ...... in many ways

At the same time, industrialization bound to generate lot of wastes at the processing stages/ after use of materials ......

In recent years, Protection of Environment is considered to be important for the industry

Environmental Legislation that controls all types of emissions as well as treatment of wastes

Legislations are based on Global Standards prepared by EU, US, Japan in collaboration with International Conventions

Basal Convention 1989, Earth Summit in Rio in 1992 were significant in the control & Prevention of Wastes

General trend is to reduce the discharge limits/ reprocess the wastes / increase the life of materials ... etc

Ultimate aim is to achieve " *The Concept of zero Industrial discharge*" in future

What are the types of Wastes ?

Solid wastes **– Solid Residues from the processing of Primary Minerals such as Flotation, Leach Residues , Land fills ..., Spent Catalysts, Spent Batteries, Electrolytic (Ni, Cd, Li, Pb), Combustion Ashes etc.....**

Liquid Wastes **– Acid Mine Waters, Tanning (Cr), Photographic (Ag), rayon Industry (Zn), galvanizing, Etching industry .....**

Gaseous Wastes **– Chemical / Metallurgical Industries, Mercaptans, SO_2 , CO, CO_2 emissions etc ...**

To days lecture, **I restrict my talk on treatment and recovery / recycle of solid & liquid wastes from metallurgical industries**

Particular reference **to Applications of SX technique to some**

Industrial a wastes with some examples –
Plating, pickling, etching.....
Scrap metal, Alloy wastes, Spent automobile, Spent catalyst, Spent batteries ...

SX technique **is efficient, highly selective, easy to operate & versatile in terms of scale of operations**

What are the objectives to treat a waste ?

To remove metals effectively to produce a liquid stream capable of reuse or finally meeting regulations of discharge limits

To recover the metals for recycling within the plant or at appropriate purity for sale

To separate other impurities in the form for resale as by-products

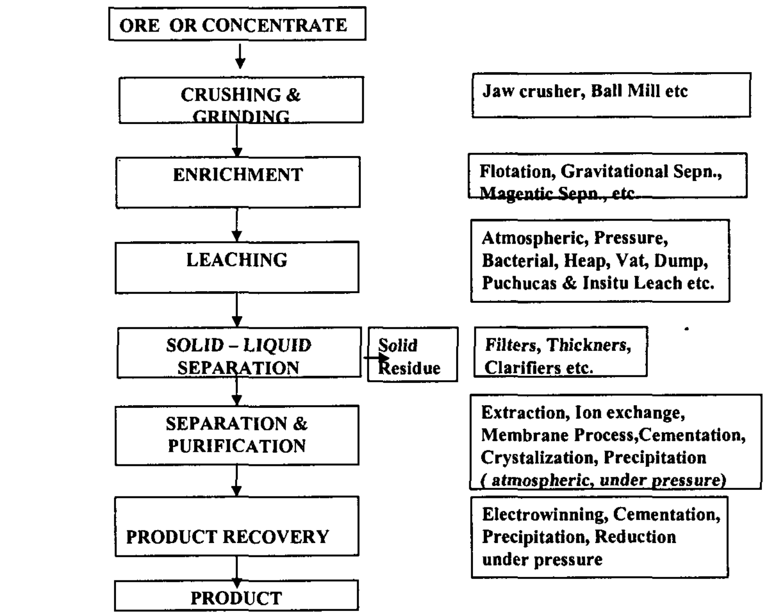
These principles are incorporated in the concepts of "Zero discharge & sustainable technology"

Hydrometallurgy means ....

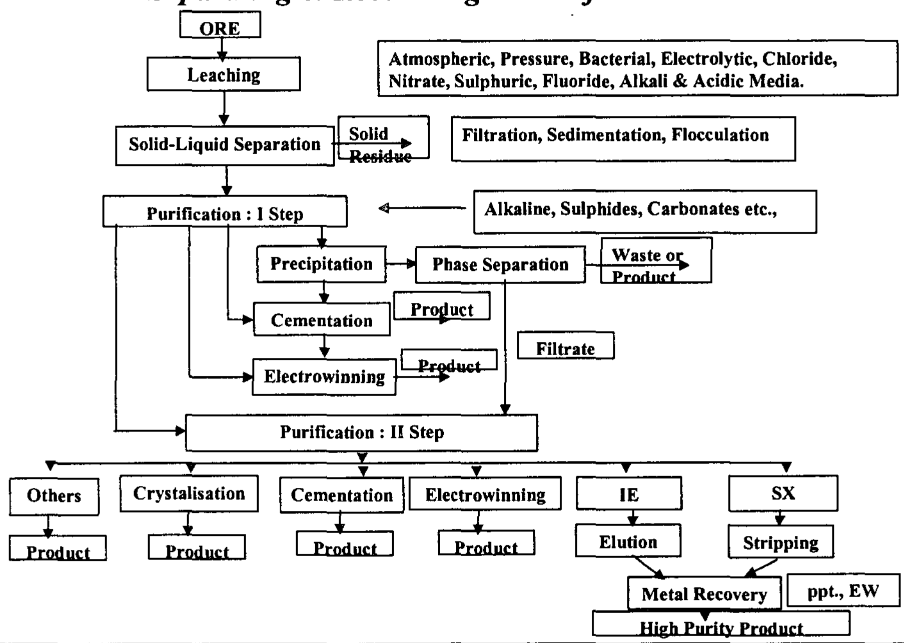
Hydrometallurgy deals with the processing of ores, concentrates and other metal- containing materials in ' *WET*' processes associated with the dissolution of some components

It represents an alternate way of processing of primary raw materials of unfavorable composition that can not be effectively processed by pyrometallurgical procedures or when such processing of primary resources is associated with significant difficulties

Block Diagram of Hydrometallurgical Process



Variants of Hydrometallurgical Processes with Various Ways of Separating & Recovering Metals from solution



What is Solvent Extraction (SX) ?

SX / or Liquid- Liquid extraction (LLE) refers to the distribution of a solute between two immiscible liquid phases in contact with each other

Distribution can be *Physical* or *Chemical* type

Physical- Extraction of simple, uncharged covalent molecules
Distribution is independent of Solute concentration & Phase Ratio
$D= (S)_{org}/(S)_{Aq}$
Depends on solubility of metal species in solvent phase.
Examples- Halides of Sb(III), Hg(II), As (III)

Chemical – Chemical reaction between metal species in the aqueous phase and components of organic phase
Examples- Cu- Oxime, Ni, Co- P based extractants

Historical Developments of SX

1900-1940 : Organic Chemists for Separation of organic substances

1900-1940: Reactive reaction with organic acids (HA) giving color

- Analytical chemists as tool for analysis of metals by colorimetry

1940-1950 – First application for U production by ether in USA (>99.9% pure, 1942)

- Explosion, development of alternate MIBK, TBP, TOA extractants

1950-early 1960 – Chemical & Metallurgical industry

Ex: Low grade Copper ore leaching- Oxime based LIX reagents

- Today ~ 30% Copper Produced in World Annually
- Entire Rare Earth metals are produced by SX technique

Applications & Uses of SX

Chemical Industries – To produce pure compounds
Pharmaceuticals ; Biomedicals
Metals – in Metallurgy
Waste Streams purification - Environmental

To understand metal transfer, classify the systems into

A. Systems involving compound formation:

1. Chelating extractants:
   $M^{n+} + n\,HA = MA_n + nH^+$
2. Acidic Extractants:
   $M^{n+} + m\,HA = MA_n + nH^+$ or
   $M^{n+} + m/2\,H_2A_2 = (MA_n.(m-n)HA) + nH^+$

B. Systems involving ion association

Mechanism of metal extraction:

$MA_n^{(m-n)-} + (m-n)(R_3N.HA) = (R_3N^+H)_{m-n}MA^{-m} + (m-n)A^-$

In these systems in order to complex a metal, first convert amine to salt to provide anion to exchange with the metal anion species

$R_3N + HX = R_3NH^+.X^-$

$R_3NH^+.X^- + MY^- = R_3NH^+.MY^- + X^-$

C. Systems Involving Solvation:

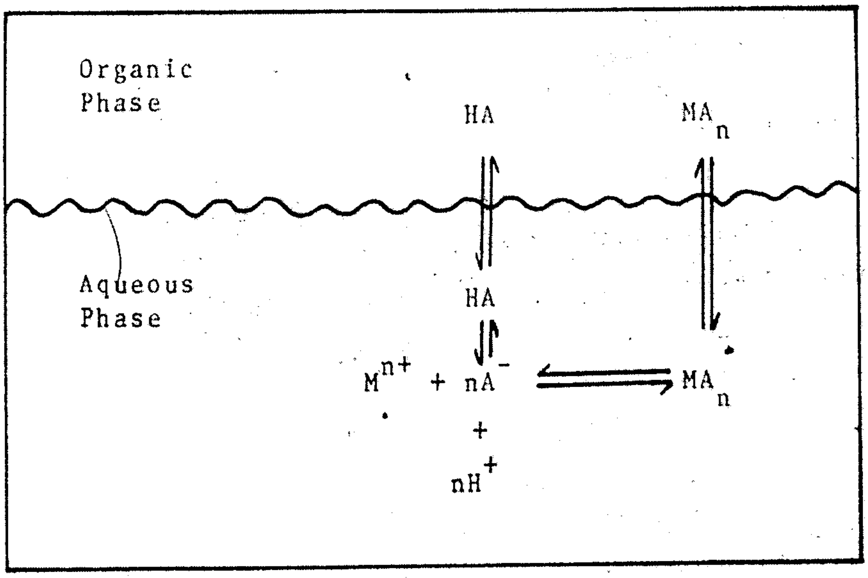
Oxygen bonded to Carbon such as Ethers (C-O-C), Esters (-COOR), Alcohols (C-OH), ketones (C=O)

Alkyl phosphonate esters (P=O)

Terms used in solvent extraction

Distribution Ratio, D
Percentage Extraction, E= 100 D/ (D+1)
$pH_{1/2}$ Extraction (50% extraction of metal)
Separation factor, β ($\beta = D_{M1}/D_{M2}$)
Kinetics of Extraction / Stripping
pH Isotherms
McCabe-Thiele Diagram
Counter- Current extraction / stripping
Raffinate & Loaded Organic Phase
Scrubbing
Stripping
Crud/ Third phase
Modifiers
Regeneration (Solvent Pre-Treatment)
Pregnant electrolyte (PE), Spent electrolyte (SE)

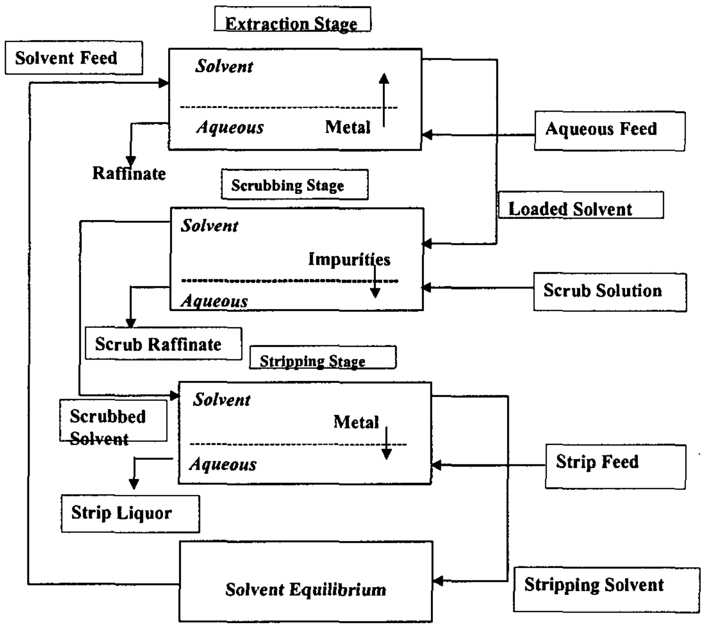
Metal transfer by Ion Exchange type Extractants



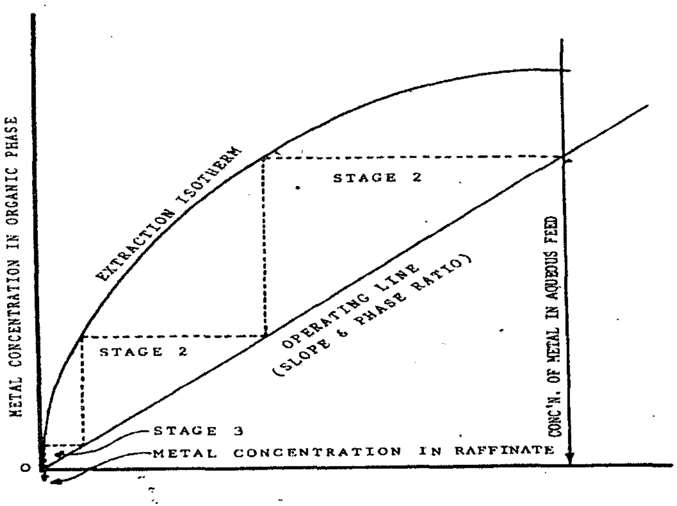
What are the requirements of an extractant ?

1. **Relatively inexpensive**
2. **Very low solubility in Aqueous Phase**
3. **Good Stability**
4. **Not to form stable emulsions with aqueous phase**
5. **Good coalescing properties when mixed with a diluent**
6. **High metal loading capacity**
7. **Easy stripping of loaded metal**
8. **Non-flammable, non-volatile, non-toxic**
9. **High solubility in aromatic & aromatic diluents**
10. **Good kinetics of extraction**

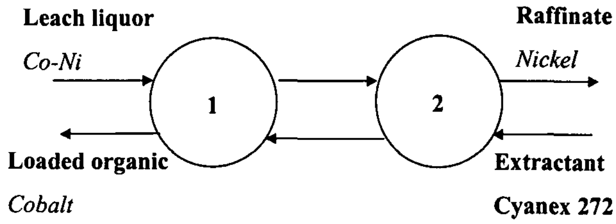
Basic Processing Steps in Solvent Extraction



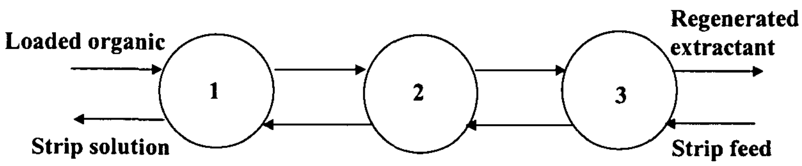
Extraction isotherm or McCabe- Thiele plot



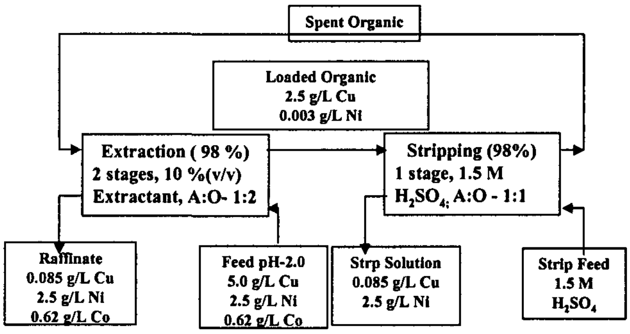
Two stage counter current simulation for metal extraction



3 stage C-C simulation for metal stripping from L.O



Recovery of copper from Copper Converter Slag Leach Liquors using MOC 45 Extractant



MOC 45 developed by ALLCO Chemicals

B.R. Reddy et al, Hydrometallurgy 57 (2000), 269-275

Hydrometallurgical Processing of Superalloy Scrap

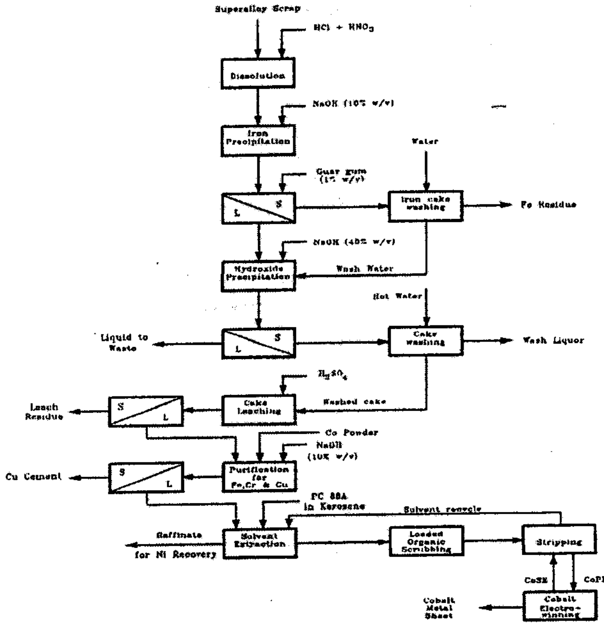
co10

A Case Study on Co recovery from Super Alloy Scrap

Sulfate Process

Rene 95: **Co-8, Ni-42, Fe-29, Cr-14 %, Ni/Co-5**

Inco-903: **Co-12, Ni-35, Fe-42%, Ni/Co-3**



Flowsheet for Solvent Extraction Separation of Cobalt (Pilot Plant)

LL composition:

31,000 liters processed

Co: ~10 g/L

Ni: ~ 33 g/L

Cu, Fe : < 1 ppm

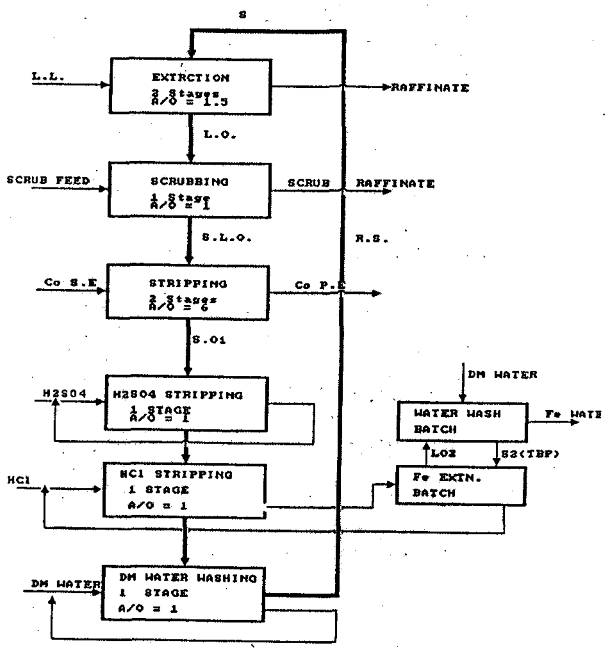
Zn: 100 ppm

pH: ` 4.4

1 M PC 88A 60 % neutralised

CoSE: ~40g/L Co, pH-1.3

CoPE: ~ 45 g/L Co, pH: 2



EW conditions & purity

CoSE: ` 40g/L Co, pH-1.3

CoPE: ~ 45 g/L Co, pH: 2

Cathode: SS

Anode: lead

Cell Temp.; ~ 60 °C

Current Efficienc :75-85%

Co produced:104 Kgs

Metal purity: 99.6 %

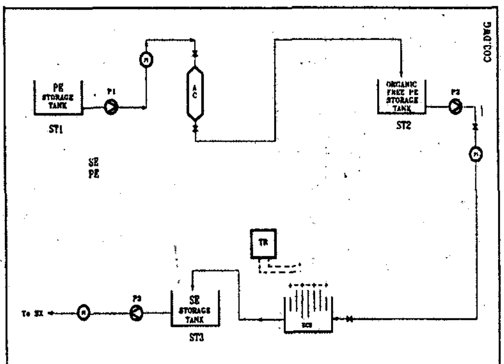


Fig.4.1 EFD FOR ELECTROWINNING OF COBALT

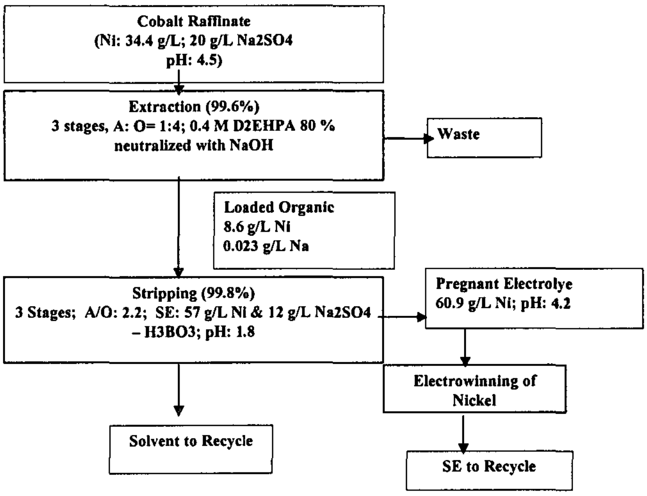
Status: Process commercialized; (Rubamin Industries, Baroda, India)

Production: 200 t/a Cobalt

Indian patent granted

B.R. Reddy, R.P. Das et al., SX-EW of Cobalt using PC 88A- A Case Study; Proc. Ni-Co 97, Int. Symp. 1997, Ontario, Canada, Vol.1, pp.263-272.

A Case Study on Recovery of Nickel as metal from Cobalt raffinate of Superalloy Scrap



B.R.Reddy & Sarma,
Hydrometallurgy 60 (2000) 123-128

Recovery of nickel from Solutions containing Ammonium Sulphate using PC 88A / LIX 84 I

Source Raw Materials : Superalloy Scrap, Coablt Sludge, Spent catalyst

LL Compn: 10-20 g/L Ni, Co, Fe, Cr & minor impurities

Fe, Cr, Al Removal by Lime pptn.

Cobalt: Na^{+}/ NH_4^{+} form of PC 88A/Cyanex 272

Co raff: Ni: 25.5 g/L; 18.1 g/L $(NH_4)_2SO_4$; pH: 5.0

50 % Ammonia Neutralised 1 M PC 88A as Extractant

Extraction: 3 stages; A:O= 1:2.2; 99.4 %

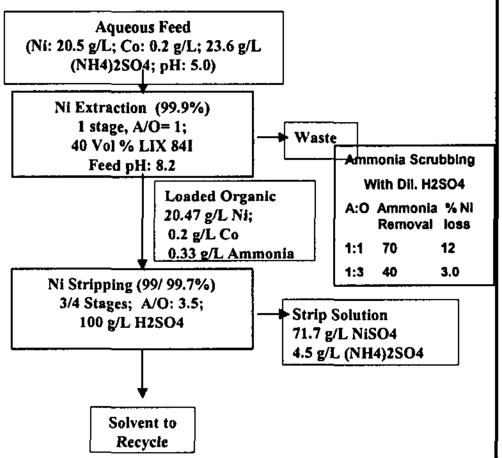
L.O: 11.5 g/L Ni; 1.37 g/L Ammonia

Scrubbing: 3 g/l H_2SO_4, 2 stages; A/O=1; 60 % ammonia removed; 1.8 % Ni loss

Stripping: 82 g/L H_2SO_4; 2 Stages; A:O= 1:5

99.98 % efficiency; SS: 55 g/L $NiSO_4$; pH= 3.0

B. R. Reddy et al., *Hydrometallurgy 53 (1999) 11-17*



B. R. Reddy et al., *Hydrometallurgy 49 (1998) 255-261*

A Case study on Co- Ni separation from spent batteries

Chloride Leach Liquor of Spent Ni- Cd Batteries
Cd-6.27 g/L; Ni- 21.56g/l; Co-0.14 g/L; pH- 1, Cyanex 272

Cobalt: Extraction, Scrubbing and Stripping data

Parameter	Equilibrium pH	Phase ratio	No.of. Stages	Efficiency, %	Ni, co-extraction, %
Extraction	5.70	1.5:1	3	99.8	0.4
Scrubbing	5.33	1:1	1	100	-
Stripping	1.60	2:1	2	100	-

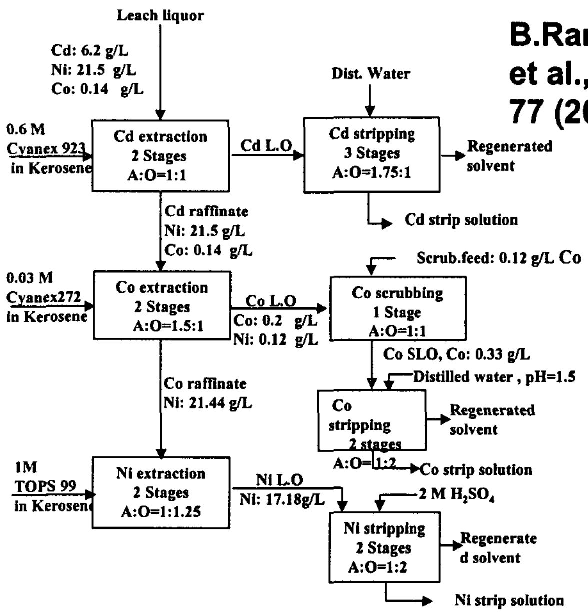
Nickel: Extraction and Stripping data

Parameter	Equilibrium pH	Phase ratio	No.of. Stages	Efficiency, %
Extraction	6.0	1:2.5	2	99.95
Stripping	2.11	1.1:1	2	99.95

Solvent extraction separation and recovery of Cd(II), Ni(II) and Co(II) from chloride leach liquors of spent Ni-Cd batteries using Cyanex 923 and Cyanex 272, *B. Ramachandra Reddy et al,*

Hydrometallurgy ,77, 2005, 253-261.

Flow sheet for separation of Cd, Co, Ni from spent batteries



B.Ramachandra Reddy et al., Hydrometallurgy 77 (2005) 253-261.

Processes for Zinc (and Cadmium)

Zinc extraction from Rayon manufacturing effluents *(Valberg process)*
Zinc extraction from used iron chloride pickling liquors *(MeS process)*

Processes for Copper

Copper extraction from an industrial waste water stream
Continuous on-line treatment of ammoniacal etch liquor and rinse water in the manufacturing of printed circuit boards for the electronics industry *(the MECER process)*
Copper recovery from wire scrap

Processes for Copper and Zinc

General hydrometallurgical concept for the recovery of copper and zinc from brass and steel mill flue dust (Sulphuric acid route- H-MAR process)

Processes for Copper, Zinc and Nickel

General hydrometallurgical concept for the recovery of copper, nickel and zinc from metal containing galvanic sludges and flue dusts *(Ammoniacal route – AmMAR concept)*
General pyro-hydro metallurgical concept for the treatment of metal containing slimes and flue dusts *(UddaMAR process)*

Processes for Nickel and Cadmium or Chromium

Recovery of Ni & Cd from accumulator scrap and production waste *(NIFE process)*
Ni & Cr extraction from plating baths -a mobile unit for bath cleaning operation

Processes for Cobalt and Nickel (Mo, W, V)

Recovery of Co & Ni from scrap alloy, using solvent extraction *(Gullspang process)*
Recovery of Co, Ni, Mo and/or W from super alloy grindings
Recovery of Co, Ni, Mo and V from spent catalysts
Processes for Vanadium (Ti)
Recovery of V from flue ash (soot) emanating from oil burned power stations (SOTEX process)

STATUS:
Process development, design and engineering
Pilot plant test
Economical and technical evaluation
Process evaluation

Recovery of Zn & Fe from Pickling Liquors

Source: **Spent HCl pickling liquors from Galvanizing Industry**

Composition: **100-130 g/L Fe (as FeCl2) & 20-70 g/L Zn**

SX: **Zn as chloride complex with TBP**

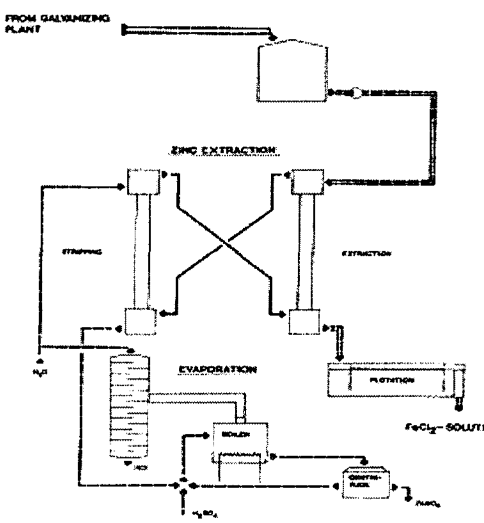
Stripping: **water / dil. HCl; 250 g/L Zinc chloride**

FeCl2 **– Pyrolysis to produce product as flocculation chemical used in sewage water treatment**

PP **operated in Sweden, Germany, Holland, technically practicable, well proven**

Important: **economics strongly depend on cost for deposit of spent pickling liquors**

THE MeS PROCESS



Recovery of Zinc from weak Acid Effluents

(ZINCEX PROCESS)

Source: Rayon Industry Rinse Water & other Zn containing Effluents

Compn: 0.1-1.0 g/L Zn; pH: 1.5-2.0

Extraction: 25 Vol% DEHPA; 2/3 Stages; 95 % efficiency;

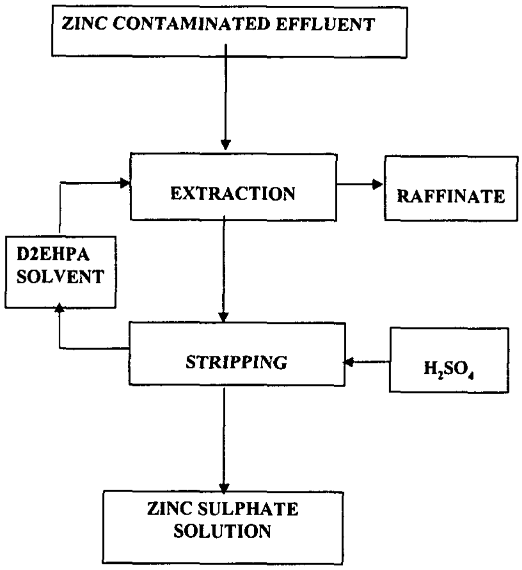
Eq. pH; 2

Stripping : Dil. H_2SO_4; SS: >50 g/L Zn SO_4

Use: Reused directly in the Spinning Bath

Application: Extraction of Zn & Cr from Electroplating bath waste Waters

Controls: SX without neutralisation results residual Zn, too high to meet environmental standards



Extraction of Cu & Zn from weak H_2SO_4 Leach Liquors

Cu: LIX 84; Zn: DEHPA

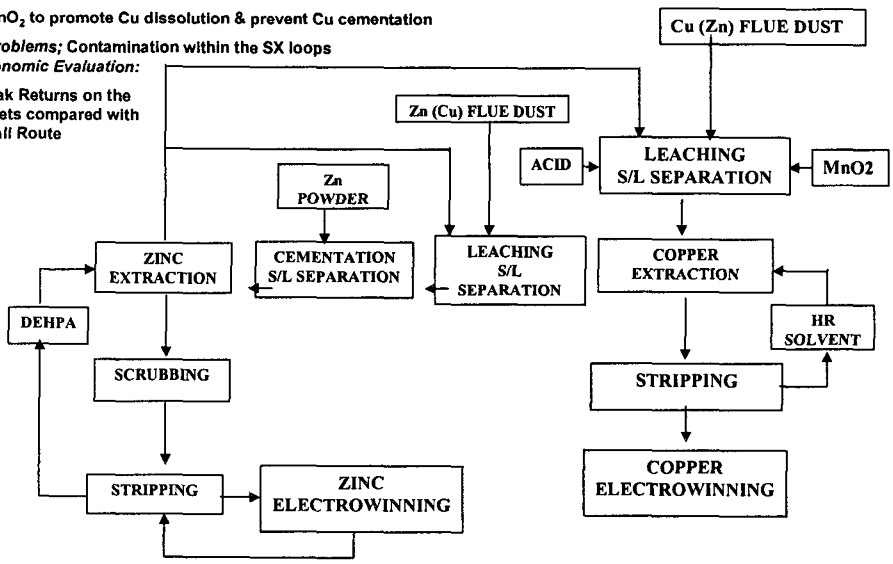
Status: Pilot Plant 10-20 Kg Zn per day

MnO_2 to promote Cu dissolution & prevent Cu cementation

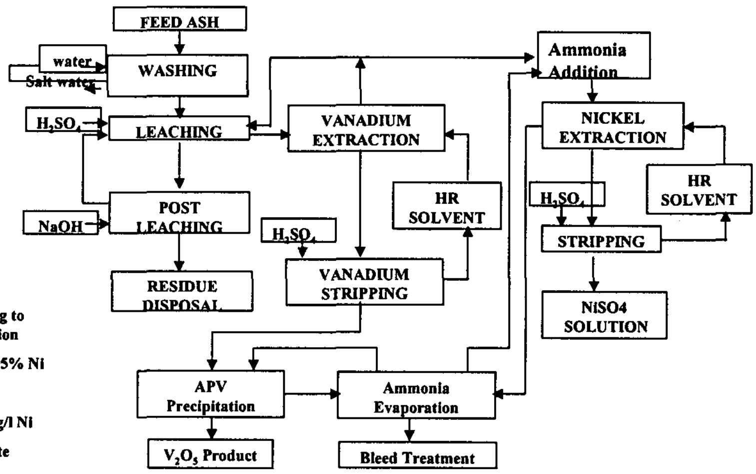
Problems; Contamination within the SX loops

Economic Evaluation:

Weak Returns on the assets compared with alkali Route



Extraction of V & Ni from Power Plant Soot & Flue Dust



Source: ash & Soot residues from Power stations

Washing: Remove Mg to avoid acid consumption

1 st leach:55% V^{4+}, 95% Ni

2 nd leach: V^{5+}

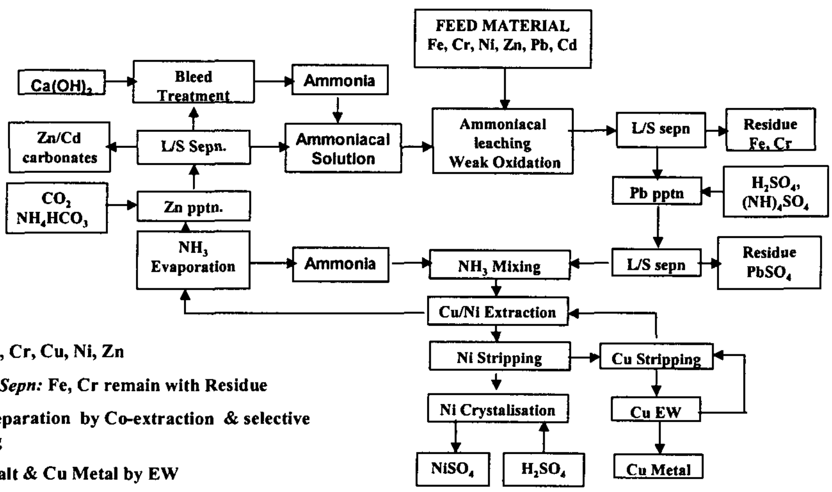
LL: ~25g/L V & ~12g/l Ni

Fe removed as jerosite

V extraction: DEHPA+TBP

Ni extraction; LIX 84

General Solvent Extraction Flowsheet from Ammoniacal Feed Solutions by AmMAR Concept



Feed: Fe, Cr, Cu, Ni, Zn

Primary Sepn: Fe, Cr remain with Residue

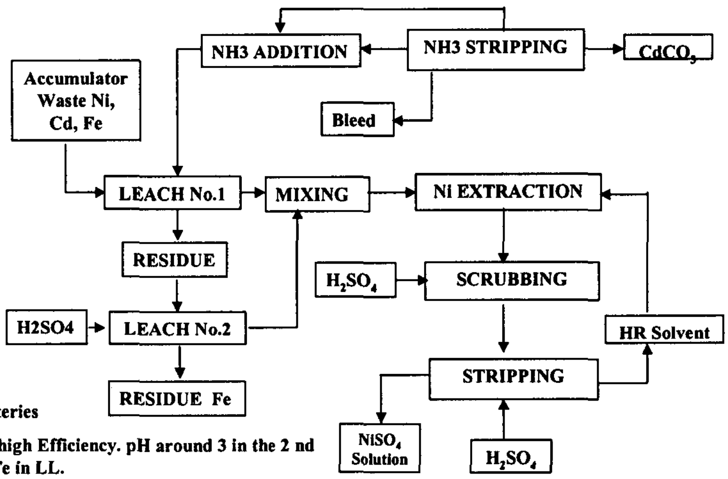
Cu, Ni separation by Co-extraction & selective stripping

NiSO4 Salt & Cu Metal by EW

Excess Ammonia is recovered by Evaporation to recycle o leaching circuit

Zn is recovered as Zinc carbonate

Recovery of Ni & Cd from Accumulator Scrap (NIFE process)



Source: Ni-Cd Spent batteries

Leaching: 2 stage to get high Efficiency. pH around 3 in the 2 nd leach results negligible Fe in LL.

Ni extraction: LIX 84

Product: 90-100 g/l $NiSO_4$ Solution to produce new accumulators

$CdCO_3$ precipitate directly used in the main production

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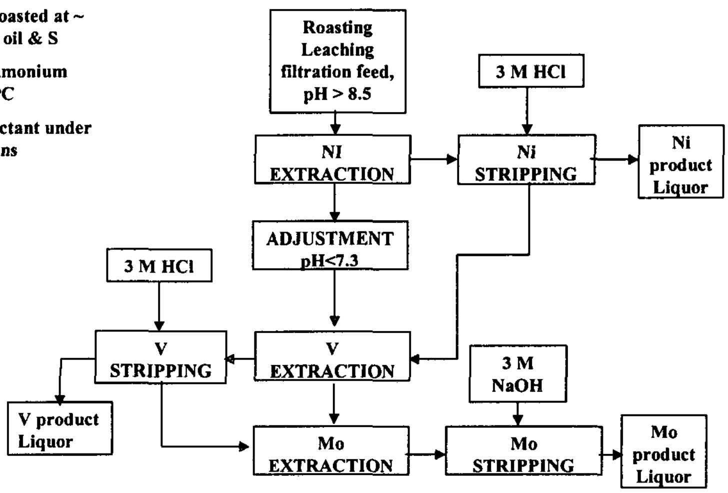
Recovery of Nickel, Vanadium and Molybdenum from Spent Desulphurisation Catalyst

Spent catalyst: Roasted at ~ 300 °C to remove oil & S

Dissolution in ammonium Carbonate at 80 °C

DEHPA as Extractant under *different conditions*



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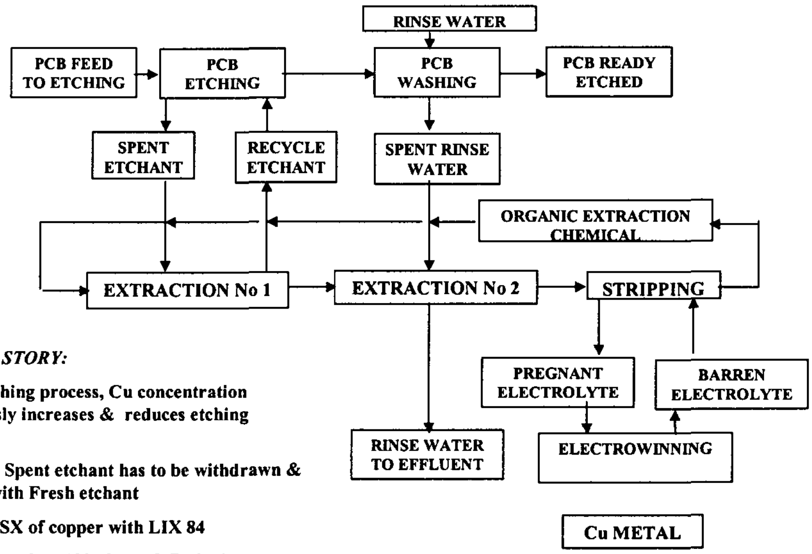
Recover of Copper and Recycle of Ammoniacal Etching liquors

(MECER Process)



SUCCESS STORY:

During etching process, Cu concentration continuously increases & reduces etching efficiency

Method 1: **Spent etchant has to be withdrawn & replaced with Fresh etchant**

Method 2: **SX of copper with LIX 84**

Status: **More than 100 plants & Reducing consumption of chemicals by 95%**

CONCLUSIONS :

Proposed HM methods of flowsheets are attractive, technically feasible

Most of the flowsheets are tried on pilot plant scale

But their commercial viability depends on many factors ....

- **Availability of wastes and their valuable metal contents**
- **Source of wastes, collection methods , its cost...**
- **Processing plant size and location**
- **Finally, fluctuating prices of end products**
- **Above all, needs financial support from the Governments/ production industries**

14.10.2005