

V). SEPARATION PROCESSES-SOLVENT EXTRACTION/ ION EXCHANGE FOR METAL IONS

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INTRODUCTION

In the hydrometallurgical processing of complex ores/ concentrates/ secondaries/ wastes, the solutions containing different non-ferrous metals are obtained during leaching the materials in acidic, ammoniacal or alkaline lixiviants. The spent solutions and effluents are also generated in different process industries and contain metallic values. Their discharge in the sewage or river is major concern for environment. In order to meet the strict environmental regulation and conserve the natural resources, metallic values are to be recovered. The leach solutions, spent solution and effluents are usually processed to recover metallic values following precipitation, solvent extraction, ion exchange, electrolysis, evaporation, crystallization, electro-dialysis etc. Solvent extraction (SX) is one such proven technique in the hydrometallurgical processing for selective extraction and separation of metals due to the ease of applicability, versatility and ability to produce high value products. It is used on commercial scale for the recovery of different metals from different solutions viz. copper, nickel, cobalt, zinc, tungsten molybdenum, uranium, rare earths etc. The effluents from waste streams are also processed to recover metals using organic extractants. With the development of improved design of SX equipment and material of construction and newer organic extractants, it is possible to recover metals as value added products even from the complex solutions containing various ionic species. The process has been used first time in USA for nuclear application for extraction of uranium from nitrate solution using ether. Subsequently, developments were made for efficient extraction of uranium from other complex solutions.

In the solvent extraction process, the extraction of metal ions, or uncharged species in the aqueous phase takes place by ion pair transfer, ion exchange with the extractant. In the case of ion-pair transfer, electrically neutral molecules interact with the extractant to form an addition compound. The most suitable extractants for such interaction are those having an oxygen atom with a lone pair of electrons viz. ether, alcohols, and the neutral phosphoric acid esters. For example, tri-butyl phosphate extracts uranium from nitric acid solutions as follows:



Similarly, the metal is transferred from the aqueous phase as simple ion, and at the same time an ion from the extractant is transferred stoichiometrically to the aqueous phase in the ion exchange process. The ion present in the aqueous phase may be either cationic or anionic form. The extraction of metal takes place by cation or anion exchange mechanism.

The present paper briefly highlights the application of solvent extraction (SX) for recovery of different non-ferrous metals such as copper, nickel, cobalt, tungsten etc from different ores, secondary resources/ industrial wastes using different commercially available organic extractants such as hydroxyoximes, hydroxyquinoline substituted phosphoric acid and other phosphatic molecules, tertiary amine, etc. R & D efforts put up at NML for separation and recovery of valuable metals by SX is also mentioned.

EXTRACTION OF METALS ON COMMERCIAL SCALE

Copper :

The solvent extraction process has been used for the production of copper first time in 1964 from dilute leach solutions containing low metallic values obtained during processing of low grade ores. In this process copper is extracted from the leach solution using substituted hydroxyoxime, LIX64N. The metal is stripped from the organic phase with spent electrolyte containing high acid (200 g/L H_2SO_4) and metal produced by electrolysis [1]. Subsequently several large copper SX plants were set-up in different parts of the world. The process is usually operated in close-loop with leaching, SX and electrolysis (EW) to produce metal while recycling the reagents in the system (Fig. 1).

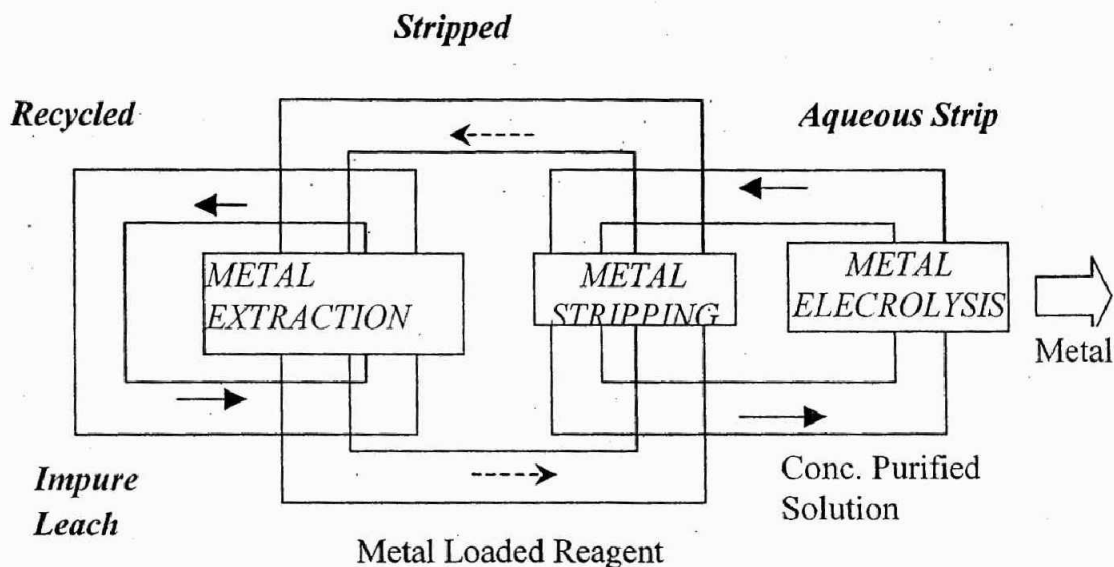


Fig. 1 : SX-EW operation in close cycle

The oxime type reagents, usually employed for copper extraction, have undergone constant improvement to suit different leach solutions. Other reagents such as Kelex100 (a substituted 8-hydroxyquinoline), aldoximes, SME 529, Acorga P1 were also used for Cu-SX. The solvents basically ketoximes, aldoximes and mixture of these are mostly employed for the extraction of copper. Ketoxime reagents are moderately strong copper extractant and they act best when the pH of leach solution is relatively high (>1.8). Modified aldoximes extract copper even at low pH or when copper content is high. But these reagents cause higher entrainment and/ or greater crud generation resulting in increased carry over of impurities to the electrolyte causing higher reagent losses. The non-modified aldoxime-ketoxime mixtures have less entrainment loss and crud formation. However, mixtures are not as effective as modified aldoximes for

copper extraction [2]. To recover copper from the ammoniacal medium, oxime based reagent or a B-diketone (LIX54 available with Cognis) can be used. It can transfer over 30 g/L Cu and remains highly fluid with low ammonia loading on the reagent. LIX54 reacts with ammonia at $\text{pH} > 9.5$ to give surface active molecules and thus increasing entrainment of aqueous in the loaded solvent. This results in carry over of ammonia to the wash stage. To overcome this problem, Cognis now have a new extracting molecule called XI-57 [3].

Cobalt and nickel:

SX has extensive application in different plants for the extraction and separation of cobalt and nickel from the chloride, ammoniacal and sulfate solutions. As cobalt forms the chlorocomplex ($\text{CoCl}_3^- / \text{CoCl}_4^{2-}$), tri-isooctylamine or tri-n-octylamine (Alamine 336) selectively extracts cobalt leaving nickel in the aqueous raffinate. The corrosion problem of chloride system is now mitigated by use of special corrosion resistant composite materials. In ammoniacal medium, LIX64N was employed by SEC Corporation at El Paso Texas to extract copper first followed by pH adjustment to 9-10 using ammonia for Ni extraction [4]. The Yabulu refinery of QNI removing Co as sulphide earlier, switched over to SX route for nickel recently. A LIX87QN developed by Cognis (Henkel) is employed for nickel extraction from ammonia solution. The loaded nickel is stripped with high concentration ammonia-ammonium carbonate solution to produce basic nickel carbonate-oxide. Sulfuric acid leaching being the most predominant medium for metal recovery, SX process for separation of Ni-Co has been used extensively. The cation exchange type reagents such as DEHPA (di-2-ethylhexyl phosphoric acid), PC88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester), Cyanex 272, Cyanex 301, Versatic-10 have been employed for extraction and separation of Ni-Co on industrial scale from different solutions.

Zinc:

In the solvent extraction of zinc, DEHPA has been used for zinc extraction in Zincex [5], the modified Zincex (Diaz and Martin, 1994), the CENIM-LNETI [6] processes. In the Zincex process, zinc chloride is first extracted with secondary amine from the chloride leach liquor of pyrite cinders, followed by second stage zinc extraction with DEHPA from the stripped solution of the first stage extraction. Zinc metal is produced by electrolysis from pure sulfate solution in close-loop solvent extraction - electrowinning (SX-EW) operation. The process was modified for recovery of zinc with DEHPA from the sulfuric acid leach solution of secondaries viz. Waelz oxides, galvanizing ashes and electric arc furnace dust (modified Zincex process). Recently, SX process has made it possible to produce zinc on commercial scale in Namibia from oxide/silicate ores as DEHPA selectively extracts zinc leaving chloride and fluoride ions in the solution [7]. A reagent, ZNX-50 (bisbenzimidazole) [3] developed by Avecia has also been found to selectively extract zinc from the chloride solution.

Tungsten:

SX has been used for recovering tungsten from leach solution obtained during processing of low and medium grade concentrate by pressure leaching methods using different reagents Primene JM-T, Aliquat-336, Amberlite LA-2, Sulphoxides, di (2-ethylhexyl) phosphoric acid, amines

etc [8-10]. In this process, tungsten is extracted using secondary and tertiary amines after purification of the solution produced in the leaching of wolframite/ scheelite ores. The solution is acidified to a pH of 1.5 to 3.5 leading to the formation of oxy-anionic complex of tungsten which is extracted by the amine. The loaded organic is stripped of the tungsten values using 5% ammonia solution to yield highly purified ammonium tungstate solution. The ammonium tungstate solution obtained is processed further by evaporation under atmospheric pressure. APT crystallizes out as a pentahydrate containing 89% WO_3 which is a precursor of pure WO_3 . A generalised flow sheet for alkali pressure leaching of the concentrate produced from the ore by solvent extraction-crystallisation is given in Fig-2. It was possible to produce APT of 99.6% purity by this process route and metal in this form is the precursor of almost all tungsten applications.

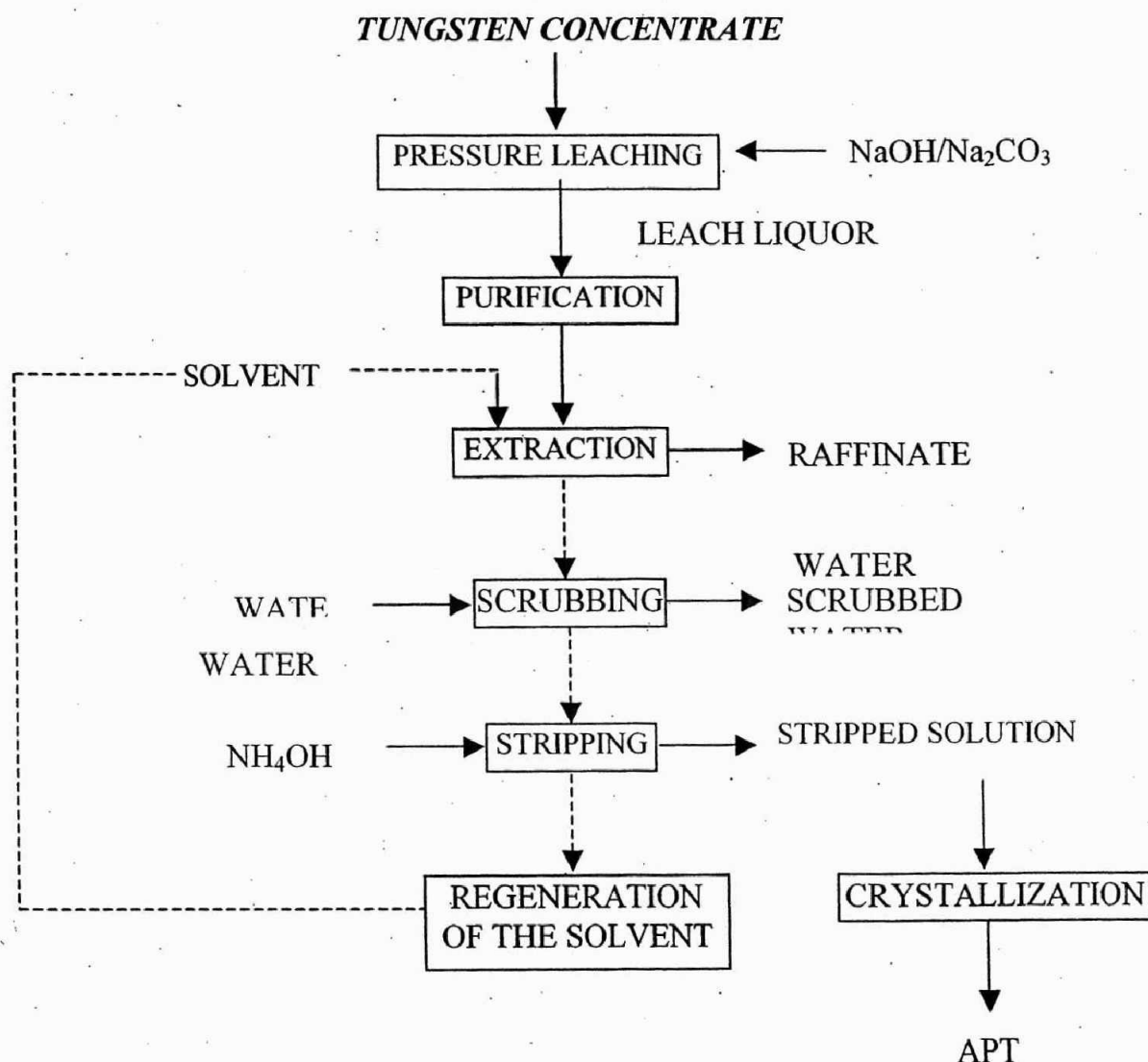


Fig 2 : General scheme for extraction of tungsten from tungsten concentrate

SOLVENT EXTRACTION STUDIES IN INDIA

Besides the above commercial application of the SX process, a number of research and review papers are appearing in open literature for the extraction and separation of different metals from the complex leach solutions and industrial effluents [11-13, 3, 7]. The studies have been

made for the extraction and separation of metals such as tungsten, gallium, titanium, chromium, etc from the different leach solutions and industrial effluents [14-16]. Details of some the developments are mentioned below for extraction of metals using different extractants in India.

In India, solvent extraction process is used on commercial scale for the extraction and separation of Zr and Hf from its leach solution at Nuclear Fuel Complex, Hyderabad. Indian Rare Earths Ltd. has also developed SX based processes to separate and purify individual rare earths at their Rare Earths Division near Cochin. However, very little of such expertise was available to metal extraction industry in the private sector. Hindustan Zinc Ltd, Udaipur was the first to enter this field, and has been operating small plant to recover Co from their process wastes. They later on planned to establish a SX operation using know how from abroad, to recover Cu values from their Pb-dross at Chittorgarh Imperial Smelter plant.

Only few plants were set-up for the production of base metals utilising solvent extraction process from different low-grade ores/ secondary materials/ wastes. These plants are of small capacity less than 2 T metal/day. The largest among them has been set up by Sunrise Zinc Ltd. (SZL), and is located at Cuncolim, Goa. It has a design capacity to produce 12.5 T/day of SHG electrolytic Zn and 2T/day of LME grade Cu metal, both via SX. The basic raw material is zinc ash, brass ash, die casting ash etc. A simplified flow sheet of this plant is shown in Fig. 3. The reagents used are DEHPA for Zn, LIX 984 for Cu and Alamine336 for Fe extraction [17]. In this process, zinc from the purified leach liquor with respect to iron is extracted with DEHPA diluted in kerosene leaving other impurities in the solution.

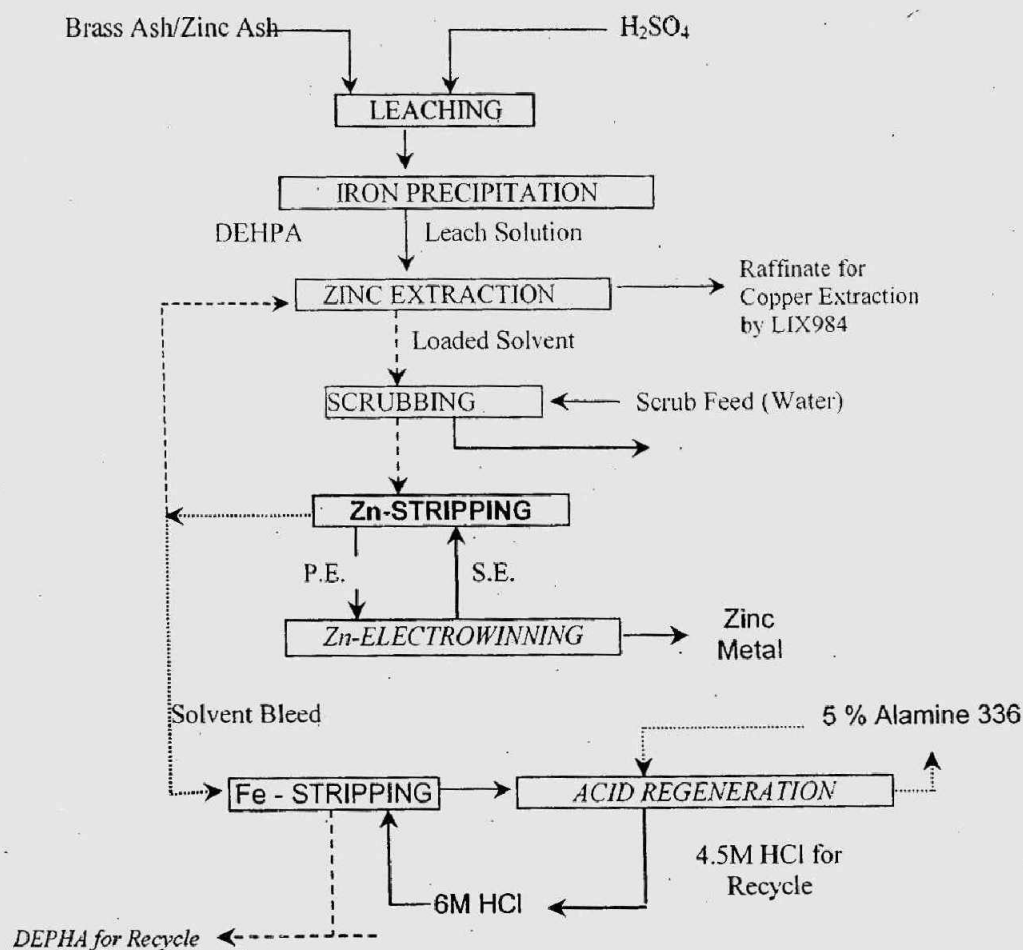


Fig- 3 : Simplified flow sheet for recovery of zinc and copper from brass and zinc ash.

Any iron remaining in the solution is extracted by DEHPA in preference to zinc. Aqueous raffinate retains all other impurities except iron along with some zinc. In case of brass ash or similar inputs, the raffinate contains copper, which is recovered in second SX circuit using LIX984 as the solvent. Copper and zinc are recovered as cathodes by electrolysis (EW). The iron extracted in the DEHPA was stripped with 6M HCl to regenerate the solvent for the recycle. The plant has utilised mixer-settlers of three different designs. The zinc circuit is provided with mixer-settlers of unique concept with gravity flow for both aqueous and solvent streams, with axial flow marine type impellers, which consume low power. SZL later on used available low-grade brass ash (16-18% Zn), since only they had the SX technology for purification. SX is now accepted process for zinc recovery as an environment friendly technology; consequently imported raw material is also now permitted.

Following the success of zinc SX-EW process, another plant was set up at the same location by Nicomet Industries Ltd (NICCO), Cuncolim, Goa. This is the first commercial cobalt refining plant to be set up in India with a design capacity to produce around 200 TPY of HG cobalt cathodes. This modern cobalt refinery was commissioned in April 1997 and now has separate SX circuits for Cu, Co and Ni and is in a position to produce cobalt metal of the high quality (99.98% pure). It is the only plant in India, which recovers nickel from basic raw material and produces NiSO_4 crystals of almost four nine purity. A simplified flow sheet followed at this refinery is shown in Fig. 4.

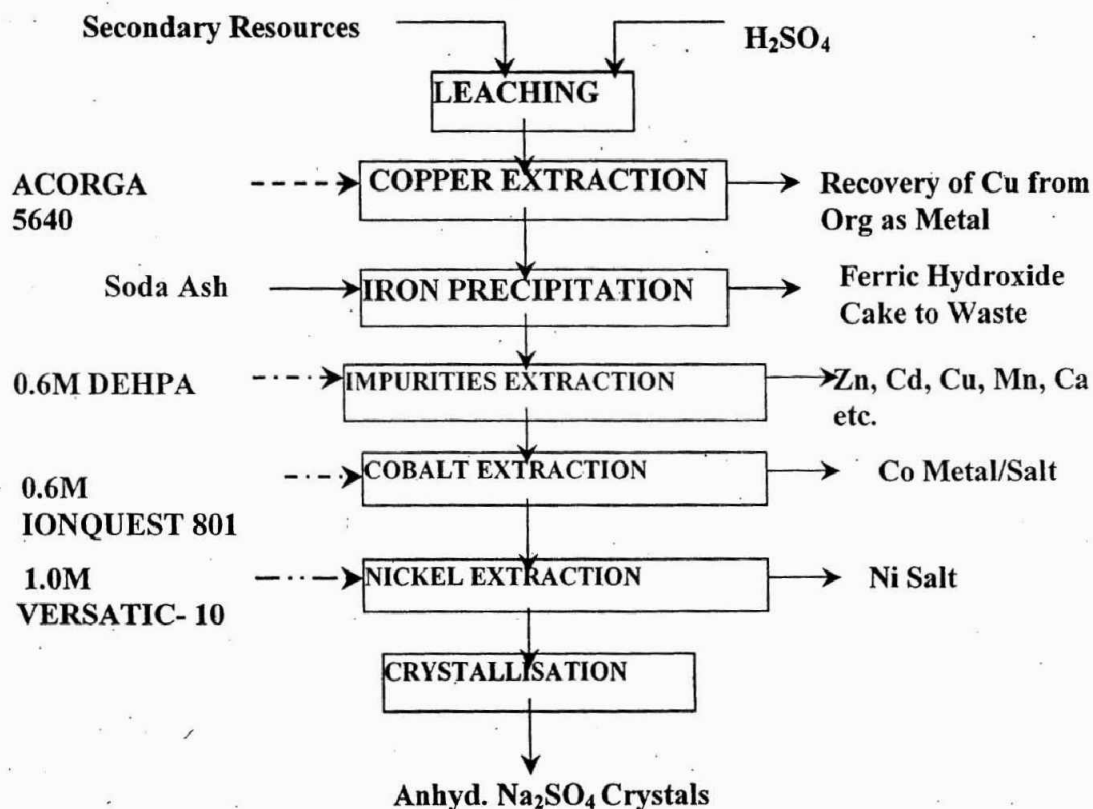


Fig-4 : SX process for the recovery of metals/salts from secondary resources

Soon after, two more Co refineries based on SX process [18] were also set up in 1998 at Baroda (M/s Rubamin Ltd) and Talaja near Mumbai (M/s Conic Metals Ltd). These plants produce cobalt cathode and various salts. M/s Rubamin Ltd uses the acid (sulfuric acid with and without SO_2 or in HCl-HNO_3) leaching of cobalt sludge/ supper alloy scrap to dissolve the metallic

values [19]. After removal of iron as hydroxide, cobalt-nickel cake is obtained. The cake is re-dissolved in sulfuric acid. The solution is then purified with respect to iron by precipitation and copper by cementation. The purified solution is then separated using PC 88A. The extracted cobalt in the organic phase is stripped with spent electrolyte of electrowinning cell. Nickel is recovered as salt in the form of carbonate.

In addition to this refinery production, cobalt metal powder was recovered from mented carbide scrap by M/s Sandvik Asia Ltd. At a pilot plant in Pune, spent catalysts from plants producing terephthalic acid were reprocessed by more than a dozen small cobalt chemical processors. Cobalt containing a waste product, beta-cake is generated during production of zinc at M/s Hindustan Zinc Ltd, Udaipur [19]. In order to recover the valuable metals from such product, roasting, sulfuric acid leaching, iron precipitation and solvent extraction process has been developed. DEHPA has been used for extraction and separation of zinc and cobalt. The purified cobalt solution obtained after stripping was used to produce cobalt metal by electrolysis. The developed process has been used at HZL plant to recover the valuables. Copper SX-EW plants have also been set up- one near Chennai and another near Hyderabad. They produce about 2-3 TPD copper metal. Raw material availability is a one of the reasons for low productivity in these plants. Looking into the progress of SX technology over the past few years, one can optimistically expect several metal SX plants to be in operational in India in coming years.

SX in the processing of different solutions:

The solvent extraction process has been extensively studied in India (NML- Jamshedpur, RRL- Bhubaneswar, RRL-Trivandrum, BARC- Mumbai, HZL-Udaipur, NFC-Hyderabad and other research institutions) for the extraction and separation of metals from the acidic and ammoniacal solutions obtained after leaching of lean grade and unexploited ores/ wastes. The effluents generated during the processing of materials also contain heavy and toxic metallic ions along with other anionic complexing ions. The presence of these ions creates environmental pollution and treatment of such solution by the conventional methods is also not possible. In order to treat such solutions, solvent extraction is an alternate approach to recover the metallic constituents. The results of these developments are detailed below.

Ammoniacal solutions:

Ammoniacal solution is extensively employed in the hydrometallurgical operation to recover the metallic values as it rejects the iron and manganese in the residue. The solution free from such impurities could be processed for the metal separation by solvent extraction. Different authors studied the solvent extraction process to recover valuable constituents from the leach solutions obtained after treatment of the low grade ores/ wastes such as polymetallic sea nodules, chromite overburden, lateritic nickel ore, sulphide concentrate, supper alloy scrap etc.

At NML, extensive studies have been carried out for the extraction and separation of copper, nickel, cobalt from the ammonia ammonium carbonate leach solution (in g/L, 2.40 Cu, 2.41 Ni, 0.163 Co, 0.008 Mn, 0.002, 70 NH₃ and 60 CO₂) of polymetallic sea nodules obtained after leaching roasted nodules [20-23]. The co-extraction and selective stripping of nickel and copper has been used for extraction and separation of copper, nickel and cobalt from ammoniacal

solutions. The solvent, LIX64N was found excellent for the treatment of the ammoniacal solution of ocean nodules on bench and continuous operation, with the phasing out of the LIX64N and marketing of the superior reagent, LIX84 (5-Nonyl 2-hydroxy acetophenoneoxime) for copper extraction by M/s Cognis, USA, the process was modified for the utilization of LIX84 for the purpose. The simplified flow sheet adopted for the metal separation by SX-EW is shown in Fig.-5. Further, ammonia ammonium carbonate solution containing Ni and Co obtained from the lateritic nickel ore of Sukinda valley as well as chromite ore overburden was processed using LIX84 [24] and LIX64N [25] for the selective extraction of nickel leaving cobalt(III) in the raffinate. A process developed on bench scale for extraction of copper, nickel and cobalt from ammonia ammonium sulfate solution and nickel and cobalt from ammonia ammonium carbonate solution tested in a demonstration plant for future exploitation of these metals from sea nodules [26] and lateritic nickel ore respectively.

A sulphide concentrate containing copper, nickel and iron is generated in small quantity at Uranium Corporation of India Ltd, Jaduguda. In order to utilise such materials, ammonia-ammonium sulfate leaching followed by solvent extraction process has been used. LIX84 diluted in kerosene

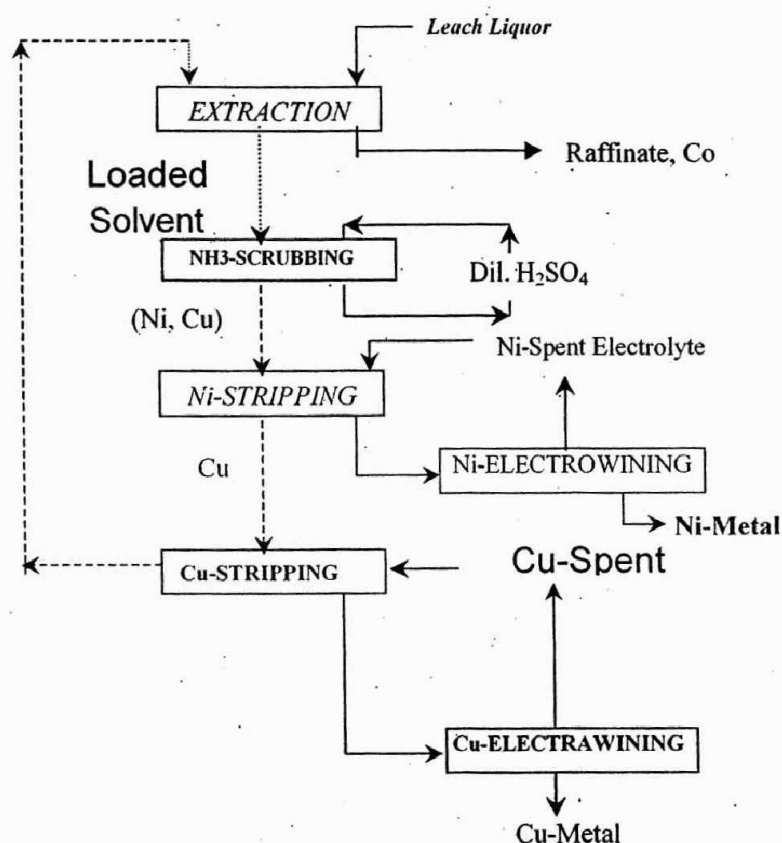


Fig-5 : Separation of metals from leach liquor by solvent extraction-electrowinning (SX-EW)

has been used for extraction and separation of metals from the leach liquor [19]. A similar by-product containing Cu, Ni and Co is also generated in the UCIL plant. Pressure leaching followed by solvent extraction route adopted to treat such materials [27]. The nickel from the aqueous raffinate solution (25.5 g/L Ni and 18.1 g/L ammonium sulfate) obtained from a super-alloy scrap was extracted with PC-88A [28-29] reported the extraction of nickel from the ammonium sulfate solution obtained in the processing of industrial wastes/ secondaries such as cobalt sludge

using LIX 84I (2-hydroxy-5-*t*-nonyl acetophenonoxime). The nickel was stripped with sulfuric acid to produce solution suitable for electrolysis.

Sulfate solution:

The solvent extraction process has also been studied for the extraction and separation of metals from the sulfate leach solution of different lean ores/ wastes such as brass ash, converter slag, complex sulphide ores etc using different organic extractants [30-31]. Copper and zinc from the leach solution obtained in treatment of complex sulphide concentrate [31-32] were also separated using solvent extraction technique. LIX64N selectively extracted copper from the leach liquor generated from the sulfation roast - leach process of the complex sulphide concentrate of Ambamata, Gujrat leaving zinc in the aqueous raffinate. The loaded copper was stripped with strong sulfuric acid and metal produced by electrowinning in a close loop SX - EW operation. The raffinate containing zinc was purified and the metal was produced by electrowinning. Separation of cobalt and zinc from the sulfate leach of cobalt cake obtained in the processing of sea nodules was studied with DEHPA. A flow sheet has been developed [33] at NML to extract and separate Zn-Co from the leach liquor of cobalt cake from ocean nodules processing.

Chloride solution :

Different authors studied the separation and recovery of metals from the chloride leach solutions generated after leaching the industrial wastes/ resources to recover the metallic values. Reddy et al., (2005a) reported solvent extraction process for the extraction and separation of Cd (II), Ni (II) and Co (II) from the chloride leach solution of Ni-Cd batteries. Cyanex 923 was used for the selective extraction of Cd(II) leaving nickel and cobalt in the aqueous raffinate. Subsequently, cobalt and nickel were extracted with Cyanex 272 and TOPS 99 respectively. Selective extraction of cobalt from acidic chloride solutions of lateritic nickel ores of Sukinda, Orissa [34] was achieved using TBP.

CONCLUSIONS

Solvent extraction is a proven technique for extraction and separation of different non-ferrous metals from various complex leach solutions and industrial effluents using different organic extractants such as DEHPA, LIX 984, PC 88A, Alamine 336 etc. A suitable organic extractant can be used for selective extraction of desired metal or impurities depending on presence of anions and cations and their concentration in the solution.

R & D efforts are also being made to develop energy efficient processes for the extraction and separation of metals from the different leach liquors and industrial effluents generated in treatment of complex lean ores/ industrial wastes which have not been exploited till date. A potential exists for the application of process with the development of newer organic extractants and mixed extractants which may be more selective for specific metals from the acidic/ alkaline leach solutions in presence of complexing agents.

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