Development of New-Concept Clean Technologies to Extract Metals from Primary and Secondary Sources

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ABSTRACT

Development of new-concept hydrometallurgical technologies promoted by Técnicas Reunidas is providing efficient and clean means for metals extraction from diverse primary and secondary sources, such as conventional or low-grade concentrates and ores, lead-acid batteries, domestic batteries, effluents from electronic industry, etc. Relevant characteristics of the recently developed processes regarding extraction of zinc, lead, silver, nickel and copper metals are the following: environmentally friendly, value added products and by-products, flexibility to a great variety of feed materials, adapted to local market requirements, easy to be combined with existing plants, available for small and large capacities and on-site installation close to the metal sources.

Key Words : Clean technologies, metal extraction, hydrometallurgical routes, value addition, environment friendly, new-concepts.

INTRODUCTION

The technological packages developed by Técnicas Reunidas (TR) during last twenty years include many individual and combined processes able to cope with very different feed materials and satisfying every application requirements.

The new-concept TR technologies respond to market demand and society needs, and are oriented to improve quality of life, to get more environmentally friendly processes and to reduce consumption of energy and natural resources.

Relevant characteristics of the new-concept clean technologies promoted by TR are as follows:

- Flexibility to a great variety of primary and secondary feed materials
- Environmentally friendly and eco-efficient processes
- Adapted to local market conditions and needs
- Value added products and by-products
- Easy to combine and complement with existing plants or processes
- Available for small and large capacities
- On-site installation, close to the metal sources

This paper describes the last and current hydrometallurgical developments regarding extraction of metals such as zinc, lead, nickel and copper from diverse sources, for instance, ores and concentrates, low-grade or dirty or mixed concentrates, spent domestic batteries, lead-acid batteries, electronic industry effluents, etc.

The main objective of this paper is to establish the concepts and meanings of the various TR's technologies, but only some of them are described because of space limitations. Interested customers are kindly invited to contact us to study in more detailed each particular case or application.

ZINC EXTRACTION PROCESSES

Extraction of zinc is carried out from primary or secondary materials by applying two kinds of technologies, Zincex® in sulphate media and Zinclor® in chloride media. Some typical applications are as follows.

Zincex® Technology[1-4]

- Oxidised, silicated and carbonated zinc ores and concentrates
- Zinc sulphide ores and concentrates based on ferric sulphate leaching
- Electric arc furnace dusts from steel making industries (sulphate based)
- Drosses, ashes and fumes from galvanic industries
- Spent domestic batteries containing zinc and manganese
- Zn-enriched ashes from combustion of tyres and municipal wastes
- Zn-enriched effluents or bleeds from industrial plants and mines

Zinclor® Technology[5-6]

- Zinc sulphide ores and concentrates based on ferric chloride leaching
- Complex Cu-Zn-Pb and Zn-Pb ores and concentrates
- Electric arc furnace dusts from steel making industries (chloride based)
- Pickling liquors and effluents from surface treatment plants

ZINCEX TECHNOLOGY-BRIEF DESCRIPTION

This process is being industrially applied to recover zinc from diverse secondary feed materials with total success (Fig. 1). The modified Zincex process is an essential part of the Skorpion project, which is presently under construction in Namibia, aiming to produce 150,000 t/y SHG zinc from zinc ores. It is envisaged that Skorpion plant will have the lowest unit operating cost in the world.

The Zincex process consists essentially in a combination of atmospheric acid leaching (sulphuric), zinc solvent extraction (D_2EHPA extractant) and zinc electrowinning, yielding SHG quality zinc (Fig. 2). When convenient, pure zinc oxide or hydroxide, or pure zinc sulphate can be produced instead of zinc metal.

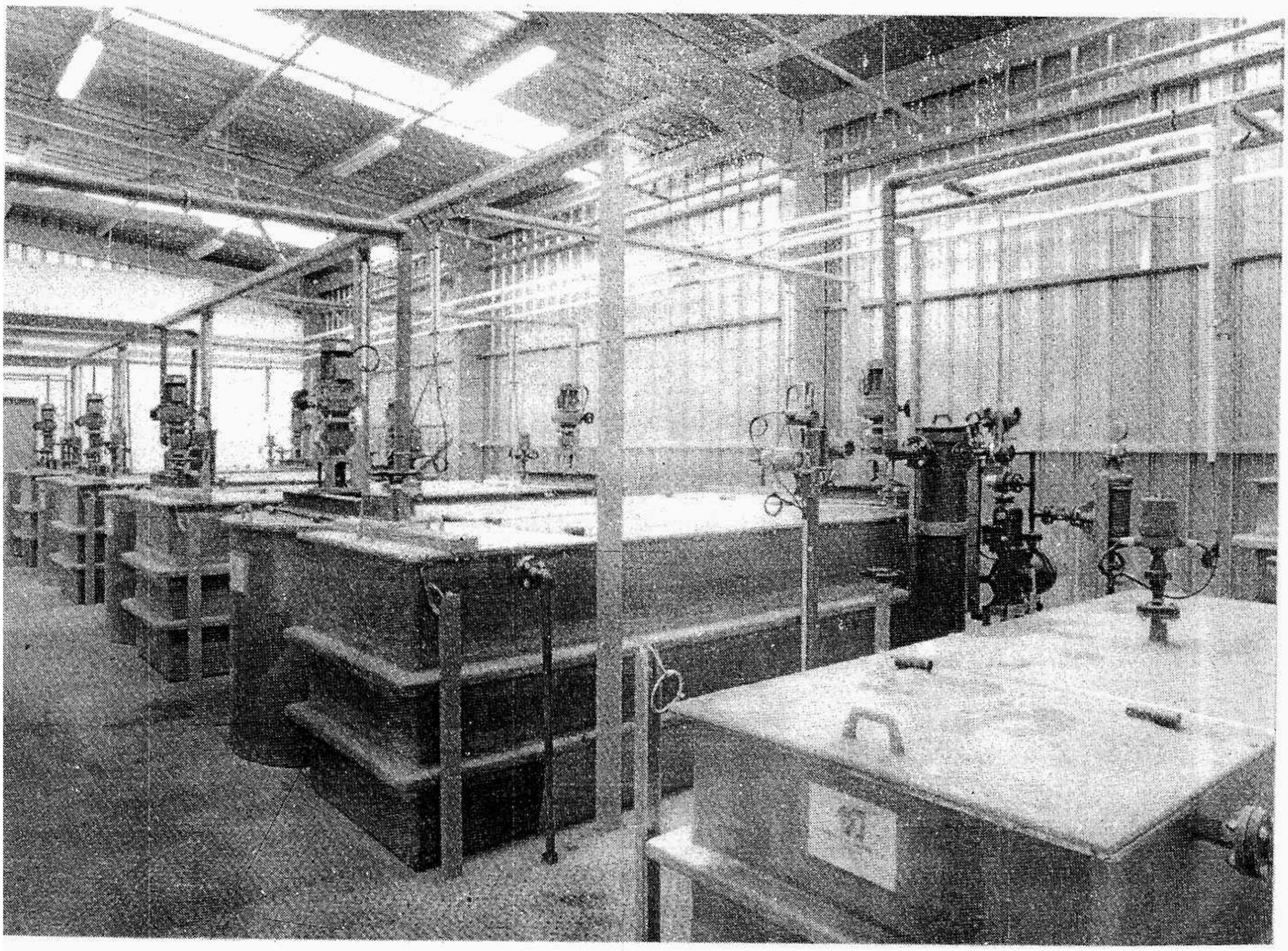

Fig. 1 : Spent domestic batteries recycling plant, Barcelona, Spain

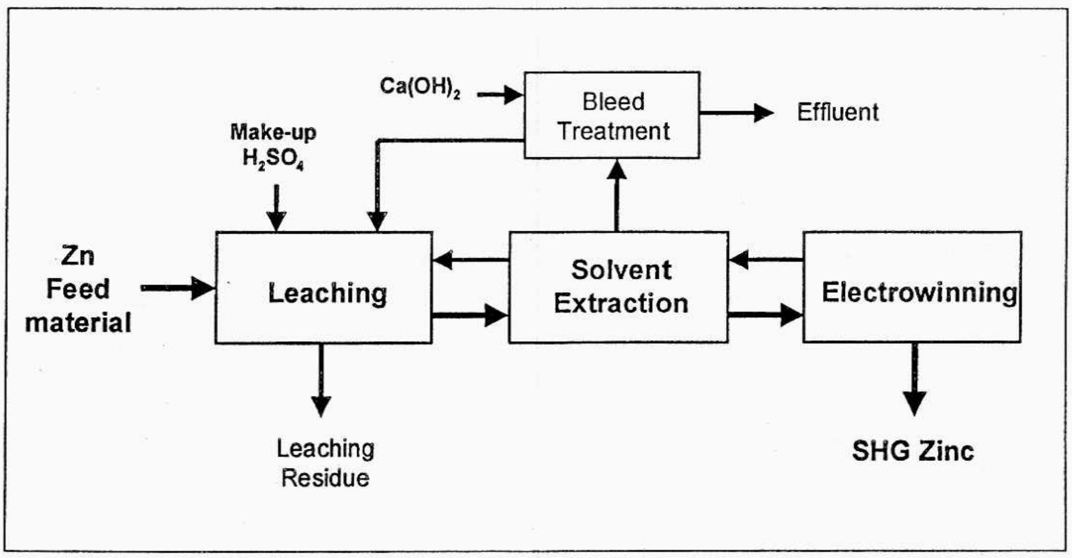

Fig. 2 : The Zincex process - Conceptual block diagram

LEAD EXTRACTION PROCESSES

Several technologies developed by TR are applied to extract lead from primary or secondary materials, such as Leadclor®, Placid® and Placid Intermediate (Plint®). Silver that usually accompanies lead in those feed materials is also recovered, improving substantially the process economy. Some typical applications are as follows.

Leadclor® Technology[7-9]

- Lead sulphide ores and concentrates based on ferric chloride leaching
- Complex Cu-Zn-Pb and Zn-Pb ores and concentrates

Placid® and Plint® Technologies[10-12]

- Oxidised, sulphated and carbonated lead ores and concentrates
- Electric arc furnace dusts from steel making industries
- Lead-acid batteries
- Slags, drosses and fumes containing lead
- Pb and Ag enriched residues from zinc and copper refineries

PLACID AND PLINT TECHNOLOGIES BRIEF DESCRIPTION

Those processes are useful for lead (and silver) recovery from lead oxide secondaries. "Four-nines" pure lead is obtained when Placid or Placid Intermediate (Plint) processes are applied to the recycling of lead acid batteries.

The leachant is dilute acid brine, where lead oxides and lead sulphate are dissolved. In the Placid process, hydrochloric acid is regenerated in the electrowinning section, just lime is the only consumption. In the Plint process, addition of acid is required, but cheaper sulphuric acid is used, instead of hydrochloric acid.

Placid or Plint process would be perfectly integrated if they were used in parallel with a pyrometallurgical smelter. In this way, any lead fumes, drosses and slags from the pyrometallurgical line would be passed to the leaching bath of the hydrometallurgical line. Important gain would be obtained from environmental, process efficiency, product quality and economics points of view (Fig. 3).

Placid pilot plant development in the laboratories of TR's R&D Centre was carried out in several campaigns (above 1000 hours total operation), during which 10 tonnes of pure electrolytic lead were produced. Representative samples of electrolytic lead gave above 99.99% Pb, containing 3 ppm Cu, 6 ppm Sb, 2 ppm As, 1 ppm Sn and 2 ppm Bi. Those data would likely be improved in a continuous industrial plant.

The Plint process is ideal to recover silver and lead from industrial residues coming from zinc and copper refineries (Fig. 4). Typical materials to be processed are leaching and jarosite residues from RLE conventional zinc refineries, leaching residues from zinc concentrate pressure-leaching plants, dusts and fumes from copper, zinc and lead smelters, bioleaching residues from copper and zinc plants, etc.

The leaching step is very flexible and can be adapted to work under acid. neutral or alkaline conditions, so virtually, any lead-silver enriched oxidised or sulphated material can be suitable as feed for this process. Even more, gold would be also recovered by applying high oxidant leaching conditions. This process can be easily combined with any existing metal refinery and is able to treat low to large tonnage.

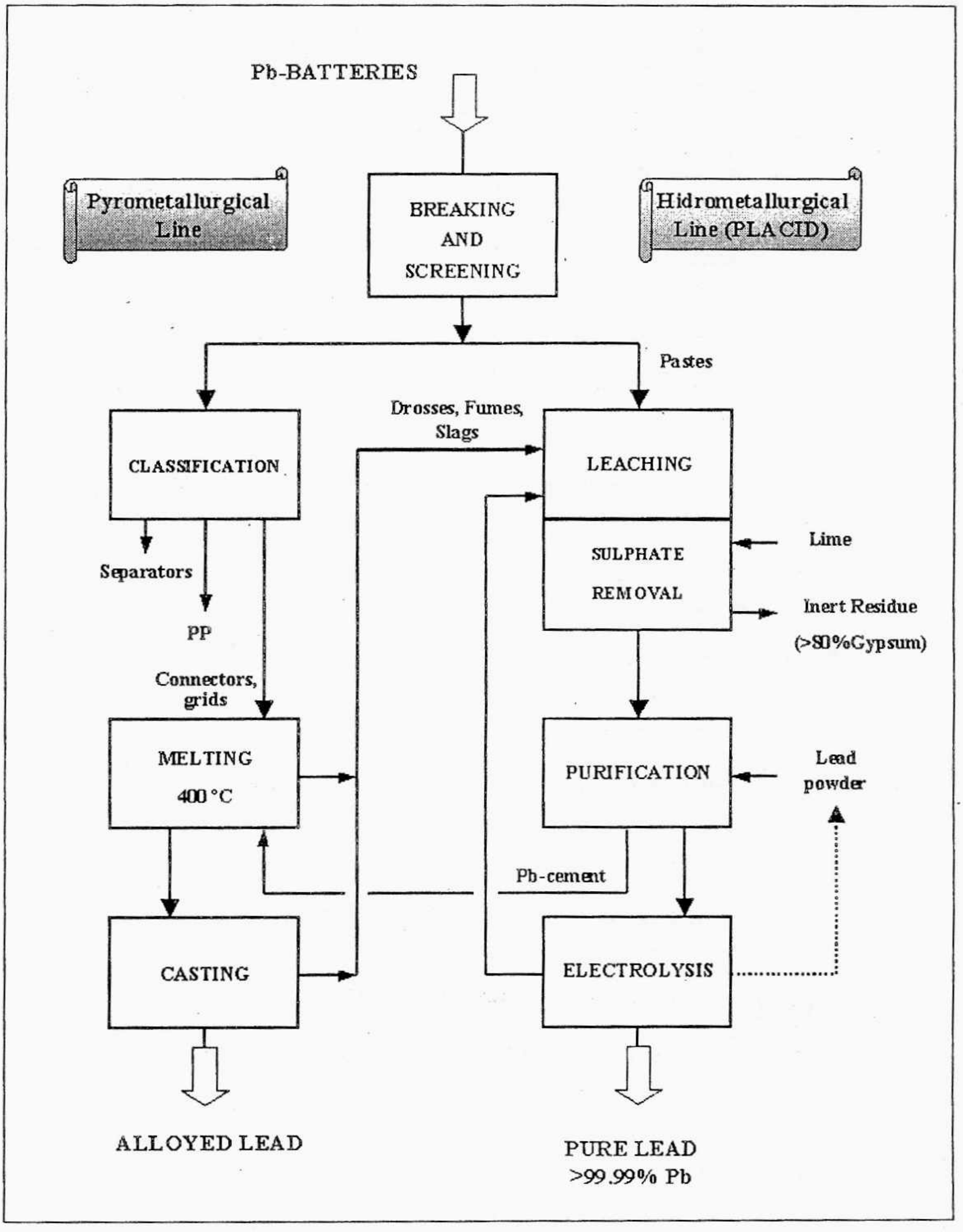

Fig. 3 : Combination of Placid process and smelting plant

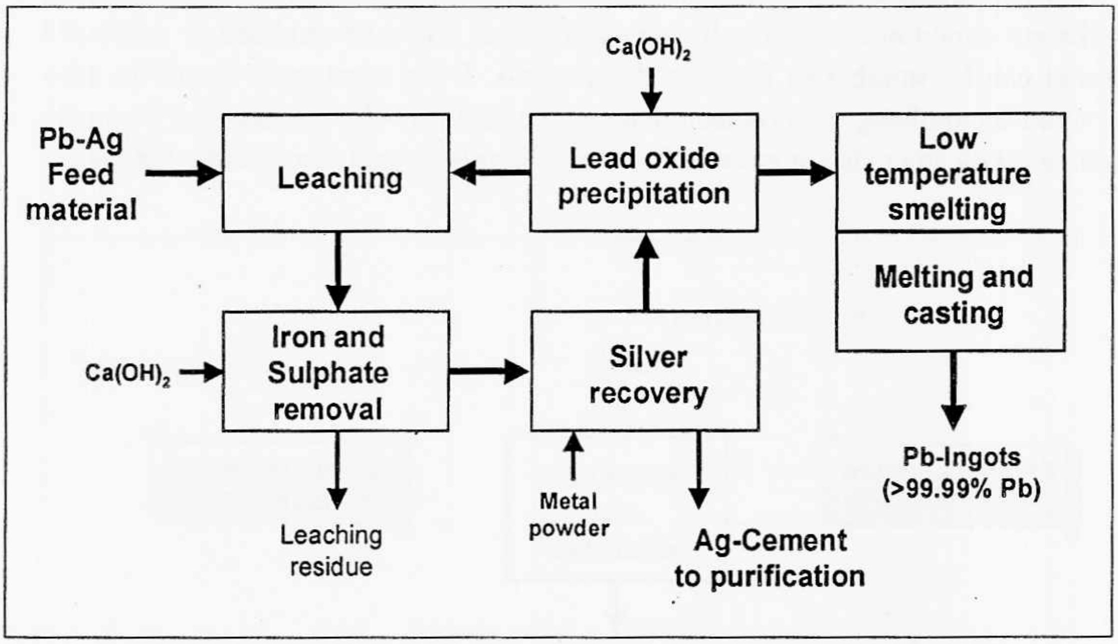

Fig. 4 : Plint process applied to lead-silver enriched industrial residues

COPPER EXTRACTION PROCESSES

Extraction of copper is carried out from primary or secondary sources by means of various technologies, adapted to every case, for instance Cuprex® and Rosel® in chloride media and Cu-SX in sulphate media. Some typical applications are as follows.

Cuprex® Technology[13]

- Copper sulphide ores and concentrates based on ferric chloride leaching
- Complex Cu-Zn-Pb ores and concentrates

Cu-SX Technology

- Oxidised copper ores and concentrates (sulphate based)
- Cu-enriched effluents or bleeds from industrial plants and mines

Rosel® Technology for Cu, HCl/Cu and Cu/Fe (Chloride media)

- Pickling liquors and effluents from surface treatment plants
- Etching liquors from printed circuit board manufacturing

ROSEL-Cu TECHNOLOGY : BRIEF DESCRIPTION

Fabrication of p: nted circuit boards (PCB) is based on the following etching processes to dissolve the remaining copper from the plate:

- Ferric chloride: $Cu + 2\ FeCl_3 = CuCl_2 + 2\ FeCl_2$ (1)
- Cupric chloride: $Cu + 2\ CuCl_2 = CuCl \cdot HCl$ (2)

  $CuCl \cdot HCl + H_2O_2 = CuCl_2 + H_2O$ (3)
- Alkaline media: $Cu + Cu(NH_3)_4Cl_2 = 2\ Cu(NH_3)_2Cl$ (4)

$2\ Cu(NH_3)_2Cl + ½O_2 + NH_4OH + NH_4Cl = 2\ Cu(NH_3)_4Cl_2 + 3\ H_2O$ (5)

Worldwide application of the various techniques is distributed as follows:

Cupric chloride	50 %
Ferric chloride	30 %
Ammonium chloride	10 %
Others	10 %

Tecnicas Reunidas has developed specific technologies for in-line or on-line regeneration of the spent etching liquors, avoiding typical neutralisation option. Copper is recovered in the form of valuable copper plate while reagent consumption of hydrochloric acid or hydrogen peroxide is minimised. This Technology is named Rosel Technology, and it is conceptually shown in Fig. 5.

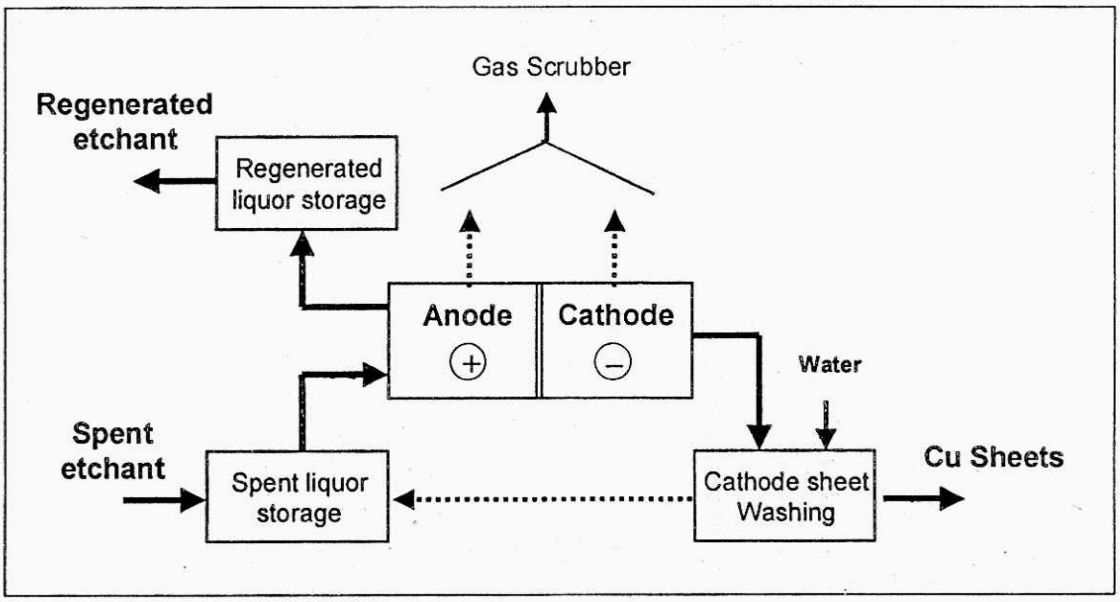

Fig. 5 : Regeneration of Cu-etching liquor by applying Rosel technology

Economic figures obtained for a Rosel plant able to regenerate and recover 25 kg/h copper plates is very attractive, giving a payback period lower than two years.

NICKEL EXTRACTION PROCESSES

Extraction of nickel from primary or secondary feed materials is performed by applying various technologies developed by TR, such as Nichlor® and Rosel®, both in chloride media. Some typical applications are as follows.

Nichlor® Technology[14]

- Nickel sulphide ores and concentrates based on ferric chloride leaching
- Complex Ni-Cu and others metals ores and concentrates

Rosel® Technology for Ni and Ni/Fe (chloride media)[15-16]

- Pickling liquors and effluents from surface treatment plants
- Etching liquors from shadow mask manufacturing for cathodic tubes

ROSEL-Ni TECHNOLOGY : BRIEF DESCRIPTION

This technology has been developed by TR aiming to regenerate spent etching solutions coming from shadow mask manufacturing for cathodic tube uses (maimly television and computer monitors application).

Spent etchant has an approximated composition of 125 g/l Fe and 100 g/l Ni in chloride media. The aim of regeneration is to produce a renewed liquor containing below 5 g/l Fe (II). Técnicas Reunidas has developed a new-concept electrolytic cell based on the following reactions:

- Anode: $2\ Fe(II) = 2\ Fe(III) + 2\ e^-$ (6)
- Cathode: $Fe(II) + 2\ e^- = Fe$ (64 %) (7)

  $Ni(II) + 2\ e^- = Ni$ (36 %) (8)

A nickel-iron alloy is produced in this process, which is a valuable Invar metal. An industrial size electrode cell, containing 11 cathodes, 1 m² each, is shown in Fig. 6. This cell prototype has been tested by Philips Components in The Netherlands, giving very satisfactory performance.

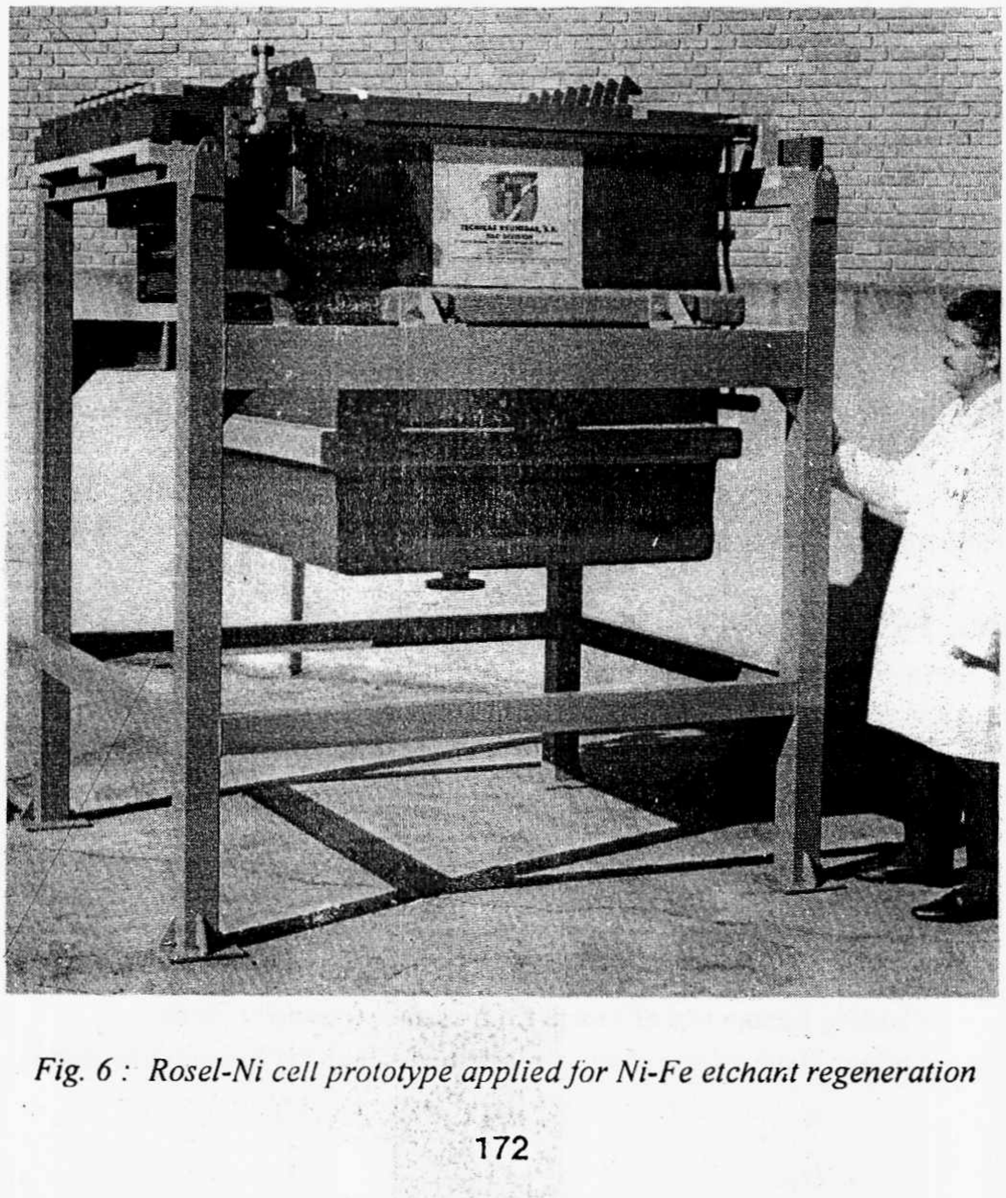

Fig. 6 : Rosel-Ni cell prototype applied for Ni-Fe etchant regeneration

CONCLUSIONS

The hydrometallurgical processes developed by Técnicas Reunidas during the last few years represent advanced and new-concept clean technologies, which can deal efficiently with diverse primary and secondary materials to extract metals such as zinc, lead, silver, copper and nickel.

Application of the new-concept TR´s technologies would improve substantially all environmental, technical, and economic aspects of the project.

Those technologies are simple and flexible, and can be adapted to customer requirements aiming to get a profitable application.

REFERENCES

[1] *M.A. García, A. Mejías, D. Martín and G. Díaz (2000) : "Upcoming zinc mine projects: the key for success is Zincex solvent extraction", Lead-Zinc'2000 International Symposium, TMS Pittsburgh, Pennsylvania, USA.*

[2] *D. Martín, M.A. García, G. Díaz and J. Falgueras (1999) : "A new zinc solvent extraction application: spent domestic batteries treatment plant", International Solvent Extraction Conference (ISEC), Barcelona, Spain.*

[3] *G. Díaz and D. Martín (1994) : "Modified Zincex process: the clean, safe and profitable solution to the zinc secondaries treatment", Resources, Conservation and Recycling, 10 Elsevier Science B.V.*

[4] *D. Martín, M.A. García and G. Díaz (2001) : "Zinc recovery from tyre ashes: a profitable and clean solution to the problem", International Symposium on Recycling and Reuse of Used Tyres, University of Dundee, U.K.*

[5] *G. Díaz and C. Frías (1994) : "The Zinclor industrial electrowinning cell", European Metals Conference'94, Freiberg-Dresden, Germany.*

[6] *G. Díaz, C. Frías and F. Parrilla (1994) : "New developments in Zinclor technology applied to complex sulphide concentrates", International Minerals and Metals Technology, published by M.I.R.O., U.K.*

[7] *D. Martín and G. Díaz (1991) : "Hydrometallurgical treatment of lead secondaries and/or low grade concentrates: the Leadclor process", Recycling lead and zinc, the Challenge of the 1990's, International Conference organised by ILZSG, Rome, Italy.*

[8] *J.L. Alvarez, E. Hermana, D. Martín and F. Martín (1990) : "Leadclor process for low grade concentrates and wastes", Tenth International Lead Conference, Nice, France.*

[9] *Técnicas Reunidas Internal Report nº P-4698/021/1998 (1998) : "Application of the Leadclor process to lead concentrates from Boliden-Apirsa".*

[10] *G. Díaz and D. Andrews (1996) : "Placid - A Clean Process for Recycling Lead from Batteries", Journal of Metals, Vol. 48.*

[11] *C. Frías, M.A. García and G. Díaz (1997) : "Industrial Size Placid Electrowinning Cell", TMS Annual Meeting at Orlando, Florida, USA, Aqueous Electrotechnologies: Progress in Theory and Practice, D.B. Dreisinger (Ed.).*

[12] *C. Frías, M.A. García and G. Díaz (2000) : "New clean technologies to improve lead-acid battery recycling", Lead-Zinc'2000 International Symposium, TMS Pittsburgh, Pennsylvania, USA.*

[13] *R.F. Dalton, G. Díaz, R. Price and A.D. Zunkel (1991) : "The Cuprex metal extraction process: recovering copper from sulphide ores", Journal of Metals, Vol. 43.*

[14] *D. Martín (1992) : "Treatment of residues, secondaries or low grade concentrates of lead zinc and nickel", International Congress on Hydrometallurgy, Vancouver, Canada.*

[15] *G. Díaz, C. Frías and J. Palma (1999) : "Nickel and iron removal from concentrate solutions by electrowinning", TMS Global Symposium on recycling, waste treatment and clean technology, San Sebastian, Spain.*

[16.] *G. Díaz, C. Frías and J. Palma (2001) : "The Geniall process for generation of nickel-iron alloys from nickel ores or mattes", Electrometallurgy'2001 Conference, Toronto, Canada.*