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Cobalt recovery from metallurgical wastes of zinc industry

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ABSTRACT

*Cobalt is a metal of great strategic importance for super alloys which are used in aerospace. Cobalt is also extensively used in the manufacture of cemented carbide tools, magnetic alloys and even in ceramics as a colouring agent. During the hydro-metallurgical process for extraction of zinc, valuable metals can also be recovered as by-products from the waste materials. Under the '**Home Grown Technology Programme**' of TIFAC, a flow sheet has been developed and process optimised for cobalt recovery from metallurgical wastes from the zinc industry. The work was done jointly by HZL & BARC and has not only resulted in increased yield of cobalt to more than 60% but also improved the product quality to achieve 99.8% pure cobalt. This paper briefly outlines the modified process flowsheet consisting of washing, roasting, three stage leaching, oxalate precipitation and solvent extraction. Results of the market survey for cobalt metal and powder carried out as a part of the study are also enclosed.*

Keywords : Cobalt recovery, Wastes from zinc industry, Home grown technology programme.

INTRODUCTION

Cobalt occurs in nature in a widespread but dispersed form, almost exclusively in admixture with ores of other metals. The main potential sources for cobalt are the residues generated during the extraction of zinc.

Cobalt is associated with zinc and gets concentrated as 'cobalt alpha nitroso betanaphthol chelate' complex during zinc sulphate purification. This is commonly known as 'β cake' and contains about 1 to 2% cobalt metal, besides 10-17% zinc, 2 to 4% iron, 0.1 to 0.4% copper and 0.05 to 0.25% cadmium.

The production of cobalt metal in India is around 140 tonnes compared to the world output of around 26,600 tonnes, thereby accounting for a mere 0.5% world production. The domestic price of cobalt metal powder is about Rs. 3500 to 4000 per kg. The minimum purity required by customers is 99.6 to 99.8% of cobalt.

Strategic Importance of Cobalt

- Cobalt ranks high in respect of its strategic importance though not being one of the major industrial metals in terms of tonnage and value.
- Its strategic use is derived from the ability to impart hardness and corrosion resistance at high temperatures.
- High speed tools are the essential cutting tool materials in the engineering industry. Cobalt is one of the major alloying elements in those tools.
- The cobalt powder is being used as binder in cemented carbide and diamond tools.
- Cobalt is used in super alloys for industrial and aircraft gas turbine engines.
- In rare earth permanent magnets cobalt is used along with samarium (e.g., $SmCo_5$).
- Its non metallic applications are as pigment in paints, ground coat in porcelain, enamelling and colouring agent in glass, and ingredient in some catalysts.

UTILISATION OF ZINC INDUSTRY WASTES

The cobalt bearing residue resulting during zinc extraction by hydro-metallurgical route is called 'β cake'. The development work for recovery of cobalt from beta cake was carried out at the Central Research and Development Laboratory (CRDL), Hindustan Zinc Limited (HZL), Udaipur. As a result of extensive laboratory tests, a cobalt recovery process based on solvent extraction was developed. Hence, with the commissioning of a solvent extraction plant, HZL utilises its entire cobalt bearing wastes generated at Vizag and Debari Smelters. As regards availability of waste material (beta cake), the annual treatment of zinc concentrate at the two smelters of HZL is around 1,65,000 tonnes/year which would enable production of about 1.24 tones of cobalt metal per year at the pilot plant.

Role of TIFAC

Technology Information, Forecasting and Assessment Council (TIFAC), an autonomous organisation under Department of Science and Technology (DST), Govt. of India plays a crucial role in technology development in the country. With an objective of looking ahead towards technology options, TIFAC has carried out a number of Technology Forecasting/Technology Assessment and Techno-Market Survey studies. TIFACLINE is an important activity which aims at developing databases on specific technology areas such as composites, non-ferrous materials, environmental technologies etc.

Home Grown Technology (HGT) activity is another major programme which promotes commercialisation of indigenous technologies in the country. The HGT activity is catalysing research and development efforts and strengthening linkages between research institutions and industry. On behalf of TIFAC, in order to review each project, a Monitoring Committee (MC) comprising of experts from industry, research and academics has been set up. The MC meets periodically at the demonstration plant site in order to discuss the progress of the project and also give valuable advice towards meeting the objectives. So far, five projects have already been successfully completed under the HGT activity and are in the process of commercialisation. In addition, 17 more projects are in progress and at various stages of completion.

DEVELOPMENT WORK AT BARC AND HZL

HZL has given major R&D thrust for recovery of values from residues obtained at various stages of zinc metal extraction. Based on extensive laboratory scale experiments by scientists of HZL and BARC, a process was developed for recovery of cobalt from β cake through the following route. The flowsheet is given in Fig. 1.

ß-cake
↓
Washing
↓
Drying and Roasting
↓
Leaching at 95°C
↓
Iron Precipitation
↓
Solvent Extraction
↓
Zinc Extract
↓
Electrowinning
↓
Cobalt Metal

With the above process, an overall cobalt recovery of around 40% from beta cake was achieved with the quality in the range of 98-99% purity cobalt.

PILOT PLANT AT HZL

In view of the importance of cobalt as a strategic material required for the country's industrial development, it was decided by HZL that a plant would be put up based on the process developed by scientists of HZL and BARC. The basic and detailed engineering work was carried out by Fertiliser Engineering and Design Organisation (FEDO), Cochin. The plant is designed to recover:

i) Cobalt sulphate from β–cake, and

ii) Copper sulphate from copper cement

The plant has a capacity for treating 3 tonnes of β-cake and 2 tonnes of copper cement per day. The pilot plant has been operated for cobalt recovery intermittently since 1991 and producing around 1 to 2 tonnes of cobalt metal per year.

Project Objectives

An analysis of the process carried out by HZL during the operation of the pilot plant reveals that the capacity of the plant can be increased and also the quality of cobalt upgraded by improving the recovery efficiency and addition of balancing facilities for handling the increased output. Also, the cobalt cathode produced at the pilot plant had a purity of 98.5% cobalt which is adequate for many uses. However, for applications in maraging steel and super alloys, cobalt of 99.8% purity is required. The quality can be improved by optimising the leaching and solvent extraction stages.

Accordingly, HZL took up a project under the HGT Scheme of TIFAC with the following objectives:

a) Up-gradation of demonstration plant by increasing the overall cobalt recovery from β-cake from the existing level of around 40% to 60%.

b) To improve product quality from 98.5% to 99.8% purity of cobalt metal

c) Development of process for production of cobalt metal powder

PROCESS OPTIMISATION

With the above mentioned objectives in view, a project was initiated by HZL in June 1993, and since then different alternative process variants were tried out

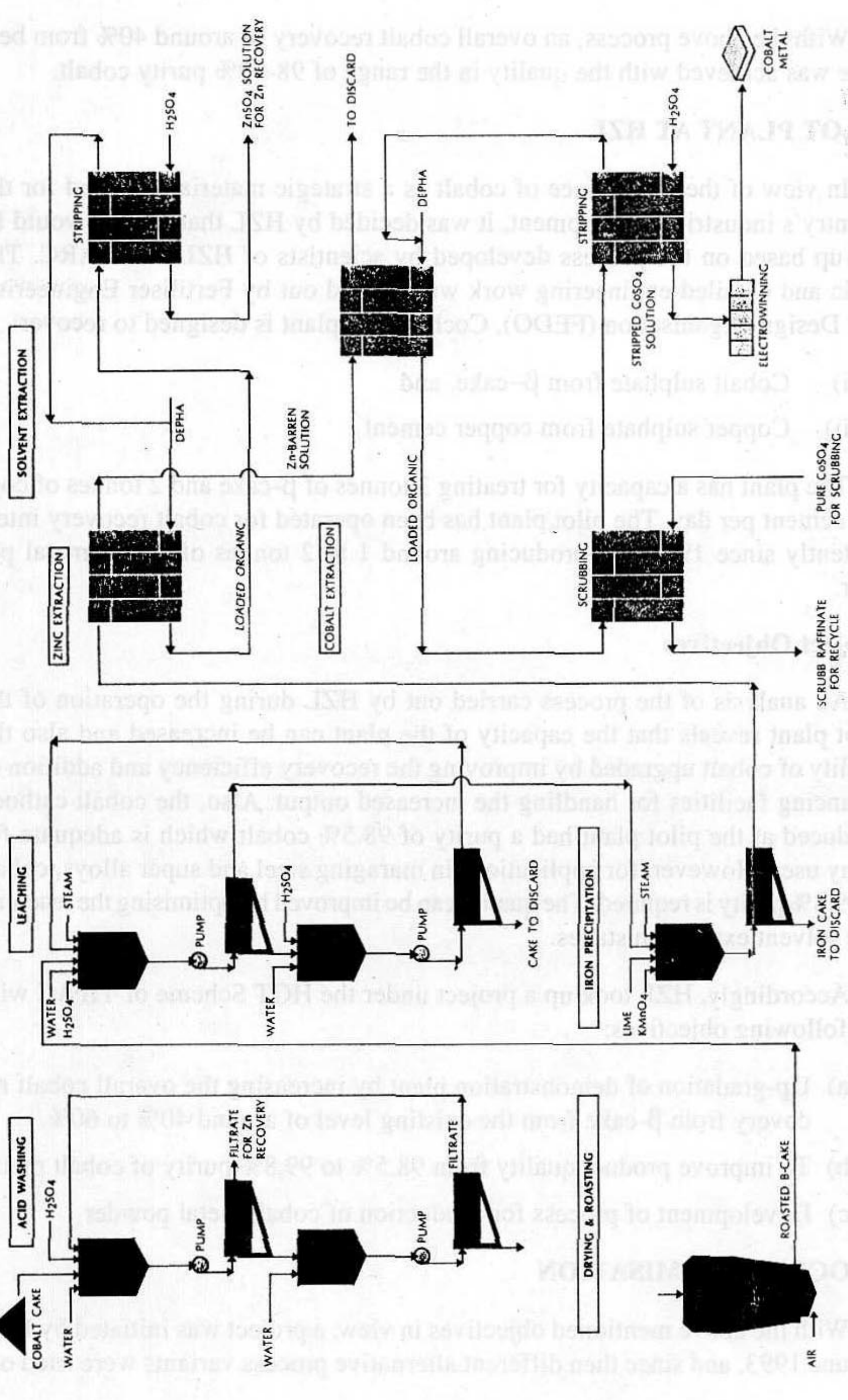

Fig. 1 : Existing flowsheet for cobalt recovery plant.

by scientists at CRDL with technical assistance from the Rare Earth Development Section of Bhabha Atomic Research Centre (BARC). The process flow sheet has now been finalised and the various steps involved in the modified flow sheet are given below:

Washing

The β-cake contains appreciable amounts of zinc and manganese. These impurities are partially removed by washing the β-cake in dilute sulphuric acid along with required amount of ferrous sulphate at room temperature for two hours. The cake loses about one-third of its weight in this washing step and the cobalt content in the cake is enriched accordingly.

Roasting

The washed β-cake is subsequently roasted on sand bed in a fluidised bed roaster at around 750°C for one hour. During roasting, organic matter decomposes. The roasted mass gets reduced to about 60-70% and cobalt content in roasted mass gets upgraded to about 7%.

Leaching

The roasted mass is leached in dilute sulphuric acid. To improve Co-recovery further, a three stage counter-current leaching of roasted beta cake has been recommended instead of the existing two-stage leaching.

Beta Cake →	Ist stage	→ 2nd stage	→ 3rd stage
	130 g/l H_2SO_4	150 g/l H_2SO_4	170 g/l H_2SO_4

The acid concentration at each stage was analysed and then make up acid is added to maintain required concentration in first, second and third stages respectively. The results indicate that about 250 gm of H_2SO_4 is consumed while processing 500 gm of beta cake and 40-50 gms/litre of free acid is present in the leach liquor. At this acidity, almost all iron is solubilised, giving rise in iron concentration in the leach liquor. The analysis of tailings indicate that cobalt recovery is about 97% during the leaching stage.

Iron Precipitation

The separation of iron was carried out using the leach liquors obtained from counter current leaching as well as from conventional leaching practised at HZL. At present, the iron separation method adopted at HZL is based on the fact that Fe^{3+} gets precipitated as hydroxide at pH ~3.5. However, cobalt loss in this method is quite high (~20%). Hence, different methods were investigated. One of the proposed method is iron separation by oxalate precipitation. More details about this process is given below.

Iron Separation by Oxalate Precipitation

The separation of Fe from base metals is possible by taking advantage of high solubility of ferric oxalates and low solubilities of most of the base metal oxalates including Co. It is important to note that while ferric oxalate is highly soluble, ferrous oxalate is insoluble. Hence it is necessary to convert all the Fe in the leach liquor to trivalent state to achieve its effective separation by the oxalate route. This first involves addition of required quantity of MnO_2 and then saturated solution of sodium oxalate/oxalic acid. Since such a method call for use of comparatively costly reagent such as oxalic acid (cost Rs. 22 per/kg), attempts have been made to optimise the amount of oxalic acid required for the selective precipitation of base metals. During trials it was revealed that complete precipitation of base metals took place only when excess of oxalic acid over that required for precipitation of iron and base metals was added. For example, use of 25 and 50% excess oxalic acid over that required to convert all the metals to their respective oxalates resulted in 95 to 97% of Co recovery respectively. The oxalate precipitate on calcination at 300°C results in a crude oxide concentrate analyzing 30% Co and representing 97% Co recovery. On comparison with other methods, iron separation by oxalate precipitation was considered as most appropriate.

Solvent Extraction

The solution, obtained after Fe separation by oxalate precipitation, metathesis of oxalate to hydroxide, and acid dissolution was diluted to get a feed solution. The analysis shows:

Elements	Concentration (g/l)
Co	10.6
Mn	6
Ni	1.5
Fe	< 0.05
Zn	3.8

The purification of cobalt from such a solution is feasible by solvent extraction processing using cation exchanger type extractant like DEHPA and PC88A.

A separation scheme was worked out to separate better extracted metals like Zn, Cu and Mn in first step (zinc circuit) followed by extraction and separation of Co from Ni in second step (Co-circuit).

Cobalt Circuit

The raffinate obtained from zinc circuit was extracted in four stages using partially saponified PC 88A in kerosene. The co-extracted nickel was scrubbed with dilute H_2SO_4 in two stages and scrub solution was fed back along with feed in extraction section. The extract coming out from the scrubbing circuit was stripped with 1 M H_2SO_4 in two stages. The composition of reffinate-2 and cobalt strip liquor indicate >99.8% cobalt purity with 96% recovery.

Electrowinning of Cobalt

The cobalt sulphate solution containing about 60 gms per litre of cobalt is electro-won to get cobalt metal using stainless steel cathodes. The optimum electrowinning parameters are: Bath pH 2.0, bath temperature of 60°C and current density 200-250 Amp/m^2. The spent electrolyte generated is recycled to solvent extraction section.

Final Recommended Flow Sheet

Based on the extensive laboratory work carried out at BARC as well as HZL, and discussed in the meetings of TIFAC Monitoring Committee, following recommendations are made:

a) Three stage leaching of the roasted beta cake with maximum acid addition in the last stage.

b) Iron removal by oxalate precipitation in preference to hydroxide precipitation. This has twin advantages of higher recovery and crude-free operation of mixer-settlers.

c) Oxalate conversion to hydroxide in a once through process, i.e., without filtrate recycle.

d) Solvent extraction by the dual solvent process involving PC88A in second cycle.

e) Adoption of scrubbing in the solvent extraction circuit. Scrubbing is essential for high purity product. Scrubbing unit must have internal recycle for maximum efficiency.

f) Pure cobalt solution to be used for powder production by precipitation as oxalate and decomposition in a reducing atmosphere.

The modified flowsheet is given in Fig. 2.

FURTHER ACTION PLAN

The recommendations also include detailed list of equipments like reaction tanks with agitators, pumps, storage tanks, heating coil for the reaction tank etc. The project is now under implementation at the pilot plant installed at CRDL, HZL, Udaipur and is likely to be fully commissioned and operated by end of June 1999.

Techno Economics

Based on the flow sheet optimised as a result of this project and present cost structure, HZL has worked out that the variable cost for recovering cobalt metal would come to around Rs. 2000 per kg. This does not include the fixed costs, which will vary significantly with the scale of operation.

MARKET SURVEY

In order to assess the market demand, availability and shortfall for both cobalt metal and cobalt powder as a part of this project, HZL had assigned a market survey study to MECON, Ranchi. The projections as mentioned in the market survey report are as follows:

Unit : Tonnes

Year	Demand	Availability	Gaps(-)/Surpluses(+)
Cobalt			
1997-98	330	110	(-)220
2001-02	480	220	(-)260
2006-07	660	220	(-)440
Cobalt Powder			
1997-98	137	58	(-)79
2001-02	197	82	(-)115
2006-07	287	82	(-)205

From the above figures, it is evident that there will be a considerable increase in demand of both cobalt metal and powder in the years to come.

Price

The report also gives domestic prices of cobalt metal in the range of Rs. 2200 to 2800 per kg., and that of cobalt powder in the range of Rs. 3500 to 4000

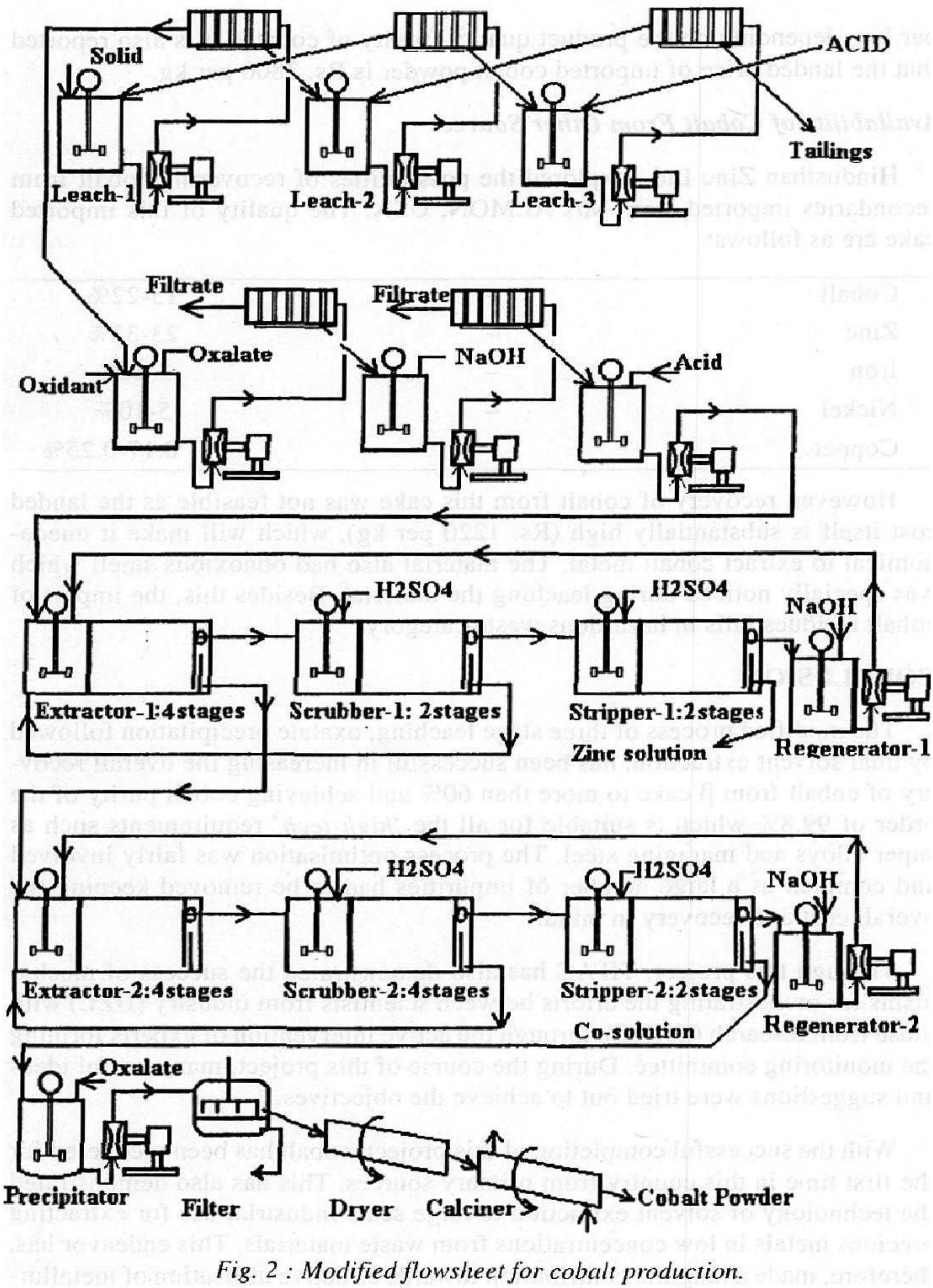

Fig. 2 : Modified flowsheet for cobalt production.

per kg., depending on the product quality (purity of cobalt). It is also reported that the landed price of imported cobalt powder is Rs. 3800 per kg.

Availability of Cobalt From Other Sources

Hindusthan Zinc Ltd., explored the possibilities of recovering cobalt from secondaries imported from M/s ALMON, USA. The quality of this imported cake are as follows:

Cobalt	–	13-22%
Zinc	–	23-33%
Iron	–	3-10%
Nickel	–	5-10%
Copper	–	0.17-0.25%

However, recovery of cobalt from this cake was not feasible as the landed cost itself is substantially high (Rs. 1220 per kg), which will make it uneconomical to extract cobalt metal. The material also had obnoxious smell which was specially noticed during leaching the material. Besides this, the import of cobalt residues falls in hazardous waste category.

CONCLUSION

The modified process of three stage leaching, oxalate precipitation followed by dual solvent extraction, has been successful in increasing the overall recovery of cobalt from β cake to more than 60% and achieving cobalt purity of the order of 99.8% which is suitable for all the *'high-tech'* requirements such as super alloys and maraging steel. The process optimisation was fairly involved and complex as a large number of impurities had to be removed keeping the overall cost and recovery in mind.

Through this project, TIFAC has also demonstrated the success of mechanisms for orchestrating the efforts between scientists from industry (HZL) with those from research (BARC), through the active intervention of experts forming the monitoring committee. During the course of this project, many useful ideas and suggestions were tried out to achieve the objectives.

With the successful completion of this project, cobalt has been recovered for the first time in this country from primary sources. This has also demonstrated the technology of solvent extraction to large scale industrial use for extracting precious metals in low concentrations from waste materials. This endeavor has, therefore, made a tangible contribution towards effective utilisation of metallurgical wastes from zinc industry and a modest step *"towards a cleaner world"*.

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