



Solvent extraction in the primary and secondary processing of zinc

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Synopsis

An unprecedented expansion of the global zinc industry is currently under way. While most new projects and plant upgrades remain committed to traditional processing technologies, recent advances in zinc solvent extraction (SX) have created opportunities for new process routes for both primary and secondary materials. The first commercial plant to use zinc SX for the mainstream processing of a low-grade ore is under construction and promises to become one of the lowest cost zinc producers. Several other oxide and sulphide projects in various stages of feasibility are considering the inclusion of SX in their process flowsheet. Zinc SX has also proved advantageous in the reprocessing of secondary materials, particularly for the treatment of zinc residues and furnace dusts. This review focuses on recent installations and projects under development that feature zinc SZ as the key separation step.

Introduction

The traditional roast-leach-electrowin(RLE) zinc production route was developed for the processing of sulphide ores. It can prove inefficient for some complex sulphides and is not readily applicable to the treatment of other ore types. Inherent to this route is the generation of SO₂ gas that has to be fixed for environmental reasons, usually resulting in the production of sulphuric acid. These limitations have encouraged the search for alternative processing routes for both sulphides and other ores.

Approximately 30% of global zinc production arises from recycled zinc. With increasing awareness of secondary zinc materials as a valuable resource and stricter environmental legislation that restricts dumping of these hazardous materials, interest in their recycling has increased¹. Direct retreatment of such materials via the process of origin is not always cost effective and can deleteriously affect the operation of the primary plant due to high levels of impurity species.

The development of process routes for the treatment of both primary and secondary sources of zinc has been hindered by the very

stringent requirements for production of high-purity zinc by electrowinning (EW)². Zinc EW from sulphate medium is extremely sensitive to the presence of trace impurities and requires a highly purified electrolyte. The selectivity of modern solvent extractants, an improved understanding of the process chemistry, and engineering innovations, have today enabled SX to provide unique advantages as a purification step ahead of the EW circuit in hydrometallurgical process flowsheets.

In most of the new applications involving SX processing in sulphate media, di(2-ethylhexyl)-phosphoric acid (D2EHPA) is used. This extractant is selective for zinc over most of the species deleterious to EW (Cu, Cd, Co, Ni, and the halides) and is readily stripped by acid concentrations typical of the spent tankhouse electrolyte (~180 g/l H₂SO₄). Circuit configurations generally include an organic-phase scrub to further ensure electrolyte purity. Iron build up in the organic phase is controlled by a concentrated HCl treatment. The selectivity of D2EHPA for zinc over selected base metal and alkali cations is illustrated in Figure 1.

In contrast to the zinc industry itself, zinc SX has found wider application in the refining of other base metals, providing an efficient means for the removal of zinc as an impurity species. These applications are surveyed elsewhere⁴. This review focuses on recent installations and developmental projects featuring zinc SX. Some historical perspective is provided by brief descriptions of earlier processes.

Primary processing of zinc

Flowsheets involving zinc SX for the primary processing of zinc sulphides have been the

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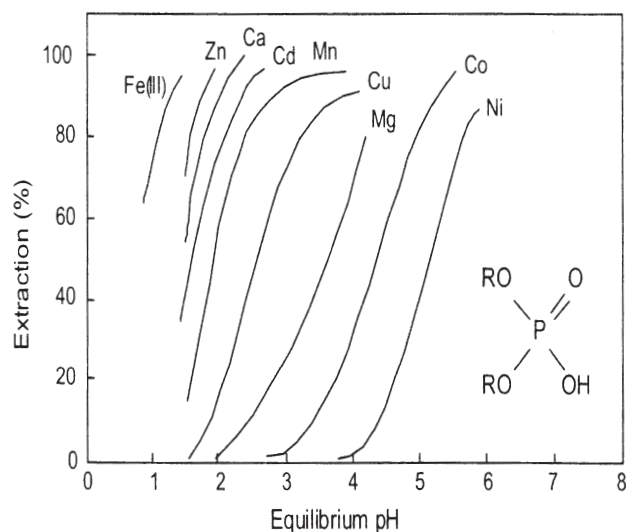


Figure 1—pH dependence of the extraction of selected cations by D2EHPA³

subject of investigation for some time. Interestingly, however, the first commercial application of zinc SX on the mainstream process liquor will be for the exploitation of an oxide orebody.

Sulphide ores and concentrates

Most zinc ores occur as sulphides and, as such, are amenable to upgrading by flotation. The traditional treatment route includes smelting of the concentrates, followed by hydrometallurgical processing to produce electrolytic zinc metal. Direct ore processing via a hydrometallurgical route could enable the economic exploitation of complex ores that yield low upgrading recoveries, while hydrometallurgical processing of concentrates would avoid the generation of SO₂ and would be more flexible with respect to the grade of feed material that can be treated. The inclusion of an SX separation step in potential process flowsheets could also accommodate difficult-to-treat concentrates, such as those with high lead or halide contents.

Chloride routes

Chloride routes for the treatment of sulphides have been known for over a century, however, few have been commercialized because of the associated corrosion problems. Although modern materials of construction have improved this situation considerably, there are currently no known plants that use this technology for zinc. There have, however, been several process developments that have made use of SX for the treatment of zinc sulphides.

The Zinclor Process was developed by Técnicas Reunidas (TR), for the treatment of concentrates⁵. Leaching with ferric chloride was followed by SX with pentylphosphonate and EW in their patented Metclor cell. Another process for the treatment of concentrates proposed leaching in concentrated ammonium chloride, followed by zinc SX using D2EHPA modified with isodecano⁶. The ammonia fixed in the metal-ammine complex provided neutralization of the acid released during extraction.

More recently, a detailed engineering design for a plant based on ferric chloride leaching of a complex sulphide New

Brunswick ore was reported⁷. The process featured zinc SX using the zinc-selective bisbenzimidazole extraction, ZNX 50, developed by Zeneca (now Avecia). Zinc metal was electrowon in a divided cell in which chlorine gas was also generated for recycle. Interestingly, this process route was reported to be more cost effective for treating the whole ore than for treating the concentrate, generating approximately 10% more revenue.

Sulphate routes

Pressure leaching for the hydrometallurgical processing of zinc sulphides has been applied commercially for many years but purification of these liquors has, to date, relied on a series of precipitation steps to achieve the electrolyte purification required for the production of high-purity zinc. Indications are, however, that SX may be used in future installations, with pilot-plant studies having been carried out by TR on pressure leach liquors using D2EHPA¹.

An alternative approach to the hydrometallurgical treatment of sulphides is the use of bacterial leaching for solubilizing the valuable metals. Following a bulk iron-removal step (typically by precipitation), SX has been shown to be successful in producing ultrapure electrolytes suitable for the production of special high-grade (SHG) zinc metal (>99.995% purity) from a variety of bioleach liquors. In pilot-plant studies, MIM Holdings of Australia have proved the feasibility of this route for treating concentrate, demonstrating that the simplified zinc-recovery flowsheet can provide low capital and operating costs with high overall zinc recoveries (96%)⁸. For the development of the Lanping deposit in China, BHP Billiton have proposed bacterial leaching of the sulphide concentrate, an atmospheric leach of the oxide material, and the treatment of the combined leach liquor by SX for the recovery of zinc⁹. A process for the treatment of Mexican polymetallic (Cu/Zn) and chalcopyrite copper concentrates, developed by BacTech and Mintek, includes bioleaching, copper recovery by SX/EW, and zinc recovery by SX/EW¹⁰.

Non-sulphide zinc ores

Extensive feasibility studies have shown that oxide, silicate, and carbonate-based zinc ores, not amenable to conventional processing, can be viably treated using zinc SX technology in a purely hydrometallurgical processing route⁹. A key feature that contributes significant economic advantage to these projects is that SHG zinc cathode is produced at the mine site. This is rarely seen for the processing of sulphide ores. Use of SX enables the entire process stream to be treated for the selective recovery of zinc, with a single SX circuit capable of processing in excess of 150 000 t/a zinc¹. This means that the impurity-removal operations are small, treating only a bleed stream of the main circuit, rather than the entire process stream as in traditional flowsheets.

Skorpion project

Anglo American's Skorpion project will be the first commercial application of zinc SX for primary zinc processing, involving a capital investment of US\$ 454 million to develop the mine and refinery near Rosh Pinah in southern Namibia¹¹. A simplified flowsheet of the proposed process is given in Figure 2¹².

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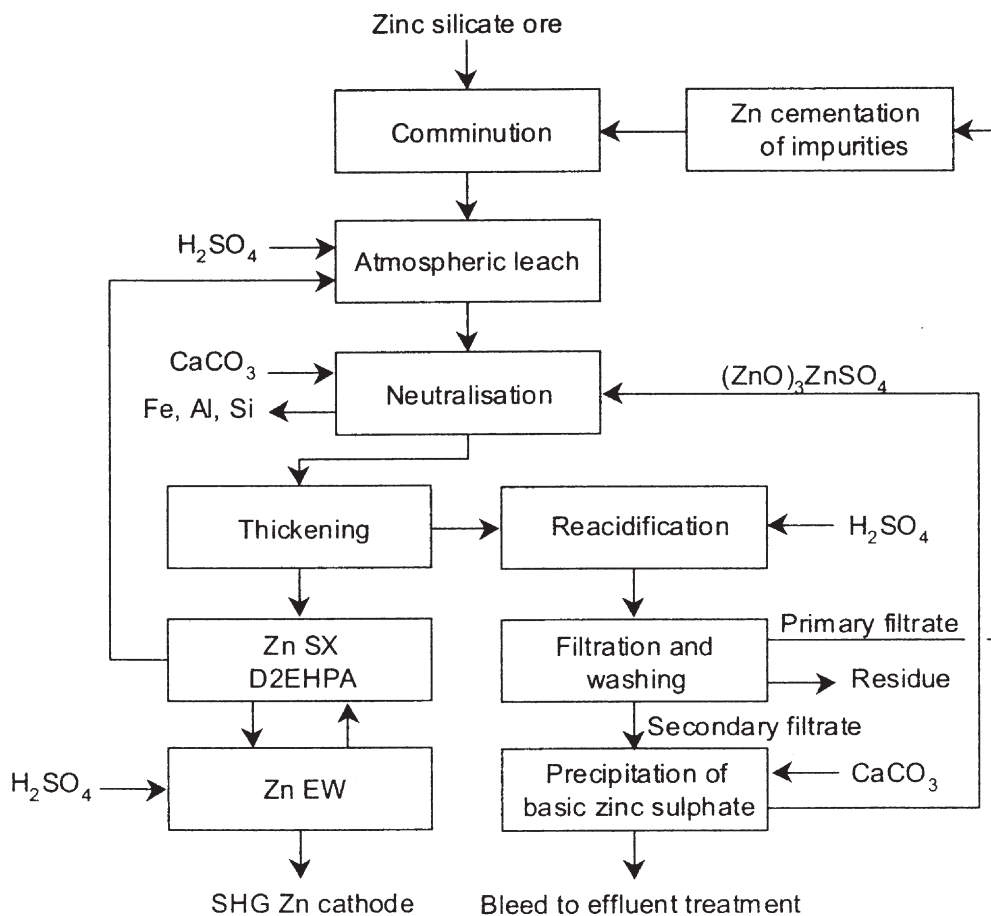


Figure 2—Simplified flowsheet for the Skorpion zinc project¹²

Following atmospheric leaching in sulphuric acid, iron, aluminium, and silica are removed from solution by precipitation. Zinc is then selectively extracted by SX with D2EHPA, enabling the electrowinning of SHG zinc. The selection of SX as the purification step serves several purposes. The ore is a low-grade oxidized silicate containing soluble chloride and fluoride minerals. The choice of D2EHPA as the extractant and the inclusion of a scrubbing circuit ensure the rejection of the halides, as well as the base metals that are deleterious to zinc EW. SX also successfully upgrades the rather dilute leach liquor (30 g/l Zn) (produced as a consequence of the leach conditions dictated by the elevated silica content (~26%) of the ore) to an advance electrolyte containing 90 g/l Zn that is suitable for EW. Soluble losses of zinc in the filtration step are minimized by employing a dilute leach liquor, and the problematic formation of silica gel is avoided. Operation with a high extractant concentration ensures minimal calcium co-extraction and allows high zinc transfer in the extraction circuit without the need for neutralization. The acid generated by the extraction reaction is then available for leaching on recycle of the raffinate.

TR was responsible for providing the SX technology¹¹ and the plant will be the largest yet built for zinc SX. The circuit comprises three extraction, three scrubbing, and two stripping stages, and an organic regeneration stage. Zinc transfer of 20 g/l across the extraction circuit is achieved, yielding a raffinate of 10 g/l Zn. The first two stages of the

scrubbing circuit use demineralized water to wash out physically entrained impurity species; spent electrolyte is employed as the scrub liquor in the third wash stage to 'crowd off' co-extracted impurity species from the loaded organic phase. Treating a bleed stream with 6 M HCl controls iron build up in the organic phase. Residual HCl is removed from the regenerant solution by distillation, producing concentrated FeCl₃ liquor, which is neutralized prior to disposal to tailings.

Construction of the full-scale plant commenced in May 2001, and the first metal is expected in December 2002. The feasibility study conducted for the planned capacity of 150 000 t/a zinc showed that the Skorpion project will be the most profitable zinc facility in the world⁹, with an expected production cost of US\$ 0.25/lb.

Projects under development

Several non-sulphide ore projects in various stages of development and feasibility studies intend to use zinc SX for primary ore processing (Table I).

Zinc recovery from geothermal brines

A process originally developed by BHP for the recovery of zinc from geothermal brine that has been used for power generation is currently being commissioned by Kvaerner Metals for CalEnergy Minerals in the Imperial Valley of California. High-temperature underground brine is brought to

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Table I

Non-sulphide primary ore processing projects under development that use zinc SX

Project	Capacity (t/a Zn)	Ore type	Process route
Shairmerden, Kazakstan ¹³	100 000	Oxide, silicate, carbonate	Sulphate leach, zinc SX
Angouran, Iran ¹⁴	100 000	Carbonate, silicate	Sulphate leach, zinc SX
Sierra Mojada, Mexico ¹⁵	-	Oxide	Sulphate leach, zinc SX
Accha, Peru ¹⁶	-	Oxide, carbonate	Chloride leach, zinc SX

Table II

Composition of furnace dusts and upgraded zinc solution produced by SX at Met-Mex Peñoles²²

Element	Blast furnace dust%	Reveratory furnace dust (%)	Upgraded zinc SX solution (mg/l)
Zn	10.6	15.6	95 000
Cd	23.8	1.1	128
As	1.1	8.8	<1
Pb	39.1	30.2	<2
Fe	0.1	0.1	<2
Cl	4.3	0.4	7
F	0.5	0.3	2

the surface and flashed down in pressure vessels to produce steam to drive electricity-generating turbines. Zinc is recovered from the brine before it is pumped back underground. Very hot geothermal brine (19 t/h) is passed through an ion-exchange column to adsorb zinc. A conventional anion-exchange resin (DOWEX 21K XLT) selectively complexes zinc, as it is unique among the species present in forming multivalent anionic complexes in brine solution; other elements remain in solution as cations. The resin is eluted with water. The application of reverse osmosis to the eluate produces a concentrated zinc solution that is purified by SX using D2EHPA, prior to EW to produce zinc cathode. The operation is expected to yield 30 000 t/a zinc¹⁷ in one of the cleanest zinc-recovery operations ever undertaken.

Secondary processing of zinc

Several pyrometallurgical processes have been implemented for the treatment of secondary materials, however, these are generally only efficient for a constant composition feed and need to have a high production capacity to be economically viable¹⁸. Some materials are not amenable to treatment by these routes, and environmentally acceptable discharges are not always assured. Hydrometallurgical processes are potentially less sensitive to these constraints; the most successful of these include an SX step to purify and upgrade the zinc.

TR has been at the forefront of developments in the processing of secondary zinc materials. Recycling plants, now closed, were built in Spain and Portugal based on their Zincex process^{19,20}. This was superseded by the Modified Zincex Process (MZP), which has found application and is the instrument of numerous new investigations into the treatment of secondaries such as Waelz oxides, galvanizing residues, and electric arc furnace dusts (EAFD)^{18,21}. The process uses D2EHPA for the selective extraction of zinc from the acidic sulphate liquor produced on the leaching of these

materials. Advantages claimed for the MZP include the high selectivity over species such as halides and magnesium, the production of an electrolyte from which SHG zinc can be produced, high zinc recoveries, and safe and environmentally friendly operation. Gypsum precipitation in the SX circuits remains a problem, with the production of 80 to 150 kg per tonne of material treated. However, by using a source of pure lime for neutralization in the SX circuit, 'white gypsum' can be produced, which may be sold for certain applications in the plasterboard industry.

Re-processing of furnace dusts

Electric arc furnaces produce 10 to 15 kg of dust per tonne of steel produced, representing one of the more contaminated zinc residues. The steel industry has approved the MZP as 'technically, economically and environmentally suitable for the solution of the EAFD problem'²¹. A project for the treatment of 82 000 t/a EAFD in Spain has been proposed, but to date this has not been implemented, despite several successful pilot-plant trials on different EAFD compositions.

Dust generated from blast and reverberatory furnaces at the Met-Mex Peñoles lead smelter in Torreón, Mexico, has since 1998 been treated in a zinc SX plant built at the site²². The material was previously recycled, causing saturation of undesirable species such as cadmium, arsenic, and halides in the main circuit. Installation of the SX plant is reported to offer operating, economic, and environmental advantages: greater flexibility now allows the treatment of 'dirty' lead concentrates; increased revenues are realized from the sale of impurity species recovered; and airborne dust generation has decreased. Production is 5000 t/a zinc cathode of 99.99% purity. Table II compares the composition of the high-impurity feed material with an assay of the upgraded zinc solution produced by SX.

Italian trials to recover zinc from EAFD by SX have also been reported²³. In this process, iron was not removed from the leach liquor prior to SX. Zinc and iron were co-extracted

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using D2EHPA; zinc was stripped with 1 M H₂SO₄ and iron was periodically removed from the organic phase by treatment with HCl. It was reported, however, that HCl stripping introduced partial degradation of the extractant, and a reductive stripping process for iron was under development.

Fluor Daniel Wright has also carried out development of an SX process to recover zinc from EAFD. The extraction of zinc chloride by ZNX 50 was evaluated²⁴.

Process residues and tailings

In 1988, Española del Zinc in Cartagena, Spain, integrated SX into a conventional zinc refinery flowsheet for the recovery of water-soluble zinc from stockpiled and fresh leach residues^{25,26}. The main refinery treats a mixed sulphide concentrate to produce 40 000 t/a zinc via a RLE circuit. The iron hydroxide precipitate exiting the primary leach circuit contains about 20% zinc. These solids are leached, along with previously dumped material, in a secondary leach using sulphuric acid and the loaded strip liquor generated in the SX plant. Iron is removed as ammonium jarosite. The secondary filtrate from the washing of the jarosite solids (containing 14 g/l Zn, 0.03 g/l Fe, 0.7 g/l Cu, 0.3 g/l Cd, pH 3) is not suitable for EW and is treated by SX to upgrade and purify the zinc into a concentrated (120 g/l Zn) strip liquor for recycle.

Zinc tankhouse bleeds

Most operating zinc refineries use precipitation methods for zinc purification, followed by metal recovery by EW. In such processes, there is usually a gradual accumulation of impurities in the electrolyte, especially of species such as magnesium and manganese. Since zinc EW is extremely sensitive to the presence of impurities, it is necessary to bleed the electrolyte to control the composition. Several studies have looked at the use of SX for the recovery of both sulphuric acid and zinc from this bleed. These have involved recovery from both sulphate media with D2EHPA²⁷ and from chloride media using tri-*n*-butylphosphate²⁸.

Zinc recovery from spent batteries

The R.F. Procés plant, commissioned in the Spanish province of Cataluña in 1997, is the only plant in the world applying a hydrometallurgical process to the recycling of spent domestic batteries. The MZP is applied as the core separation step, producing a high-purity zinc sulphate solution suitable for electrowinning SHG zinc metal²⁹. The loaded strip liquor is transported to Española del Zinc for zinc recovery.

A similar process for the recovery of zinc and other hazardous elements from spent batteries has been investigated in Switzerland. The initial flowsheet used D2EHPA for the purification of the leach liquor³⁰, however, it was found that the process was too difficult to operate continuously because of the fine pH control required. CYANEX 301 was also tested for this application³¹, and, although the extraction behaviour of this system was appropriate, the difficulties of stripping the irreversibly loaded copper and iron from the organic phase mitigated against it. The process has not been commercialized.

Another hydrometallurgical scheme for recycling of battery waste was developed by PIRA GmbH, Germany³².

The BATENUS process, which also used D2EHPA Sx for the recovery of zinc, was fully piloted and commercialization was expected in 1995; the reason why this did not go ahead is unknown.

Conclusions

The advantages afforded by hydrometallurgical processes that feature SX have only recently been realized in the zinc recovery industry. The commissioning of the Skorpion refinery, as the first plant to use SX for the recovery of zinc from a primary source, will add further impetus to this development. An increase in the application of zinc SX technology can be expected during the next decade, particularly in the processing of non-sulphide primary materials and for the treatment of an increasing variety of secondary materials.

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Business edge implements fingerprinting system for TEBA*

Business Edge Systems (BES) has been awarded the contract to develop and implement a fingerprint administration system for TEBA Limited that allows the company to capture and verify fingerprint forms. TEBA administers fingerprints for its mining clients and for Rand Mutual Assurance (RMA).

TEBA, a private company that provides employment support services to labour-intensive industries such as mining, construction and agriculture, currently verifies the annual Certificates of Life (COL) issued by insurance company, RMA. These certificates serve as confirmation for RMA to pay out pensions to mining industry employees injured in the course of their employment history.

TEBA required a database solution to serve RMA's needs cost-effectively and more efficiently, and rid TEBA of their backlog of outstanding fingerprint forms that still requires capture and verification. 'The old fingerprint verification system is not consistent with TEBA's new technology infrastructure, not supported and difficult to maintain. The fingerprint verification process is also extremely time consuming, the system is difficult to develop and extend, and not scalable to handle the large volume of requests we receive from different organizations,' says Wendy Kraemer, manager of Manpower Data Centre at TEBA.

The new fingerprint administration system project, managed by BES, is part of the company's ongoing system development at TEBA. Business Edge is designing and implementing the scalable fingerprint identification facility using Delphi and IBM's Universal DB2 on a Microsoft Windows platform. Being TEBA's preferred technologies, the solution will be simple to support and maintain by TEBA's in-house IT department. 'While the first phase of the fingerprint identification solution will still require manual intervention by TEBA technicians, it is designed with the aim of including further automation at a later stage using biometric technology,' says Karen Malkin, account director at BES. 'It does however, offer significant benefits, in its first phase. With the new system, TEBA will be able to verify that the unique fingerprints of the current RMA

pension recipients collected by TEBA field workers in rural communities match those of the workers originally captured on the old system,' she says.

New beneficiary details and fingerprint images can be effortlessly captured on the new system, and linked for future Certificate of Life verification. All unknown and mismatched data will be flagged for reporting to RMA. With TEBA's new verification system in place, RMA will be able to take the necessary steps to suspend, continue or commence the correct payment of pensions.

The new fingerprint administration system will allow TEBA administrators to log into a secure system that is access controlled. Personal data of workers, pensioners and dependants can be maintained and linked to fingerprint images and fingerprint classification codes. The new database will have extensive search capabilities that allow users to filter beneficiary information into different categories and classifications such as name, district, country, mine, closest TEBA office and specified classification codes of one or more fingers.

The software will be able to provide detailed reports of individuals, dependants and relatives, employment history, specific classification codes, search results, fingerprint images. The system will allow TEBA to print standard TEBA fingerprint forms for its field workers, and RMA can print and analyse information relating to COL information e.g. matches, mismatches and unknowns. 'The solution now being developed by BES allows TEBA and the RMA to retain control over their business processes which will be supported by the fingerprint administration system, taking advantage of TEBA's infrastructure. The projects duration is expected to be four months and will be completed in December 2002, concludes Malkin'. ◆

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