

Solvent Extraction Developments in Southern Africa

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Abstract: The largest solvent-extraction plant in the world at the time, the Nchanga Copper Operation, was in Zambia. The first commercial process using solvent extraction for the refining of the platinum-group metals was in South Africa. More recently, the Southern African region has seen the implementation of solvent extraction for other base metals, precious metals, and specialty metals. These include the world firsts of primary production of zinc at Skorpion Zinc in Namibia and the large-scale refining of gold by Harmony Gold in South Africa. Several other flowsheets that use solvent-extraction technology are currently under commissioning, development, or feasibility study for implementation in this part of the world, including those for the recovery of copper, cobalt, nickel, tantalum, and niobium.

Key words: solvent extraction; zinc recovery; gold refining; copper; cobalt; nickel

Introduction

Solvent extraction (SX) has been an integral part of the hydrometallurgist's arsenal in Southern Africa for many decades^[1]. In the early 1970s, several SX plants were built to recover uranium, commonly occurring with the gold-bearing minerals of the Witwatersrand reef in South Africa. AngloGold Ashanti's Vaal River South Uranium Plant is still operational today. The first primary uranium producer in Southern Africa was Rössing Uranium, Namibia. The construction of the Nchanga copper plant in 1973 in the Zambian Copper Belt marked the beginning of a new era for large-scale copper SX operations. This was the world's largest SX plant for more than a decade and remains operational. At the other end of the scale, the commercial refining of the platinum-group metals (PGMs) by SX was first implemented at Rustenburg, South Africa, in the 1980s. More recently, the region has seen commissioning of

the first plants for the primary production of zinc and for the large-scale refining of gold, both using SX technology. This review discusses some recent hydro-metallurgical developments involving SX in Southern Africa.

1 Primary Zinc Recovery

Anglo American's Skorpion Zinc refinery^[2], located in southern Namibia, produced its first metal in May 2003 and is currently approaching full production of 150 000 t/a. The oxidized silicate ore (also containing soluble chloride and fluoride minerals), not amenable to treatment by conventional processes, is viably treated in a purely hydrometallurgical processing route that includes the first commercial application of SX for primary zinc processing. A significant economic advantage is realized by the production of special high-grade (SHG) zinc cathode (>99.99% purity) at the mine site. Skorpion zinc promises to be one of the lowest cost zinc facilities in the world with an expected production cost of US\$ 0.25/lb.

Following atmospheric leaching with sulphuric acid,

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iron, aluminium, and silica are removed from solution by precipitation. Zinc is then selectively extracted by di(2-ethylhexyl)phosphoric acid (D2EHPA), enabling the electrowinning (EW) of SHG zinc. The SX step serves several purposes. The choice of a cation exchanger like D2EHPA ensures rejection of the halides as well as the base metals (such as Cu, Ni, Co, and Cd) that are deleterious to zinc EW. SX also upgrades the zinc from the relatively dilute leach liquor (30 g/L)—a consequence of the leach conditions dictated by the elevated silica content (~26%) of the ore—to an advance electrolyte containing in excess of 90 g/L Zn that is suitable for EW. Soluble losses of zinc in the filtration step are minimized, and the problematic formation of silica gel is avoided. Iron is prevented from entering the electrolyte as it will not be stripped with the return electrolyte, despite its elevated sulphuric acid content (180 g/L). The use of 40 vol.% D2EHPA allows high zinc transfer in the extraction circuit (~20 g/L) without the need for neutralization. This ensures that the acid generated by the extraction reaction is available for leaching upon recycle and minimizes co-extraction of calcium. Using a conventional mixer-settler design and a high-density polyethylene (HDPE)-lined concrete construction, the SX circuit comprises three extraction, three washing, and two stripping stages. The plant is the largest yet built for zinc SX, with an aqueous feed flowrate of 960 m³/h.

2 Gold Refining

The Minataur™ process is a novel route for the refining of gold, developed and commercialized by Mintek, South Africa. Gold-bearing materials are leached in HCl, and the leach liquor purified by SX. Gold recovery from solution is via precipitation with a suitable reducing agent, such as SO₂. Gold of 99.999% purity can be achieved.

The first refinery, established at Harmony Gold Mine in Virginia, South Africa, in 1997, processed gold slimes from the EW circuit (~80% Au, 8% Ag). The circuit was designed to produce 24 t/a high-purity gold. Following the significant commercial success of this project, the ease of operation of the process, and the forgiving nature of the technology, a new refinery was commissioned in 2001 which currently produces up to 400 kg/d of gold powder^[3]. The production of this high-purity gold on site at the mine has enabled a

variety of other value-added products to be manufactured, including ten-tola (1 tola=0.4114 oz) bars, gold granules, and gold potassium cyanide.

Other refineries have since been established in Algeria (25 kg/d Au) for the processing of doré bullion and in Dubai (100 t/a on a 12-hour shift per day) using jewellery and electronic scrap as the feed material.

3 Primary Copper Recovery

3.1 Bwana Mkubwa Mining, Zambia

Purchased by First Quantum Minerals (FQM) in 1996, the original Bwana Mkubwa copper mine in the Zambian Copper Belt started operations in the early 1900s. A small plant with an agitation leach followed by SX-EW was constructed and commissioned in 1998. By processing old tailings, this plant produced approximately 10 000 t/a copper cathode. In 2000, the rights to mine copper ore at the Lonshi deposit in the Democratic Republic of Congo were secured. By the end of 2002, the plant had been expanded to treat the Lonshi ore, with the major hydrometallurgical capital expenditure being for a second SX train, another EW tank-house, and a countercurrent decantation (CCD) circuit. Bwana Mkubwa also has two sulphur-burning acid plants to produce the acid required for the operation. Excess acid is sold to other local mining operations. The plant produces approximately 45 000 t/a copper cathode, and is currently one of the lowest cost copper producers^[4].

The ore is milled and dewatered before being leached using sulphuric acid and raffinate from the high-grade SX plant. The leach slurry is thickened and the overflow clarified in a Bateman pinned-bed clarifier before reporting to the 2E-1W-1S high-grade SX circuit. The mixer settlers are constructed of stainless steel. As the ore treated at Bwana Mkubwa has a high copper grade, the high-grade PLS can contain up to 10 g/L Cu. The organic phase employed is 25 vol.% LIX 984N in Shellsol 2325. The leach thickener underflow is washed in five stages of CCD using raffinate from the low-grade SX circuit. The washed residue is discarded and the CCD overflow is clarified in a second Bateman pinned-bed clarifier before being treated in the low-grade SX plant. The mixer-settler units in the low-grade SX plant are constructed of HDPE-lined concrete. The plant is operated in conventional series-

parallel mode with a single strip stage. The organic phase in this circuit is 26 vol.% LIX 984N in Shellsol 2325, designed to handle a typical PLS composition of 3.4 g/L Cu at pH 1.7.

3.2 Kansanshi, Zambia

The Kansanshi copper deposit, containing both oxide and sulphide mineralization, in the North West Province of Zambia was acquired by FQM in 2001. A plant to produce approximately 65 000 t/a copper cathode by agitation leaching of the oxide and SX-EW has been constructed. Commissioning of the SX plant (a fibre-reinforced polymer (FRP)-lined concrete construction) commenced in March 2005. The project will also produce 25 000 oz gold annually, as well as a saleable copper sulphide concentrate. Pressure leaching of the concentrate, that could potentially provide the acid required for the oxide leach step, is being engineered.

3.3 Mopani Copper Mines, Zambia

During 2004, Mopani Copper Mines (MCM) constructed and commissioned an SX plant at their Mufulira refinery to recover copper from old underground mining operations by an *in situ* leaching program. The leach produces a PLS of 4 g/L copper at pH 2. The SX plant (a stainless-steel construction) is a series-parallel configuration using 25 vol.% LIX 984N in Shellsol 2325. As more old stopes are brought into the leaching program, a further SX train will be added. The first train of the SX plant has been designed to recover 17 500 t/a Cu, at a design volume of 14 400 m³/d. Existing electrorefining tankhouse capacity has been converted to EW for this project. The SX-EW plant also recovers copper produced by vat leaching of oxide ores. This may include ores foreign to Mufulira in the future.

At least two further copper SX projects are in development by MCM. One will treat liquor derived from heap leaching of newly mined oxide material followed by EW. The other will see copper SX replace electrolysis for the decopperization of cobalt refinery feed.

3.4 Konkola Copper Mines, Zambia

Modernization of Konkola Copper Mine's Tailings Leach Plant (TLP), situated close to the town of Chin-gola in the Zambian Copper Belt (that originally in-

cluded the world's largest SX installation for copper), was completed in December 2003 and production is now 80 000 t/a copper cathode.

The most significant process issue in the SX plant is the formation of crud, attributed to the lack of adequate clarifying facilities downstream from the agitation leach. The suspended solids' concentration in the PLS ranges from 30 to 80 ppm, compared to < 20 ppm typical for heap leach operations. Both bottom and interfacial cruds are prevalent in the settlers. The cruds are treated in a newly installed Flottweg tricanter centrifuge. This produces a relatively dry solids stream as well as clear aqueous and organic phases. The solids are disposed of and the liquids returned to the SX circuit. Organic losses are predicted to be significantly lower in the future following the installation of the centrifuge.

Water balance issues at the TLP require a significant bleed of raffinate from the circuit. The feasibility of utilizing the acid contained in this solution in a heap leach operation to solubilize copper that will then be recovered by converting one of the SX circuits to a series-parallel configuration is presently being investigated.

3.5 Zenzele O'Kiep project, South Africa

A small but novel development is taking place at O'Kiep, site of one of the oldest copper mines in Southern Africa, located near Springbok in the Northern Cape Province of South Africa. The ore body, an oxidized deposit of copper carbonates and silicates, has been worked out as far as conventional mining is concerned. An initiative by Zenzele Technology Demonstration Centre (a non-governmental organization that assists artisan and small-scale mining operations) will extend the life of mine for about 20 years and benefit the indigenous population at the same time.

The hand-picked ore, containing about 5% copper, is crushed and then leached in sulphuric acid to yield a solution containing about 40 g/L Cu. The leach liquor is refined by means of SX (3E-1S) with 30 vol.% LIX 984N to separate copper from iron and other impurities. Using technology first demonstrated by Zenzele, the loaded strip liquor (LSL) then becomes the electrolyte in a special electrochemical cell designed to electroform a variety of copper artefacts. These include items such as bowls, ornaments, plaques, and jewellery,

which are sold to tourists and the export market.

4 Primary Cobalt Recovery

4.1 Kasese Cobalt, Uganda

Kasese Cobalt Company Ltd. treats a cobaltiferous pyrite concentrate stockpiled at the Kilembe copper mine in Uganda for the recovery of cobalt, copper, and nickel via a bioleaching route^[5]. Commissioned in 1999, the plant processed approximately 1 Mt/a pyrite until mid-2002, when production was suspended, due to low base metal prices. The plant was recommissioned in early 2004 and now produces 1000 t/a cobalt cathode.

Following solubilization of the base metals by bacterial oxidation, the bulk of the iron is removed in a two-stage neutralization circuit. The iron-free solution is processed through a first SX circuit (2 extraction, 1 scrub, and 2 strip stages) where zinc and some manganese are removed using 2 vol.% D2EHPA. After treatment of the raffinate with caustic soda to remove copper as the hydroxide, the solution is passed to a second SX circuit (4 extraction, 1 scrub, 3 strip, and 1 wash stages) in which cobalt is selectively extracted from nickel and magnesium using 7 vol.% Cyanex 272. This produces an advance electrolyte that reports to the cobalt EW circuit to produce cobalt cathode of >99% purity. The mixer settlers are Krebs units, manufactured of glass fibre and are completely enclosed to limit the evaporation of the organic phase (PLS temperature 40°C).

4.2 Chambishi Metals, Zambia

The Chambishi cobalt plant, near Kitwe in Zambia, treats two feed materials: a sulphide concentrate *via* a roast-leach process and a cobalt-rich copper slag *via* a smelt-pressure oxidation process (nominal production of 7000 t/a cobalt and 18 000 t/a copper). The initial flowsheet for the cobalt refinery comprised an extensive series of precipitation steps employing limestone and quicklime slurry to sequentially remove base metals from the cobalt electrolyte. The associated cobalt losses were high; furthermore, the increasingly stringent demands on the cobalt cathode purity could not be met. These problems were greatly alleviated by the implementation of SX (in 1991 with upgrade in 2001) and ion exchange (IX) steps for the removal of

zinc (D2EHPA) and nickel respectively from the cobalt solution^[6]. Chambishi is currently exploring the use of cobalt SX to improve overall plant performance and copper SX to deal with a possible increase in copper throughput to 40 000 t/a. Copper SX would replace the electrolytic process presently employed for decopperizing the cobalt refinery feed solution. Copper electrolysis produces a poor grade product and is expensive due to low current efficiencies. SX-EW will allow production of LME-grade copper cathode.

4.3 Knightsbridge Cobalt, South Africa

In 2001, Knightsbridge Cobalt Corporation upgraded their cobalt refinery (based on classical precipitation techniques) with the addition of two SX steps that enabled the production of high-grade cobalt oxide powder^[7]. Impurity elements such as Zn, Mn, and Ca are removed selectively from cobalt using 20 vol.% D2EHPA (3 extraction, 1 scrub, and 1 strip stages). Ni, Mg, and trace Zn and Fe impurities are rejected in a subsequent SX step using 15 vol.% Cyanex 272 to produce a substantially upgraded cobalt solution (5 extraction, 2 scrub, 2 strip, and 1 re-strip stages). This refinery ceased operation in 2002, but the plant was purchased by Umicore and relocated to Mogale City, South Africa, where operations continue today.

4.4 Kolwezi Tailings, Democratic Republic of Congo

The flowsheet developed to recover copper and cobalt from the Kolwezi copper flotation concentrator tailings includes several SX steps^[8]. The tailings are leached in a primary circuit to solubilize copper and cobalt, and copper recovered by SX-EW. A bleed of this circuit is treated in a secondary circuit to remove iron and manganese by precipitation with air/SO₂, followed by SX with Cyanex 272 to remove zinc, IX using an aminophosphonic acid cation exchanger to remove trace Cu and Zn, and finally the cobalt stream is upgraded by SX with Cyanex 272, enabling high-purity cobalt cathode to be electrowon. Current owners Adastra have recently secured finance for a feasibility study and preferred contractors have been selected. This project is expected to produce 40 000 t/a copper and 7000 t/a cobalt during the first phase, with possible expansion to double this capacity.

4.5 Kakanda Tailings, Democratic Republic of Congo

A similar processing philosophy has been proposed by International Panorama Resource Corporation to recover copper and cobalt from the Kakanda tailings^[9]. In a primary circuit, copper is recovered by SX-EW. A bleed is treated in a secondary circuit to produce 3500 t/a cobalt cathode. In contrast to the Kolwezi flowsheet, however, iron precipitation is followed by SX with D2EHPA to remove zinc and a large proportion of the manganese. The cobalt stream is upgraded first by SX with Cyanex 272, and then traces of copper and zinc removed from the LSL by IX ahead of cobalt EW.

5 Primary Nickel Recovery

5.1 Tati Nickel, Botswana

LionOre's Tati Nickel operates the Phoenix Nickel Mine and Tati Nickel Concentrator in Botswana. The sulphide concentrates produced are treated offsite. Tati is currently evaluating a proposed expansion that will include the incorporation of a hydrometallurgical refinery to produce 17 000 t/a nickel metal, 8000 t/a copper metal, 1240 t/a cobalt carbonate, and a PGM concentrate. Following Activox leaching of the concentrate, copper is recovered by SX-EW. A bleed of the copper SX raffinate is treated for iron removal in two stages. The first stage provides partial iron removal but essentially no loss of nickel or cobalt, while the second stage completes the removal of iron but precipitates significant amounts of cobalt and nickel and is recycled to the leach. The liquor is then purified by cobalt SX with Cyanex 272, followed by nickel recovery by SX with neodecanoic acid followed by EW. The cobalt product is initially expected to be CoCO_3 , with metal EW as a later option. A 1/170 scale demonstration plant is currently being operated on site for process optimisation and operator training for the full-scale plant.

5.2 Nkomati, South Africa

African Rainbow Minerals produce a nickel concentrate at the Nkomati complex in Mpumalanga, South Africa. Plans are underway to exploit the massive sulphide deposit by increasing the concentrator capacity. The on-site treatment of the

concentrates has been investigated. The flowsheet evaluated is similar to that proposed for Tati^[10]. A feasibility study has been completed for 375 000 t/m run-of-mine ore producing 16 500 t/a nickel metal, 7100 t/a copper metal, and 940 t/a cobalt as carbonate. LionOre has recently acquired 50% equity in Nkomati, and a synergy between the Tati and Nkomati projects is expected.

5.3 Ambatovy, Madagascar

Ambatovy, a saprolytic laterite deposit located in Madagascar under joint development by Phelps Dodge and Dynatec, could become one of the lowest cost nickel producers^[11]. A bankable feasibility study was completed in mid-2004 and the project is currently seeking finance to proceed. The metallurgy is very similar to that at Moa Bay, Cuba, and it is understood that the flowsheet will be similar to that of Murrin, Australia, where SX using Cyanex 272 is employed, firstly for zinc removal and then for cobalt-nickel separation.

5.4 Nickel and Palladium Recovery from Spent Catalyst, Mintek, South Africa

Spent hydrogenation (Ni) and petroleum (Ni/Pd) catalysts were treated at Mintek for several years for recovery of the valuable metals^[11]. SX with di-n-hexylsulphide was used to recover a high-purity palladium product. Premium nickel metal was produced by electroless plating, a technique that requires a high-purity nickel sulphate solution as feed. SX with D2EHPA was used to remove calcium and magnesium impurities from the nickel sulphate stream. An interesting feature of the circuit was the use of a nickel preloading step. Since the addition of a base to control the pH during extraction (necessary to efficient impurity-over-nickel separations) would have introduced undesired sodium or ammonium impurities into the nickel sulphate solution, the organic phase was preloaded with nickel *prior to* extraction.

5.5 Development of Novel Synergistic Nickel Extractant, Mintek, South Africa

Disadvantages of the use of carboxylic acid extractants for nickel include poor selectivity over calcium and the high pH levels required for efficient nickel extraction.

Aqueous solubility of the extractant increases significantly with pH. Mintek, South Africa, has introduced an organic system for nickel extraction that makes use of a nitrogen-donor compound in synergistic combination with Versatic 10 that overcomes these disadvantages by reducing the pH required for nickel extraction and increasing the nickel-over-calcium separation^[12]. Extensive continuous piloting of this organic system on various nickel-containing liquors has been undertaken with a view to commercial implementation of this system in the near future.

6 Primary PGM Producers

6.1 Hartley Platinum, Zimbabwe

Hartley Platinum at Selous, Zimbabwe, began operation in 1997, ceased operation in 2000^[13], and is presently being evaluated for re-opening by Impala Platinum. Platiniferous ore was concentrated and smelted to produce a matte that was the feed to the base-metal refinery. Nickel was leached in two stages of atmospheric and one stage of pressure leaching where the solids and liquids were fed countercurrently. The three stages ensured that >99.5% of the nickel, cobalt, and iron were dissolved with out dissolution of copper. Iron was removed from the nickel pressure leach liquor and copper was removed from the nickel sulphate solution that advanced to nickel EW by cementation onto the incoming matte in the first leach stage. Cobalt was removed by SX with Cyanex 272 *prior to* nickel EW. This was the first commercial plant to use this reagent in a PGM flowsheet. An impure cobalt carbonate was precipitated from the strip liquor.

6.2 Anglo Platinum Rustenburg Base Metals Refinery, South Africa

Anglo Platinum is the world's largest producer of PGMs. Sulphide ore (rich in both PGMs and base metals) from the Merensky and UG2 reefs in the Rustenburg area of South Africa is concentrated and smelted to produce a PGM-rich matte that becomes the feed to the Rustenburg Base Metal Refinery (RBMR). Following removal from the nickel leach liquor by oxidative precipitation with nickelic hydroxide, cobalt is further refined using D2EHPA to produce premium-grade cobalt sulphate. A planned increase in PGM production is requiring Anglo Platinum to explore options

for the expansion of RBMR. One option considers Cyanex 272 for recovery of cobalt from the nickel stream. This will require modifications to the downstream D2EHPA circuit to accommodate higher manganese levels^[14].

At Anglo Platinum's Precious Metal Refinery the processing of PGM concentrate to produce high-purity individual PGMs is based extensively on SX separations^[15]. These are for gold (using methyl-*i*-butylketone), palladium (using a beta-hydroxyoxime with an amine accelerant)^[16], platinum (using an amine), and iridium (using a novel amide extractant). The refinery is currently being debottlenecked and upgraded to accommodate a significant increase in PGM production (expected to be 3.5 million oz by 2010).

6.3 Impala Platinum Base Metal Refinery, South Africa

Impala Platinum's Base Metal Refinery in South Africa produces nickel, copper, and cobalt as by-products from a PGM-containing matte using a process that relies on inefficient base-metal amino chemistry to achieve separation of nickel and cobalt. A new refinery flowsheet, featuring zinc and cobalt SX steps using Cyanex 272, was developed to accommodate a mixed nickel-cobalt sulphide concentrate that was to be produced from the Philnico deposit in the Philippines^[5]. Although the Philnico prospect is no longer an option for Impala, the flowsheet may still be considered for other opportunities. A major advantage of the flowsheet is improved overall cobalt recovery due to the introduction of the SX steps.

7 Tantalum and Niobium

7.1 Tantalite resources, South Africa

A small operation at Isithebe on the KwaZulu-Natal north coast of South Africa is recovering tantalum and niobium from mineral sands originating in Mozambique. Plant design capacity is 90 t/min ore, grading approximately 30% Ta₂O₅. The process consists of multiple stages, including published technology^[17] and some unique technology developed internally. The ore is leached in concentrated hydrofluoric acid. Tantalum is then extracted selectively from the leach liquor. Co-extracted impurities are scrubbed

from the loaded organic phase, before tantalum is stripped and precipitated from the organic phase. Calcined product purity of >99.99% has been achieved. Selectivity from impurities such as Si, Fe, Ti, Mg, and Mn is obtained. High-purity Ta₂O₅ is currently being produced (360 t/a), with high-purity Nb₂O₅ expected to follow shortly.

7.2 Tantalum Exploration, South Africa

Another small operation east of Johannesburg similarly processes minerals sands and clays originating from South Africa, Mozambique, and Cuba to produce high-purity tantalum and niobium products. Following solubilization in HF, tantalum is separated from niobium by SX using methyl-*i*-butylketone.

8 Conclusions

During the 1970s, Southern Africa witnessed the birth of many of the early commercial SX processes, including those for copper, uranium, and the precious metals. The past decade has again seen a burgeoning of SX technology with the commissioning of the Skorpion Zinc, Harmony Gold, and Kasese Cobalt operations, as well as circuit upgrades at various sites. The Zambian Copper Belt is currently experiencing renewed interest in SX for copper recovery. A variety of new projects are at advanced stages, and several new base-metal circuits are expected to come on-line within the next few years.

The Southern African subcontinent has one of the highest concentrations of mineral wealth anywhere, and the value-added recovery of a multitude of industrial minerals and metals is expected to increase into the future. The choice of SX as a processing option is likely for many systems which employ aqueous metallurgy, rather than pyrometallurgy. An interesting future ahead for SX technologies in this part of the world is predicted.

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