Physicochemical Problems of Mineral Processing, 42 (2008), 29-36
Fizykochemiczne Problemy Mineralurgii, 42 (2008), 29-36

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GROWING ROLE OF SOLVENT EXTRACTION IN COPPER ORES PROCESSING

Received May 15, 2008; reviewed; accepted July 31, 2008

Heap leaching of oxide copper ores and cathode copper recovery by solvent extraction (SX) and electrowinning (EW) has been well established as a primary low-cost hydrometallurgical copper recovery method. Subsequently, hydrometallurgy was also gradually developed and applied for sulphidic ores and concentrates. Presently, more than 20 % of total world production of copper is achieved through the solvent extraction route. The success of this method led to a significant revival in the development of hydrometallurgical processes to recover copper from ores both sulphidic and oxidized. This work reviews the major problems related to solvent extraction from pregnant leach solutions (PLS) after leaching oxide and sulphide copper minerals.

key words: heap leaching, extraction, electrowinning, copper oxide, copper ore, sulfides

INTRODUCTION

At present, there are basically two main methods employed world wide in order to process copper ores for metal production. The most important one is the “conventional” - pyrometallurgical method, comprised numerous types of shaft and flash technologies, which consists of crushing, grinding, flotation, smelting-refining and electro-refining. This method is applied to sulphide flotation concentrates rather than ores and is economically feasible for copper rich feed and for large scale operations.

A second method, “hydrometallurgical”, is applied to the rest of the world’s primary copper production. Hydrometallurgy consists of crushing, leaching (non-oxidative leaching, atmospheric leaching and pressure leaching), solvent extraction and electrowinning. Hydrometallurgical processing can be effectively applied for oxi-

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dized ores, containing CuO, Cu_2O, carbonates and some silicates, as well as for sulphide ores with chalcopyrite as a predominant copper mineral. Hydrometallurgical methods are used in countries having readily available deposits with low copper content and with surplus of oxidized forms at the same time (USA, Chile, Australia, and Peru). Recently, observed is a considerable intensification in research and development of hydrometallurgical ore, by-product and concentrate treatment as alternative to traditional pyrometallurgical processes for sulphidic ores and concentrates, particularly for small scale production and for remote metal resources - not acceptable by pyrometallurgy.

Hydrometallurgy has been used for copper recovery for more than 300 years. The most important development in copper hydrometallurgy, with respect to the growing number of its applications as well as for its future potential, has been solvent extraction. It became the achievement which revolutionized copper production all over the world and enabled to introduce hydrometallurgy for industrial scale. First SX small scale plants started in 1968 and already in 1974 copper production was expanded to a large scale of about 0.1 Tg/year (Szymanowski, 1996).

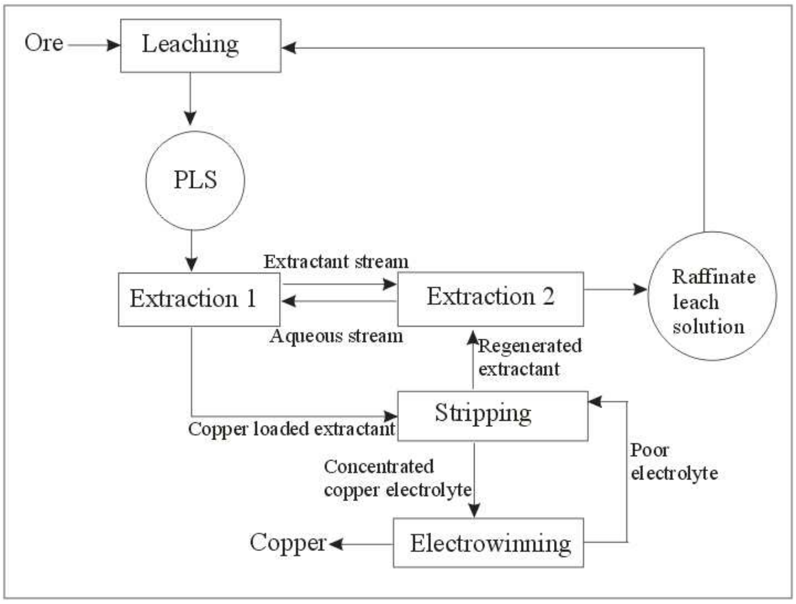

Fig. 1 Typical flow-sheet diagram of LX/SX/EW plant (Bergh and Yianatos, 2001)

Figure 1 shows a typical flow-sheet of hydrometallurgical copper processing, which consists of three fundamental unit operations:

- leaching of copper ore with a week acidic solution, which usually is sulfuric acid,

- solvent extraction, in which the aqueous pregnant leach solution (PLS) is vigorously mixed with an organic solvent, selectively recovers copper from PLS, being acidic or ammonia solution. The organic solvent is then separated and the copper stripped from it with a fresh acidic solution to produce a highly concentrated, relatively pure copper liquor suitable for the final step–electrowinnig or precipitation,
- electrowinning, where copper-rich solution is filtered to remove entrained organics, heated, and then passed through a series of electrolytic cells to form high quality cathodes, which are the market deliverable product (Bartos, 2002).

According to International Copper Study Group data, during the last decade world copper mine production increased by 30 %, from 11.5 Tg (million metric tones) in 1997 to 15 Tg in 2006. Simultaneously, production of copper in concentrates rose by 24 % while production by solvent extraction–electrowinning (SX/EW) rose as high as by 63 % (Fig. 2) (ICSG, 2007).

Furthermore, world mine production in 2007 increased by 3 % to 15.5 Tg and it is expected to increase in 2008 by 6 % to 16.4 Tg, and in 2009 of 1.5 Tg (9 %) to 17.9 Tg owing to mine developments and increased capacity utilization. For 2007–2009 higher growth rates are expected for SX/EW production (about 4.5 Tg in 2009) (ICSG, 2008).

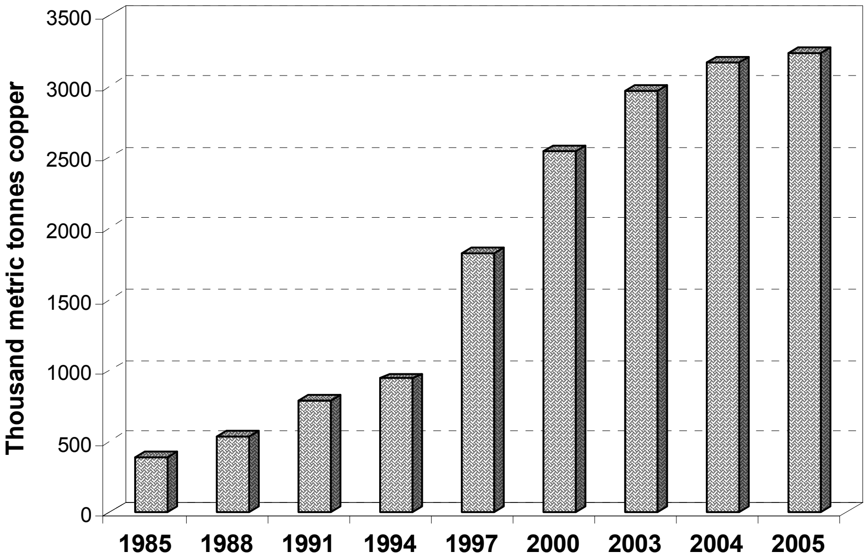

Fig. 2. World trends in SX capacities for copper from 1985 to 2005

Therefore, an enormous role of solvent extraction in growing copper production can be clearly seen. Moreover, the application of SX/EW technique for processing of waste oxide copper ores appeared to be the most economical process for copper production in the world. Typical cash operating costs for mine/heap leach/SX/EW operations are in the range of \$0.40-0.55 US/lb Cu, depending on ore grade, mining costs, Cu recovery, acid requirements and power costs (Peacey et al., 2008)

RESEARCH AREA

Implementation of hydrometallurgical technique for copper production, using solvent extraction on an industrial scale, has strongly stimulated studies on synthesis of novel extractants as well as on the extraction process. Solvent extraction provides a possible process whereby a pure feed to electrowinning could be obtained if an appropriate copper extractant is available. Until now, the most popular and unbeatable copper extractants are hydroxyoximes. It results from a number of their advantages in terms of fast extraction kinetics and high extractant strength, allowing the extraction of copper from highly acidic PLS with good selectivity over iron(III). However, increasing the extractant strength increases the acid strength required for stripping. Thus, it is not acceptable to most copper producers because the acid concentration is too high for electrowinning purposes.

To overcome these difficulties different types of modifiers can be added. Although, it ought to be mentioned, that the use of modified extractants results in more SX circuit cross –contamination and worse selectivity than it was reported for unmodified extractants. High Cu/Fe rejection ratio is very desirable feature of all copper extractants, because the appearance of iron in the tankhouse results in low current efficiency for the cathodic deposition of copper.

All advantages and disadvantages must be taken into account when selecting the best copper extractant for any particular application. It is important that each reagent should accomplish the basic requirements, listed below:

- good ability to extract the metal at the required pH
- selectivity for the required metal and rejection of undesired metals
- acceptable rates of extraction, scrubbing and stripping
- good solubility in the organic phase and restricted solubility in the aqueous phase
- high stability throughout the principal stages.

Besides finding an appropriate extractant, there are also other problems related to SX plants, like crud formation and entrainment. There is still no possible to fully eliminate these problems but scientists still work on minimizing the unwanted effects on extraction efficiency.

At present, the most up-to-date problem is application of solvent extraction for copper processing from sulphide ores. The success of SX plants in the copper recovery system results from easy leachability of oxide ores, while the main obstacle for application of hydrometallurgy for sulphide ores processing is difficulty of their leaching, relevant to scarce solubility of copper sulphides, particularly chalcopyrite. Therefore the efforts of scientists are focused mainly on finding the best efficient leaching method and then liquid-liquid extraction from received pregnant leach solutions.

DISCUSSION

At the beginning, hydrometallurgy based on solvent extraction, could not compete with conventional copper recovery methods based on smelting because the quality of copper produced was lower than that produced by smelting followed by electrorefining. By 1977, the SX/EW process had improved to such extent that most production now resulted in high-quality cathode that could be directly used by wire rod plants, without further refining. This made the SX/EW process superior to cement copper in terms of product quality and costs, production of SX/EW copper rapidly increased. When the major breakthrough of a flexible extractant was developed, there rapidly followed a whole series of minor improvements, all of which contributed significantly to SX/EW's overall productivity. New organic extractants greatly reduced iron adsorption and allowed for a much wider range of copper concentrations (Bartos, 2002).

The greatest contribution in achievements of solvent extraction provided extractants based on hydroxyoximes. As they were synthesized there were no better copper extractants, and since then all investigations were performed in order to improve their properties. The very important issue for researchers has been an increase of extractant strength and consequently an improvement of stripping efficiency. Initially, different mixtures of extractants were used, for example Cognis reagent LIX 64N (blend of LIX 64 and LIX 63). LIX 64 alone was able to extract copper selectively from iron in the pH range 1.5-2.5, but with the disadvantage of slow rate of extraction. This was solved by the addition of a small amount of LIX 63. The mixture, LIX64N, for many years was the extractant of choice for commercial copper extraction from acidic leach solution (Szymanowski, 1993).

Other extractants, based on organophosphorus compounds (Cyanex series of extractants), were also widely tested for copper recovery, but the results could not be accepted for further applications. It was shown that in order to achieve a reasonable level of copper stripping from Cyanex 302 13.5M acid was required, and in the case of Cyanex 301 even the use of concentrated (18M) H_2SO_4 did not strip copper from organic phase (Sole, Hiskey, 1995). From other paper it was clear that among all Cyanex series only Cyanex 272 can be successfully used in hydrometallurgy but only for the separation and recovery of cobalt from nickel (Flett, 2005).

As mentioned previously, to solve problems related to stripping performance the addition of modifiers to organic phase was necessary. Such modified "blend" results in a mixture that is a weaker extractant while at the same time it is easier to strip with conventional electrowinning electrolytes. As an example Avecia with their Acorga reagents have showed that addition to the hydroxyoxime of nonyl phenol, tridecanol or alkyl esters improves the stripping performance, with only little effect on extraction (Cox, Musikas, Chopin, 2004). However, what should be strongly pointed, some deleterious problems appeared, related to addition of modifiers. The very important ones are crud formation and entrainment, which result in greater contamination of electrolyte with leach solution, greater losses of extractant and solvent from the extraction circuit and worse selectivity (Merigold, 1996).

To cope with these problems a new innovation was established by Outokumpu Oyj in Finland – the Vertical Smooth Flow (VSF^{TM}), mixers which have been extensively piloted at Chuquicamata and are said to significantly reduce the amount of entrainment in the raffinate stream. The basic idea of the VSF^{TM} technology is to maintain smooth agitation throughout the SX plant to avoid oxidation of organic and development of overly small droplet size in dispersion. These principles give Outotec's SX plant the flexibility to run in widely varying conditions and to have high trough output with very little organic losses and crud formation (Outotec Oyj., 2007).

All the issues discussed above, were related to solvent extraction from solutions after leaching oxide ores. The real question is what will differ in the case of sulphide ores? If there will be any new problems, what should be taken into account? Copper sulphide minerals are not readily leached by conventional heap leach methods and require more vigorous or non-conventional conditions (the presence of oxidant or bacteria) for effective copper recovery. To solve this problem a lot of processes using different leaching agents (bacteria, sulphate, sulphate/chloride, and halides) have been developed in order to process sulphide copper ores: BioCop, Bactech/Mintek, CESL, Albion, Sepon, Mt. Gordon, HydroCopper (Peacey et al.; Dreisinger, 2006). There is, however, no hydrometallurgical technology which could be directly used for processing sulphidic copper ore, by-product or concentrate from each deposit.

At present a lot of attention is bestowed upon bioleaching methods. There are several examples of industrial bioleaching operations in Chile (Quebrada Blanca operation), USA and Australia (Girilambone Mine) (Dresher, 2004). Other solution was provided in Konkola Deeps sulphide deposit in Zambia (Avecia Notes, 2003). The sulphide material was concentrated by flotation up to 40-45 % Cu and then subjected to a high pressure acid leach. The autoclave liquid discharge contained 60 g/dm^3 Cu and 5 g/dm^3 H_2SO_4. This enabled the pregnant leach solution to be purified directly by means of SX. Another method applied for sulphide ores is total pressure oxidation process (commercialized by Phelps Dogde in 2007), which uses high temperature and pressure oxidation conditions to oxidize all sulfide minerals. The autoclave stream is merged with stockpile leach solution stream to provide a combined PLS feed to the SX/EW facility. The process has been commercially demonstrated at a large-scale and should be regarded as a “proven” technology (Dreisinger, 2006).

The development of new leaching technologies for sulphide ores has also necessitated requirements for solvent extraction of copper from more concentrated feed solutions. Until recently, typical leach solutions contained 0.5 to 8 g/dm^3 Cu at 15 to 25 °C. Leaching of high grade copper sulphide ores and copper concentrates result in leach solutions having 15 - 60 g/dm^3 Cu and 2-50 g/dm^3 sulphuric acid, at high temperatures. Therefore, significantly higher reagent strengths are required to achieve recoveries comparable to those obtained for conventional heap or dump leach liquors.

Other challenges for the solvent extraction reagents can include higher impurity levels and higher solution temperatures tolerance (Kordosky et al., 2006). The best reagent to achieve this for a number of years was Acorga P - 5100 but in recent years it has been replaced with new Acorga reagents such as M5640 and PT5050 both of which exhibit better selectivity and higher recovery characteristics. This new class of modified aldoxime extractants has greatly contributed to the growth trend in SX/EW technology. Extensive pilot plant studies and existing operations have demonstrated that current copper solvent extraction reagents are suitable for use with concentrated feed solutions but further investigations are necessary to establish optimal conditions of solvent extraction processes in copper ore processing.

SUMMARY

The leaching and SX/EW technique has been rapidly developing world-wide technology for copper production in recent years. For many years this technology was related mostly to oxide copper ores, but recently we can observe a growing interest in application of this method also for sulphide ores, by-products and concentrates processing. The success could not be obtained if there will be no good leaching method for this sulphidic material. With the recently developed technologies that are now under investigations in demonstration plants and ongoing research into improved technologies, we can safely predict that solvent extraction will eventually contribute to an increasing fraction of the copper produced each year not only from oxide but also from sulphide ores.

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Rotuska K., Chmielewski T.,*Rosnąca rola ekstrakcji rozpuszczalnikowej w przetwarzaniu rud miedzi,* Physicochemical Problems of Mineral Processing, 42 (2008), 29-36 (w jęz. ang)

Ługowanie na hałdzie (heap leaching) tlenkowych rud miedzi i odzysk miedzi w postaci katodowej na drodze ekstrakcji rozpuszczalnikowej (SX) i elektrolizy (EW) zostało uznane za podstawowy i ekonomicznie atrakcyjny hydrometalurgiczny sposób wytwarzania metalu. Hydrometalurgia miedzi została mocno rozwinięta w ostatnich latach również do przetwarzania siarczkowych rud i koncentratów. Obecnie, ponad 20 % światowej produkcji miedzi ma miejsce przy zastosowaniu metod hydrometalurgicznych, stosujących ekstrakcje rozpuszczalnikową. Osiągnięcia nowych technologii hydrometalurgicznych doprowadziły do znacznego ożywienia badań nad alternatywnym do hutniczego odzyskiwaniem miedzi z jej surowców tlenkowych i siarczkowych. Niniejsza praca jest przeglądem zasadniczych problemów związanych z ekstrakcją miedzi z roztworów po ługowaniu tlenkowych i siarczkowych minerałów miedzi.

słowa kluczowe: ługowanie na hałdzie, ekstrakcja, tlenki miedzi, ruda miedzi siarczki