

SOLVOMETALLURGICAL METHODS IN THE TREATMENT OF RARE AND NON-FERROUS METAL RAW MATERIALS

A.M. Chekmarev¹, S.V. Chizhevskaya¹, E.P. Buchikhin² and M. Cox³

¹The Chair of Rare and Dispersed Elements, D. Mendeleev University of Chemical Technology of Russia, Miusskaya sq., 9, 125047 Moscow, Russia, e-mail chekmarev@rctu.ru; chizh@rctu.ru

²Department of Geotechnology, The All-Russian Research Institute of Chemical Technology, Kashirskaya Avenue, 33, 115230 Moscow, Russia, e-mail: buchikhin@mail.ru

³Department of Physical Sciences, University of Hertfordshire, Hatfield, Hertfordshire AL10 9AB, UK, e-mail: M.Cox@herts.ac.uk

ABSTRACT

This paper discusses the position of the current state of rare and nonferrous metal raw materials and the role of solvometallurgical techniques in metallurgical development as well as the advantages of solvometallurgy for treatment of certain types of raw material. In this context solvometallurgy is defined as processes using non-aqueous solvents as the reaction media.

INTRODUCTION

The general history of metallurgy is easy to trace by considering the "solution tree" (Canterford,1985), which reflects possible routes for processing of complex ore concentrates (Pb, Cu, Ni).

Pyrometallurgy (from the Greek "pyr" – fire) is historically the first technique for the recovery of the first non-native metal used by mankind: copper. Thus this time of evolution of civilization was designated as "chalcophile" (Greek *chalkos* – copper and *lithos* – stone) or "aeneolite" (Latin *aeneus* – copper). Copper stone (copper nuggets) was successfully utilized by ancient people. As the collection of native copper did not readily satisfied the human demand for metalware, the "Bronze Age" followed the "Copper Age".

The roasting of sulfide copper ores usually occurring in combination with tin and lead sulfides led to formation of bronzes. These alloys had significant advantages over pure copper.

Iron was introduced in the same way, from native metal to ore refining processes. The more complex recovery of this metal from the ore by carbon reduction instead of simple roasting, was the reason that the "Iron Age" started later at the beginning of the first

millennium BC. Metals such as Cu, Fe, Ag, Au, Sn, Pb, Hg, are linked by the common feature of occurring in the native state and/or production solely by pyrometallurgy. Development of ore enrichment processes allows the continued current use of pyrometallurgical techniques. However the exhaustion of the abundant deposits required the need to use low-grade oxide ores that were difficult to enrich. This situation led to the development of **hydrometallurgical** methods where recovery of metals from the ore is carried out by aqueous solutions or, in a number of cases, by other solvents within the temperature range of 20-250°C (Canterford,1985). This is a significantly lower temperature than pyrometallurgy (600-2000°C) which leads to a decrease of the rate of the chemical reaction.

The industrial use of hydrometallurgy covers approximately five centuries compared to about sixty centuries of pyrometallurgy.

Evolution in the production of copper provides a typical example for the development of hydrometallurgy. The decrease in copper content of the ores from 4%, at the beginning of XX century, to currently ~0.6% as well as a change in the nature of ores requires the use of hydrometallurgy to treat these lean concentrates by acid decomposition and separation of the dissolved metals by liquid extraction. Such technology is also required for many other non-ferrous metals. Nevertheless, even today the potential for the pyrometallurgical route is not exhausted.

The historical succession of blooming and refinery processes, the blast furnace process for pig iron production, puddling, open-hearth, converter processes, arc and RF furnaces, electroslag, plasma and electron beam techniques along with advances in ore benefaction allows pyrometallurgy to be dominant in ferrous metallurgy. Currently, iron, pig iron and steel comprises more than 95% of all smelted metals. Development of the direct reduction technique for iron confirms the

SOLVOMETALLURGY AS A CONSTITUENT OF EXTRACTIVE METALLURGY

evolutionary progress of the technology. However, even in case of iron, hydrometallurgy is gaining a significant place where extremely pure metal can be obtained by liquid-liquid extraction.

Started from XVII century the studies on discovery of new elements led to a significant increase in the catalogue of metals produced in XIX-XX centuries. Some of these metals are extremely rare and widely dispersed occurring as admixtures in minerals and ores of more geochemically common elements. Application of hydrometallurgical techniques became inevitable. The need for rapid development in uranium technology led to a vigorous impact in the improvement of the technology and forced investigators to look for new ways to perfect the processes. Thus techniques of subterranean leaching, synthesis of adsorbents and extractants received their impetus from the needs of the uranium industry.

A comparative analysis of modern technology of rare metals allows the conclusion that flow-sheets involving both hydro- and pyro-metallurgy means are both advancing in parallel and often are combined. Thus the hydrometallurgical process of leaching frequently follows the pyrometallurgical processes of sintering or roasting. Similarly the production of crude metal by pyrometallurgical reduction is combined with subsequent electrowinning. Such mixture of hydro- and pyro-metallurgy is generally designated as extractive metallurgy and the topic features in handbooks, monographs and conferences (Hayes,1985; Extractive Metallurgy of Nickel,1985; Wadsworth,1983; Warren,1984).

The process of dwindling resources and the transition to more complex ores continues in spite of sporadic pleasant exclusions such as the discovery of ore layers with more than 10% uranium content in Canada and Australia. What are the ways to remedy these difficulties?

Canterford (Canterford,1985) suggested the abandonment of the most lean and complex ores until a further evolution in extractive metallurgy had taken place. In the author's opinion the application of non-aqueous solvents for recovery of metals from ore and secondary raw material can provide a promising route in a number of cases.

Currently there are many processes described for the recovery of metals from natural and technogenic raw material using non-aqueous media. The number of such processes is so great that from logical viewpoint it is not worth classifying them as hydrometallurgical (Greek "*hydor*" – water) (Canterford,1985). In a number of papers (Chekmarev et al.,1998;1999;2000;Chekmarev, Chizhevskaya and Buchikhin,2000) we have suggest the segregation of these processes into a separate branch of metallurgy which could be called **solvometallurgy** (Latin "*solvo*" – dissolve). The English word "solvent" includes many different classes of reaction media, including water. Thus hydrometallurgical processes using water as a solvent could be considered as particular example of solvometallurgy. Isolated examples of solvometallurgical processes have been known for some time. Actually the process virtually coincides with the development of the solvent extraction of inorganic compounds. Thus in 1842 a French chemist E.M. Peligot established that uranyl nitrate $UO_2(NO_3)_2$ could be dissolved not only in water but also in diethylether. Here dissolution in ether is a typical process of solvometallurgy whereas distribution of uranium between ether and water is an example of a liquid-liquid extraction process used in hydrometallurgy (McKey,1971).

It appears to be symptomatic that the development of uranium technology stimulated the improvement of hydrometallurgical processes and led first to the testing of uranium non-aqueous leaching direct from different raw materials. As early as the end of 1940's this revealed a reduction in the cost of uranium ore treatment (Ewing et al.,1955; Foley and Filbert,1957; Galvanek and Kaufman 1949;1950; Galvanek and Pelland,1955; Magner,1957; Magner and Bailis,1959).

Uranium extraction from carnotite ores with a 10% solution of a mixture of mono- and di-isooctyl esters of phosphoric acid (IOPA) in isopropyl ether acidified by sulfuric acid allowed the selective extraction of uranium into the organic phase and halved the consumption of H_2SO_4 (Magner,1957; Magner and Bailis,1959). When uranium minerals containing U(IV) as well as large amount of calcite occurred in the ore recovery can be improved by oxidization roasting at 700°C. A variation of this process involved the leaching of uranium by a combination of non-aqueous solvent with acid in the mixing step (acid-bath technique). According to (Galvanek and Kaufman 1949;1950; Galvanek and Pelland,1955) the ore was mixed with concentrated

H₂SO₄, aged, treated with nitrate and extracted by TBP in hexone. In other examples (Ewing et al,1955; Foley and Filbert,1957) the ore (-10 mesh) was treated by an acid (HCl or HCl/H₂SO₄ mixture) in a rotating tube and dried at 100°C. The product was extracted by acetone extraction at a phase ratio S:L = 1:1 in a scraping type extractor. In the lower part of this extractor the process of extraction took place and then, in the middle, uranium was extracted completely from the solid phase by fresh portions of acetone and finally, in the upper part, which was heated by steam, evaporation of acetone occurred. The acetone vapor was condensed and returned to the cycle. The general extent of uranium extraction to acetone was 91-92%.

Another example of the industrial use of solvometallurgical methods is found in lithium chloride processing. It is well-known, in contrast to the other alkali metal chlorides, that lithium chloride is soluble in many organic solvents, in particular, in alcohols forming stable solvates such as LiCl·3CH₃OH; LiCl·4C₂H₅OH, etc. In one of the technological schemes used in a German plant a mixture of the dry chlorides is treated with absolute alcohol, with the result that NaCl and KCl remain in the residue, and LiCl, together with CaCl₂, goes into solution (Ostroushko et al.,1960).

There are many other examples of solvometallurgical systems which deal with extraction and purification of rare, non-ferrous and precious metals by low-temperature halogenation in non-aqueous solvents (Buchikhin et al.,1999).

In a number of methods the efficiency of solvometallurgical approach was significantly improved by combining with mechanochemical techniques and mechanical activation. As an example, the successful use of one of the most widespread anhydrous solvents, concentrated H₂SO₄, to develop an ecologically safe variant of sulfatization of mechanically activated oxide rare metals raw materials has been described (Chizhevskaya et al.,2000).

Solvometallurgical techniques are promising to treat those types of raw material, which form stable non-filterable pulps, in particular pulps with high silica content. The results of the extractive leaching of rare elements from eudialyte, a zirconosilicate of complex composition easily decomposed by mineral acids, using 100% tri-n-butylphosphate (TBP) saturated with concentrated HNO₃ have been described (Chizhevskaya et al.,1994;1996;1998). Taking into account the complex composition of the mineral, which includes along with the metals Zr, Hf, rare earths, Nb and Ta, large amounts of silica, (≥50% SiO₂), to obtain easily filterable pulps by traditional processing requires a large expenditure of acid, high temperatures and long processing times.

The extractive leaching of mechanically activated eudialyte concentrate by 100% TBP saturated with concentrated HNO₃ allows the selectivity of the process to be improved as well as eliminating the formation of a non-filterable silica gel (Chizhevskaya et al.,1996;1998;2000).

Flow-sheets based on a combination of hydro- and solvo-metallurgical techniques have been successfully used for the recovery of metal values from secondary scrap material. Various techniques for the separation and recovery of non-ferrous metals from ash, flue dusts and cementation residues by extractive leaching using Versatic acid have been described (Thorsen et al.,1984).

The versatility of conducting a metal recovery process from ore and secondary technogenic materials allow the conclusion that the economical shortcomings related to the decreasing quality of natural raw materials will be successfully overcome. Undoubtedly, techniques that combine pyro-, hydro- and solvo-metallurgical processes provide the way forward. The extension of the scope of such combined processes, which in essence, are quite different, will guarantee further improvements in extractive metallurgy and will significantly alter the convenient practice of treating primary and secondary raw materials.

The peculiarities of the processes in non-aqueous media will be discussed in the presentation. Special attention will be paid to the shortcomings of the known solvometallurgical techniques of extractive leaching and the ways to remedy them.

ACKNOWLEDGEMENT

The studies on solvometallurgy have been supported by ISTC (Grant 1332-99).

REFERENCES

- Buchikhin, E.P., Kuznetsov, A.Yu., Chekmarev, A.M. et al. Interaction of Metallic Palladium with Iodine in Dimethyl-formamide. *Koord. Khim.*, v.25, N6, p.444, 1999. (Russian)
- Canterford, J.H. *Hydrometallurgy: Winning Metals with Water*. Chem.Eng., p.41, 1985.
- Chekmarev, A.M., Buchikhin, E.P., Chizhevskaya, S.V. et al. Solvometallurgy – New Direction of Metallurgy of XXI Century. In: *Proc. Int. Conf. Metallurgy of XXI Century: A Step into Future*, Krasnoyarsk, p.22, 1998. (Russian)

- Chekmarev, A.M., Chizhevskaya, S.V., Buchikhin, E.P. Solvometallurgical Method for Treatment of Minerals and Technogenic Materials of Rare and non-Ferrous Metals. In: R.Ramachandra Rao (Editor), A compendium of papers. Indo-Russ. Microsym. Nonferrous Extractive Metall. in the New Millennium. Nat. Metall. Lab., Jamshedpur, India, p.49, 1999.
- Chekmarev A.M., Chizhevskaya S.V., Buchikhin E.P., Cox M. Solvometallurgy – One More Independent Branch of Metallurgy? In: M.Sanchez (Editor), Proc. V Intern. Conf. on Clean Technologies for the Mining Ind., Santiago, Chile, v.2, p. 215, 2000.
- Chekmarev A.M., Chizhevskaya S.V., Buchikhin E.P. Solvometallurgy – New Direction of Metallurgy of XXI Century. *Khim. Tekhn.*, N10, p.2, 2000 (Russian)
- Chizhevskaya, S.V., Chekmarev, A.M., Klimenko, O.M. et al.: Non-traditional methods of treating high-silicon ores. In: Proc. of Hydrometallurgy'94, Cambridge, England, Chapman and Hall, London, p.219, 1994.
- Chizhevskaya, S.V., Povetkina, M.V., Chekmarev, A.M. and M. Cox. Extractive Leaching of Zirconium and Rare Earths from Solid Compounds. Proc. ARS Separatoria, Minikovo, Poland, p.69, 1996
- Chizhevskaya, S.V., Chekmarev, A.M., Povetkina M.V. et al. Effective Methods for the Hydrometallurgical Treatment of Mineral Ores with High Silicon Content. In: M.Sanchez (Editor), Proc. V Intern. Conf. on Clean Technologies for the Mining Ind., Santiago, Chile, v.2. p.523. 1998.
- Chizhevskaya, S.V., Chekmarev, A.M., Cox M. et al. New Extraction Technologies for the Treatment of Rare Metal Raw Materials Using Mechanochemistry Methods. Proc. ISEC'99, Barcelona, Spain. Soc. Chem. Ind. v.1, p.805, 2000
- Chizhevskaya, S.V., Petrova, N.V., Chekmarev, A.M., Panov, V.A. Environmental Improvements of Sulfatization Process of Resistant Oxide Raw Materials of Rare Metals using Mechanical Activation. In: M.Sanchez (Editor), Proc. V Intern. Conf. Clean Technologies for the Mining Industry, Santiago, Chile, v.2. p.257, 2000.
- Ewing, R.A. et al. Nonaqueous Extractive Methods for Western Uranium Ores. BM1279-280, 1955 (cit. Magner J. E. and Bails R.H., 1959).
- Extractive Metallurgy of Nickel. Burkin A.R. (Editor) Soc.Chem.Ind. John Wiley & Sons, N4, 150p. 1987.
- Foley, D.R., Filbert, R.B. Paper at American Nuclear Congress. Philadelphia. March 1957. (cit. Magner J. E. and Bails R.H., 1959).
- Galvanek P, Kaufman, D. Application of the Solvent Leaching Process for the Concentration of Uranium from Rand Ores. MITG-A74, 1949 (cit. Magner J.E. and Bails R.H., 1959).
- Galvanek, P., Kaufman, D. Further Studies on Solvent Leaching. MITG-225, 1950 (cit. Magner, J.E. and Bails, R.H., 1959).
- Galvanek P, Pelland M.S. A Solvent Leaching Process for the Production of High Purity Uranium Products Directly from Low-Grade Ores. WIN-31, 1955 (cit. Magner, J.E. and Bails, R.H., 1959).
- Hayes, P. Process Selection in Extractive Metallurgy. Hayes Publ. Co. Australia, 406p, 1985.
- Magner, J.E. Direct Solvent Leaching of Uranium Ores with Alkyl Phosphates. DOW-156, 1957 (cit. Magner, J.E. and Bails, R.H., 1959).
- Magner, J.E. and Bails, R.H. Recovery of Uranium from Ores by Direct Leaching with Organic Solvents. In: Proc. 2nd Int. Conf. on Peaceful Application of Nuclear Energy. Moscow, Atomizdat, p.307. 1959. (Russian)
- McKey, G. TBP in Science and Technology. In: Chemistry of Extraction, Moscow, Atomizdat, p.123, 1971. (Russian)
- Ostrousko, Yu. M., Buchikhin P.I. et al. Lithium, its Chemistry and Technology. Moscow, Atomizdat, 197p, 1960. (Russian)
- Thorsen, G., Svedsen, H.F. and Grislingas, A. Integrated Organic Leaching–Solvent Extraction in Hydrometallurgy. In: Renato G. Bautista (Editor), Proc. NATO Advanced Research Institute on Hydro-metallurgical Process Fundamentals. Cambridge, 1982, UK. Series VI, v.10, p.269, 1984.
- Wadsworth, M.E. Hydrometallurgy – Past, Present and Future. Hydrometallurgy. Research, Development and Plant Practice, Proc. 3rd Intern. Symp. on Hydrometallurgy. The Met. Soc. of AIME, p.3, 1983.
- Warren, G.W. Hydrometallurgy – A Review and Preview. J. Metal, p.61. 1984.