

## EXTRACTIVE METALLURGY

*By Dr D. S. Flett and M. T. Anthony  
Saint Barbara Consultancy Services, London*

**T**he Millennium year provided further evidence of the dramatic changes occurring in the mining industry. Globalisation continued apace with fewer owners responsible for higher shares of output. The Global Mining Initiative was launched with its implications for the future of environmental practice in the industry and Quadrem, the new e-procurement system plans to change the way mining companies purchase equipment and services. Even the London Metal Exchange became committed to radical change with its proposed demutualisation.

### **Hydrometallurgy the focus**

Events in technology during the year 2000 were rather less traumatic. Although research and development continued apace, there were relatively few major plant start-ups or new technologies revealed.

Most focus was on the continuing ramp-up of the three Western Australian nickel laterite pressure acid leaching plants. At Cawse, (capacity 9,000 t/y Ni), progress was good with reports of over 100% throughput being achieved during some months by mid-year. At Bulong, (capacity 9,000 t/y Ni), gypsum build-up in the SX plant and a leak in a flash vessel were notable among the problems reportedly experienced and which restricted output to around two thirds of capacity. Anaconda, (capacity 45,000 t/y Ni), undertook a redesign of the primary flash vessels and moved towards throughput at 75% of capacity.

A number of new nickel/cobalt projects are on the drawing board. Those confirmed include Ravensthorpe and Goro. Others include Voiseys Bay where Inco has selected pressure acid leaching (PAL) as the treatment option, Syerston, Weda Bay and Marlborough.

The UK's Mineral Industry Research Organisation (MIRO) published a major review during the year which covered in detail pressure hydrometallurgy for gold, nickel, base metals and other applications<sup>i</sup>. Details of many operations were provided, together with a look at current research and development.

Biotechnology continued its advance with major centres of expertise being established by Billiton, Noranda and Titan Resources. Another recently published MIRO review reports on the progress of a range of new processes including those developed and in operation for gold, copper and zinc<sup>ii</sup>. Bioremediation was also covered.

Although outside the scope of this article, brief reference should be made of developments in the aluminium industry. Here the potential for inert anodes (with oxygen generated in place of carbon dioxide) is being pursued vigorously by Alcoa, and Comalco, Kaiser and Reynolds are testing new, wettable anodes.

On the hydrometallurgy front, the possibility of the construction of a flexible pilot plant in Europe having permanently installed circuits for the testing of 10-15 processes including PAL and bioprocesses has been mooted.

Nothing similar exists for pyrometallurgical testing, although the technology does have a new website – [www.pyrometallurgy.com](http://www.pyrometallurgy.com) – which is building up a capability and access service of technical companies servicing the industry.

As usual, there were several hundred new technical publications during 2000 and a number of well-documented conferences took place. Those of particular interest for the major base metals are reviewed in the

following sections, where references are also provided.

### General

A very timely symposium on pressure technology applications in the hydrometallurgy of copper, nickel, cobalt and the precious metals was held as part of the TMS annual meeting, held in March in Nashville, Tennessee<sup>iii</sup>. The papers include pressure leaching of copper anode slimes (three papers); a new process for the simultaneous leaching and recovery of gold, platinum group metals (PGM) and base metals from ores and concentrates; nickel and cobalt recovery from Madagascar laterites; the high temperature pressure leaching of Guelb Moghrein chalcopryrite concentrate, nitrogen species catalysis in the processing of chalcopryrite concentrates; and the pressure acid leaching of zinc and copper concentrates by Dynatec. There were also papers on alkaline and acid pressure leaching at Barrick Gold, the optimisation of gas mass transfer in autoclaves and a review of laboratory autoclaves for hydrometallurgical research. Unfortunately some important papers presented at this mini-conference were not published in the EPD Congress 2000 proceedings.

Lead-Zinc 2000 was held in Pittsburg on October 22-25, 2000<sup>iv</sup>. Chapters on global factors affecting lead and zinc, modern lead smelting technologies, zinc operations, Imperial Smelting technologies, zinc electrowinning, new developments in lead and zinc, new zinc processing technologies, new electrowinning technologies for lead and zinc and environmental aspects of lead and zinc production, contain the papers presented at the conference. This is an important series of conferences following, for example, Lead-Zinc'80 and Lead-Zinc'90.

An interesting conference on pyrometallurgy held in 2000 was the Fundamentals of Metallurgical Processing, the James M. Toguri Symposium<sup>v</sup>. Held under the auspices of CIM in Ottawa, Canada on August 20-23, the conference volume contains the presented

papers in chapters entitled high temperature experimental methods, thermodynamics of high temperature systems, kinetics of pyrometallurgical systems, interfacial phenomena, slags and molten salts and industrial practice.

On the occasion of the 65th anniversary of the Norilsk integrated smelter, a whole issue of *Tsvetnye Metally* has been given over to papers on the history of the Russian mining and metallurgical works. Items covered included the geology, mining and processing of the copper-nickel ores, metallurgical production, automation, the company's foreign economic activity and the complex's construction, infrastructure and social policies<sup>vi</sup>. The Ni, Cu and PGE resources at the various deposits are surveyed and the precious and PGM content of the many different minerals discussed and tabulated. Mining methods are discussed and flowsheets presented for Cu-Ni bulk concentrates, a new type of Pt-containing low-sulphide ore and Talnakh magnetite wastes containing Pt, Pd and Au. Metallurgical articles cover the use of Vanyukov furnaces in copper smelting, the leaching of high-Cu mattes, iron removal in the production of anode nickel, nickel electrolysis, the refining of copper, silver, iridium and nickel, the slimes facilities and the production of mineral fertilisers.

The design of modern furnace cooling systems has been reviewed by Merry et al.<sup>vii</sup>. An integrated multidisciplinary approach to furnace design is necessary to achieve maximum production and a long refractory life. Account must be taken of the interdependence between furnace cooling elements and other furnace systems, such as binding, cooling water and instrumentation. A range of sidewall cooling technology is available: for intense processes such as flash converting, waffle coolers have copper fins and refractory-filled grooves, while in the areas around tapholes a one-piece water-cooled copper casting with a waffle pattern at the hot face is typically used. Thermocouples

in the cooling elements and water system allow fast response to process upsets, while refractory elements should be designed with the coolers. The retrofitting of the three-electrode, 13.5 MW circular furnace at Hartley Platinum's plant in Selous, Zimbabwe, and of Kidd Creek's copper converting furnace at Timmins, Ontario, are examples of a successful integrated approach to furnace cooling design.

As previously indicated, bacterial leaching remains a popular subject. Two papers consider aspects of iron oxidation. The first<sup>viii</sup> is concerned with the development of a high efficiency reactor for the bio-oxidation of ferrous iron. The bioreactor is a 1,249 mm high and 84 mm diameter column randomly packed with siliceous stone particles with inlets for fresh medium and air at the bottom. The current study examines the influence of air and liquid flowrates on the ferrous iron bio-oxidation in this flooded packed bed bioreactor. The highest ferric productivity rate attained was 11.25 g/l/h.

The second paper is concerned with a study of pyrite surfaces after bioleaching and the bioleached surface compared to that of pyrite exposed to uninoculated solutions of either sulphuric acid or ferric and ferrous sulphate dissolved in sulphuric acid at equivalent concentrations as the inoculated solution<sup>ix</sup>. The colonised surface produced an oxidised phase extending to a depth of more than 4 microns. No oxide layers of significant depth were observed for samples exposed to uninoculated solutions.

A review of insoluble lead and lead alloy anodes used in hydrometallurgy has been given. The review covers corrosion resistance<sup>x</sup> and anodic behaviour<sup>xi</sup>.

### Copper

An Alta conference was held in 2000 on all aspects of copper hydrometallurgy and included papers on a variety of projects and operations<sup>xii</sup>. Another Alta conference in 2000 was on solvent extraction and ion exchange

and included papers on Cu SX, As SX, Co/Ni separation by SX, Ni/Ca separation by SX, Co and Cu recovery by molecular recognition technology, Au SX, rare earths SX, crud problems, etc<sup>xiii</sup>.

A review of flash smelting and converting furnaces has been provided on the 50<sup>th</sup> anniversary of their development<sup>xiv</sup>. The high-intensity energy process of flash smelting was originally developed in 1949 to attain ever-increasing throughputs and intensities. Many innovations and continuous development ensued during the next 50 years, leading to today's state-of-the-art copper-making process chain and environmental benchmark technology, which includes the Outokumpu process and the Kennecott-Outokumpu flash converting process. The first two furnaces had to be re-bricked every eighth week and had no water cooling. Today's furnaces have a campaign life of more than ten years and have cooling elements designed to resist very high heat loads and to be replaced externally. Water sprays have generally given way to horizontal cast-around-tube shaft cooling elements, with more and more elements made by continuous casting. Refractory bricks are of low-Fe magnesia-chrome fired at high temperatures and direct bonded. In process control, two key pieces are the concentrate feeding system and burner.

The materials flow and energy requirement in copper metallurgy has been analysed<sup>xv</sup>. The processes used in different countries are tabulated and energy/materials flowsheets presented for the various regions. It is concluded that Asia and Australia have the highest and North America and Europe the lowest specific energy consumption, despite the low grade of concentrates treated in Europe. In Asia a large amount of oxygen is consumed. The energy for the production of oxygen, compressed air and reagents has not been taken into account. Europe has almost no unused waste products, but there is scope in America, Asia and Australia for reducing unutilised wastes, especially by installing

sulphuric acid plants. Hydrometallurgy has a high specific energy consumption, but plant sizes are much smaller than for pyrometallurgy.

The Ronnskar copper smelter and refinery, in Sweden, has been modernised to expand cathode production from 130,000 to 230,000 t/y<sup>xvi</sup>. Heavy involvement from operations and management allowed project goals to be realised while full production schedules were maintained. The project was divided into eight sub-projects linked by a co-ordination and support team. There was a strong focus on health and safety. Infrastructure included harbour extension, belt conveyors, piping and electrical distribution; new plant included an Outokumpu flash furnace, a new converter aisle, three Peirce-Smith converters, a new anode casting plant and eleven new tankhouse sections. New units were implemented system by system, eliminating large start-up problems.

Slag cleaning at Chilean copper smelters has been reviewed<sup>xvii</sup>. Each of Chile's seven copper smelters employs a different strategy for slag cleaning and obtains different results. The various systems, equipment and results at the Chuquicamata, Potrerillos, Caletones and Chagres primary smelters and the Altonorte, Paipote and Ventanas custom smelters are outlined and compared. Experience has shown that the key to recovering copper is to obtain a fluid slag with low magnetite content and without metallic copper, and to agitate it to increase the size of the metal droplets. Altonorte, Potrerillos and Caletones still have reverberatory furnaces; Paipote is temporarily using its old reverberatory furnace as a slag settler during installation of an electric furnace like the one at Ventanas; Chuquicamata has a slag flotation plant and several smelters, including Chagres, uses Teniente slag cleaning or HLE furnaces.

Commissioning of the first Australian-designed copper smelter in China has been reported<sup>xviii</sup> and it is said to have exceeded

expectations and design output is expected to be reached soon. The 35,000 t/y blister copper plant at Houma City, Shanxi, cost around US\$55 million and uses Ausmelt submerged lance technology to smelt concentrates varying in grade from 17% to 22% Cu. The installation is the first to use smelting and converting process steps in separate top-submerged lance vessels in a continuously operated process. Indications to date are that it will improve smelting economics dramatically as well as offering improved environmental performance and operator safety. A number of important environmental features were incorporated in the design.

The technical feasibility of recovering copper, nickel and cobalt from smelting and converting slags using Ausmelt's top-submerged lancing process has been demonstrated at pilot-plant scale and in several commercial applications<sup>xix</sup>. Process conditions can be tailored to achieve the maximum economic recovery of valuable metals and to yield a product composition that fits downstream processing requirements. There is strong economic justification for a slag cleaning process where the value of contained metals recovered per tonne of slag treated exceeds US\$50/t. Where this value is predominantly associated with cobalt recovery, the top-submerged lance system offers a relatively low-cost solution.

Production figures from the Guixi smelter in China for the years 1990-1997 have been examined to determine the effectiveness of various measures to reduce the Cu content of electric furnace slags: high levels of oxygen enrichment, high matte grades and a high concentrate feed rate<sup>xx</sup>. The theoretical basis is discussed for adding fine coke to the flash furnace, expanding and modifying the slag electric furnaces and managing slag dilution, three measures that proved useful in practice. The key to reducing the Cu content of the slags is to restrict output of Fe<sub>3</sub>O<sub>4</sub>; Cu content



can be reduced by ensuring that sufficient settling and segregation of slags takes place.

Computational analysis has been used in the design of ventilation and fume control systems in smelters<sup>xxi</sup>. In particular it has been used in the design of Peirce-Smith converter hoods with respect to the off-gas flow patterns exiting the converter mouth. From examination of the effects of various process and physical plant design parameters on process gas and fume capture and potential build up on the converter hoods, the optimum design and operating parameters were determined.

Process control improvements at the Kennecott Utah copper smelter have been described by Leary and Siraa<sup>xxii</sup>. The feed forward control module provides predictive control and operates in response to furnace feed input changes. The feed back control module provides responsive control and is based on furnace output deviations. To provide regular feedback information to the control room supervisors, new sampling methods were developed which provide operators with molten metal and bulk material samples at regular intervals to provide information for control. The control system was implemented on the Flash Converting Furnace in May 1999 and on the Flash Smelting Furnace in August 1999.

The case for a copper mini smelter has been put by Wesely<sup>xxiii</sup>. Despite the current trend to expand existing smelters, there are a number of conditions where a much smaller smelter could be economic. This paper examines these conditions and outlines the process concepts for a smaller smelter treating from 20,000 to 100,000 t/y of copper.

A study of the corrosion mechanism on furnace linings near the converter tuyeres and their up-side zones has been carried out. X-ray diffraction and scanning electron microscopy were carried out on samples of corroded magnesia bricks<sup>xxiv</sup>. Copper contamination was found along the crevices

and capillaries in refractories near the tuyere zone and  $\text{Cu}_2\text{S}$ , with some Cu and  $\text{Fe}_3\text{O}_4$ , near the tuyere's up-side. The change from air blow to oxygen-enriched blow resulted in evident improvement in the condition of lining corrosion near the tuyere's up-side zone, with mainly Cu accompanied by  $\text{Cu}_2\text{S}$  and  $\text{Fe}_3\text{O}_4$ . Thermodynamics and fluid mechanics were also shown to influence lining corrosion.

Combustion of copper concentrates from La Escondida, in Chile, has been studied in a stagnant gas furnace<sup>xxv</sup>. These concentrates consisted predominantly of chalcocite and pyrite, while those from La Caridad, in Mexico, contained chalcopyrite, pyrite, covellite and chalcocite. The 45-53 micrometer size fraction from La Caridad reacted to a greater extent than the 25-38 micrometer fraction because its larger proportion of pyrite transformed to open-structured pyrrhotite, whereas the chalcopyrite in the finer fraction was oxidised to an oxygen-limiting layer of  $\text{Fe}_3\text{O}_4$ . The 45-53 micrometer fraction from La Escondida had a greater proportion than did the finer fraction of particles containing both pyrite and chalcocite, which reduced the ignition temperature by forming chalcopyrite.

The reaction sequences in sulphide particle oxidation in a chalcopyrite concentrate and in two low-iron copper mattes have been studied using a laboratory scale laminar flow furnace simulating the phenomena taking place in different zones of the reaction shaft of a flash smelting furnace<sup>xxvi</sup>. In this paper, oxidation kinetics as well as ignition of particles are discussed. Changes in particle morphology, size and composition are shown to define closely the progress of oxidation and consequently to permit development of a detailed model of dust formation and reaction mechanisms. Data obtained have broadened the knowledge of the physical and chemical phenomena in flash reactions and serve as a reference for computer simulations.

A new method has been proposed for predicting Cu matte grades from plant

data<sup>xxvii</sup>. Dynamic auto-regressive and exponential smooth models are established, the former requiring that time-series data be smooth and the latter with random target data. With regard to fluctuation in matte grades, a new kind of combined model is established. The forecasting error becomes the minimum between three models; the square of the forecasting error is regarded as the target function and the best-weight numbers are obtained by the minimal least squares principle. The results showed that the combined model gives a higher degree of accuracy than either the auto-regressive or the exponential smooth model on its own.

The recovery of pollution-causing elements from copper slags has been studied by Reddy<sup>xxviii</sup>. Losses in slags account for 1-2% of the total Cu produced by a smelter, while 55% of As and Sb and 10% of Bi contained in the feed also enter the discard slags, from which they may enter the environment. Slags from four US copper smelters were treated by high-temperature techniques to recover As, Sb and Bi along with Cu in an alloy phase. Two of the slags were high in Cu and As, a third had high Sb and all four had low Bi contents. It was found that recovery of all four metals increased with reduction time, temperature in the range 1,473-1,573 K, amount of carbon added and amount of CaO flux added. Recoveries of Sb and As were strongly dependent on their initial concentrations in the slag, increasing with increased initial element concentration. Higher Sb recoveries were obtained by carbothermic reduction of the slags.

A thermodynamic database has been developed to calculate equilibria involved in copper production<sup>xxix</sup>. Zinc has now been included in the database for matte, slag and blister copper phases, allowing calculations in the eight-component system Zn-Pb-Cu-Ca-Fe-Si-O-S. Thermodynamic and phase equilibrium data from the literature have been critically assessed and optimised with the modified quasi-chemical model. When combined with Gibbs energy minimisation

software and other databases of the FACT thermodynamic computing system, the database can be used to calculate the distribution of Zn between matte, slag, copper and gas phases during copper smelting and converting, or under various conditions which are difficult to study experimentally. The calculations predict that the presence of zinc increases the solubility of copper in the fayalite slag.

An intelligent sensor for coal powder rate injection in a slag cleaning furnace has been described by Bergh et al. At the Caletones smelter in Chile<sup>xxx</sup> better control of coal addition into this batch process was reported as increasing copper recovery from slags and reducing pollution by particulate material. A hybrid expert and fuzzy supervisory control was proposed.

Silver activity in the immiscible region between the molten Cu and the Cu-Fe matte has been measured by double Knudsen-cell mass spectrometry at 1,473 K<sup>xxxi</sup>. The distribution of silver between the two phases in the miscibility gap was also determined by quenching at the same experimental temperature, to find the relationship between silver activity and composition in the two phases.

The density and surface tension of synthetic calcium-ferritic slags has been reported<sup>xxxii</sup>. These were examined to determine the possible interactions between their components. The viscosities of some binary and ternary fayalite slags, of general interest to the non-ferrous metals industry and of particular interest in copper production, have been measured and the effect of CaF<sub>2</sub> additions determined<sup>xxxiii</sup>.

Concern that spent mag-chrome furnace linings might be categorised as hazardous waste has led to research into alternative refractories for copper processing<sup>xxxiv</sup>. The microstructure of magnesia-alumina after 10 min exposure to typical molten slags is discussed.

A transpiration method has been used to evaluate the Henrian activity coefficient of bismuth in Cu-Fe mattes and white metal, gamma-Bi, as a function of Cu/Fe molar ratios from 1 to infinity, as a function of sulphur deficiency from -0.02 to +0.02 and at temperatures between 1,493 and 1,573 K<sup>xxxv</sup>. Analysis of gamma-Bi as a function of trace-element concentration reveals that the activity coefficient is independent of Bi content at values smaller than 0.3 wt%. An equation was derived for the dependence of gamma-Bi on the inverse of temperature. The results show that bismuth is stabilised in both high- and low-sulphur melts and that Bi volatility is at a maximum near the Cu<sub>2</sub>S-FeS pseudo-binary. In sulphur-deficient mattes, free copper tends to decrease Bi volatility. Failure to account for sulphur loss can lead to significant error; a method is presented whereby sulphur loss during an experiment can be accounted for in computing activity coefficients.

A furnace, designed to remove harmful impurities such as As, Sb, Bi, Pb and Zn prior to smelting, by heating the concentrate indirectly to less than 1,000°C using the thermal energy of the gases of fusion and conversion has been developed<sup>xxxvi</sup>. The concentrate heats up while sliding down a hermetically sealed vacuum tunnel. After passing through filters, the volatilised substances are conducted along a tunnel with a decreasing temperature profile, inducing step-wise condensation and recovery of the different substances. The furnace has no moving parts and is very small, even if it feeds a large smelting furnace. The main operating cost is for the electricity required by the vacuum pumps and liquid air condensers. Construction presents no great technical difficulties, as the weight of the concentrate is distributed over a large surface and operating temperatures are only moderately high.

A study has been made of the kinetics and mechanism of the chlorination of copper sulphide in the presence of oxygen<sup>xxxvii</sup>. It was found that the process was complex,

consisting of an oxidation reaction and two successive chlorination stages. A high degree of overall chlorination of copper(I) sulphide was achieved. Chlorination increased with temperature, time and chlorine flow. Increasing the oxygen flow to 20 l/h resulted in larger amounts of copper(I) and copper(II) chlorides being formed, but greater oxygen flows reduced the amount of copper(II) chloride so that overall chlorination remained approximately the same. SEM analysis confirmed that solid-state sintering and grain growth occurred with increases in temperature and time, reducing the pores between grains and the reaction surface so that the reaction would eventually slow down or stop.

The applicability to a chalcopyrite concentrate of a three-stage fluidising bed reactor process, consisting of low-temperature chlorination, selective oxidation and sulphur chloride conversion, has been studied<sup>xxxviii</sup>. Gaseous chlorination at 270°C lowered the residual sulphur to 3%; thermal curing in N<sub>2</sub> gas further lowered sulphur content and made the chlorinated products less reactive in the oxidation operation. It was found that excess oxygen was essential to stable operation in the oxidation reactor; however, this excess oxygen would cause oxidation of the sulphide concentrate in the chlorination and sulphur chloride conversion reactors. A new flowsheet is proposed separating the chlorination and oxidation steps with separate flow paths for the fluidising gases. Its feasibility was demonstrated in a laboratory-scale fluidising-bed set-up. Leaching of selective oxidation samples produces solutions analysing 115g/l Cu, with Fe/Cu ratios of less than 0.003.

An analysis has been made of the possibility of processing the copper residues from the chlorine leaching of a nickel concentrate in an autogeneous smelting unit<sup>xxxix</sup>. It is shown, with the relevant calculations, that elemental sulphur can be completely burnt from the copper residues in a unit for autogenous smelting of Cu concentrate. As the sulphur

takes a long time to heat and evaporate, the bulk of the process has to take place in the slag melt and oxidation has to be achieved by blowing oxygen into the melt with a lance. Modification of lance design may be required if complete oxidation of sulphur is to be achieved.

Copper leaching has been selected as a case study to assess the role of Life Cycle Assessment (LCA) in performance assessment in minerals processing<sup>xi</sup>. Thus LCA and established solid-waste characterisation tests have been combined to provide an assessment tool which reduces the uncertainty of LCA assumptions with respect to potential mobility of heavy metals from solid waste. LCA, unlike environmental impact assessment (EIA), can be used without site-specific information, for example in the extrapolation of findings from pilot-scale studies to full-scale plant. The copper process in the case study uses an innovative leach solution to extract copper from copper sulphide and oxide concentrates, followed, after purification, by high current-density electrowinning to produce an LME Grade A product. Sequential leach tests showed that the majority of iron and sulphur, the main components of the solid waste residues, is unlikely to mobilise under waste deposit conditions. It was found that certain environmental effect scores were sensitive to changing process conditions: feed composition affected the eco-toxicity indicator and current density affected the global climate change indicator.

An account of a winter field test for heap leaching Camacks copper ore in the Yukon has been given<sup>xii</sup>. The purpose of the test was to demonstrate that the oxide ores could be leached in an Arctic setting on a year-round basis. A crib 5 m in diameter was loaded with 250 t of composite ore from the Carmacks deposit, stacked to a height of 7 m of which 1 m was above the emitter system. The design replicated an interior segment of the planned commercial heap. Leachate flowed at 0.2 l/min/m<sup>2</sup> and was maintained at 21°C by

normal process heat transferred from electrowinning to the leachate. The winter temperatures reached -54°C and averaged -13°C over three months. Despite some problems with the flow system, leaching continued unabated and freezing was limited to the insulated over-layer and isolated points near the crib walls.

An analysis of heat conservation during copper sulphide heap leaching has been carried out with the aid of a computer model<sup>xlii</sup>. As a result a new mode of heap behaviour called "evaporative autocatalysis" has been postulated. In this mode, air is blown upward through the heap at a rate sufficient to drive the net advection of heat upward through the heap, resulting in much higher and more uniform internal heap temperatures than can be achieved in the absence of forced aeration. The effect of flow rate, heat generation rate, solution and air heating and application of an evaporative shield to the heap surface have also been investigated.

A review of leaching as part of the mineral concentration process has been reviewed<sup>xliii</sup>. Leaching is the first stage in concentration for minerals that cannot be beneficiated by conventional methods. The efficiency with which the desired ions are dissolved determines the success of subsequent cementation, ion exchange, solvent extraction or electrolysis. The processes involved and the influences on dissolution speed and overall solubility are discussed, as well as the formation of anionic complexes, the use of bacterial leaching and the advantages of the Thin-Layer copper leaching process. Different lixiviants and their properties are surveyed and the solubility products of different compounds tabulated.

Current research projects on the development of a hydrometallurgical process for the treatment of chalcopyrite have been critically reviewed<sup>xliiv</sup>. The author believes that a new, efficient process is needed for chalcopyrite, to match the use of SX-EW for



copper oxides. Potential routes using chloride solutions include the Cuprex process and the Intec copper process, while pressure-leaching methods using sulphuric acid solutions include the CESL process and total pressure oxidation. The Cuprex process uses solvent extraction by Acorga reagents and the Intec process uses  $\text{BrCl}_2$  (Halex) for electrowinning. In the CESL process, almost all the sulphur is recovered in its elemental form by pressure leaching, whereas in total pressure oxidation sulphur is almost completely oxidised to sulphate ion. General advantages include the lack of  $\text{SO}_x$  emissions, lower costs, more compact facilities and greater tolerance of grade changes or impurities.

A study of the kinetics of sulphuric acid leaching by microwave heating has been reported by Su and Liu<sup>xlv</sup>. Acid leaching of chalcopryrite is very difficult, generally requiring the strong oxidant  $\text{FeCl}_3$  with  $\text{HCl}$  and resulting in large quantities of Fe ions entering solution. An investigation was carried out into the effects of microwave heating on a leaching solution containing sulphuric acid and manganese dioxide oxidant. A 500 ml solution containing 50 g of chalcopryrite in an ore grading 53.45 wt% Cu Fe S<sub>2</sub>, 45 g  $\text{MnO}_2$  and 106 g  $\text{H}_2\text{SO}_4$  was heated by microwave and by electric furnace. Leaching efficiency using the furnace was around 25% after two hours, whereas with microwave heating it was 50% after one hour. Leaching efficiency increased as feed size decreased. Without  $\text{MnO}_2$ , leaching efficiency was only around 20%, but it could be increased from 50 to 59% if  $\text{MnO}_2$  content was increased from stoichiometric to 77% more than stoichiometric. A kinetic equation is derived which describes total leaching efficiency.

Dynatec has carried out process development studies on Hudson Bay Mining and Smelting Co. Cu concentrates at Flin Flon, Manitoba<sup>xlvi</sup>. A conceptual process flowsheet was developed for the treatment of Cu sulphide concentrates containing

significant levels of Zn and precious metals. Pressure leaching is used to solubilise Cu and Zn and the leach solution is processed by solvent extraction and electrowinning to separate and recover Cu as high purity cathode. To recover Zn and maintain an overall sulphate balance in the plant, a bleed stream of solvent extraction raffinate solution is processed by acid neutralisation and Fe-Cu removal, to give a Zn sulphate solution relatively low in Cu and other impurities. This can be treated with lime to precipitate basic Zn sulphate, or added to an appropriate circuit in the existing plant. Laboratory results show that improved Cu, Zn, Au and Ag recoveries can be obtained.

A model for ferrous-promoted chalcopryrite leaching has been developed by Hiro Yoshi et al.<sup>xlvii</sup>. The model considers the leaching to take place in two steps: (1) reduction of chalcopryrite to  $\text{Cu}_2\text{S}$  by ferrous ions in the presence of cupric ions and (2) oxidation of the  $\text{Cu}_2\text{S}$  to cupric ions and elemental sulphur by dissolved oxygen and/or ferric ions. The intermediate  $\text{Cu}_2\text{S}$  is more amenable to oxidation than chalcopryrite, causing enhanced copper extraction. Flask-shaking leaching experimental results agreed well with those predicted from the model.

An alternative non-cyanide lixiviant, namely sodium hypochlorite, has been used for the selective extraction of gold and silver from a copper concentrate<sup>xlviii</sup>. Hypochlorite leaching of the as-received, as well as aqueous pressure-oxidised copper concentrate was carried out. Direct hypochlorite leaching yielded gold and silver recoveries of 42.7% and 45% respectively. With aqueous pressure oxidation followed by hypochlorite leaching, it was possible to selectively recover 90% of gold and 92.5% of silver from the copper concentrate.

A study has been made of the leaching of copper(I) sulphide with calcium chloride with added  $\text{HCl}$  and the introduction of gaseous oxygen<sup>xlix</sup>. The effect of temperature, concentration of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{HCl}$  and total

chloride ions, stirring speed, phase ratio and time, on the leaching of copper was studied. The quantity of copper dissolved increased with increasing values of all parameters. The role of chloride ions is to disrupt the passive sulphur layer on the particle surface by promoting the formation of crystalline sulphur. The leaching reaction was concluded to be second order with respect to total chloride ion concentration and the leaching rate was found to be diffusion controlled.

The leaching of tetrahedrite in ferric chloride solutions has been studied by Correia et al.<sup>i</sup>. The results show that, for temperatures below the normal boiling point of the solution, the leaching of tetrahedrite is reaction controlled. From the analyses of the solutions and X-ray and microprobe analyses of the solid residues, it was concluded that the leaching of tetrahedrite involves the complete breakdown of the sulphide structure.

Dissolution of chalcopryrite in HCl medium in the presence of  $\text{MnO}_2$  (manganese ore containing pyrolusite) has been studied at different temperatures, acid concentrations and mineral proportions<sup>ii</sup>. Chalcopryrite underwent oxidative dissolution in the presence of  $\text{MnO}_2$  via (i) galvanic interaction, (ii) cyclic action of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple and (iii) chlorine gas generated by  $\text{MnO}_2$  dissolution. The extent of occurrence of these phenomena was evaluated and the last one was observed to be the most effective. Kinetics and mechanisms of the process have been discussed.

The electrochemical oxidation of a  $\text{CuFeS}_2$  concentrate in a mixed chloride-sulphate electrolyte was studied using carbon paste electrodes<sup>lii</sup>. This technique was found to give very reproducible results. It was shown that, during the initial stages of leaching, the oxidation of chalcopryrite at low overpotentials was hindered by the formation of a metal-deficient sulphide surface. When chloride ions were present the oxidation of the mineral was significantly enhanced. In further work<sup>liii</sup> it was found that excellent leaching kinetics

existed for the leaching of chalcopryrite with solutions containing chloride, while for solutions without chloride, the leaching was very slow. It is believed that the role of chloride is to promote the formation of a more porous sulphur product, thus permitting the dissolution reaction to proceed at a reasonable rate. Very good leaching kinetics were obtained at  $95^\circ\text{C}$  with 86% of the copper extracted in six hours and 97% in nine hours at an oxygen pressure of one atmosphere.

A study has been made of the influence of mechanical activation on the alkaline leaching of an enargite concentrate in the presence of sodium sulphide<sup>liv</sup>. The rate of leaching was influenced by mechanical activation of the concentrate in a stirring mill (attritor). XRD and XPS studies have shown that, after removal of arsenic by leaching, the enargite transforms into  $\text{CuS}$ . It is concluded that this work provides the potential of de-arsenification of sulphide concentrates and preparation of a charge suitable for further processing.

Chinese work in copper biohydrometallurgy has included several papers. Leaching pure minerals with a culture of *Thiobacillus ferrooxidans*, *T. thiooxidans* and *Leptospirillum ferrooxidans* increased Cu yields after 28 days from around 5% to 29.2%, but bio-leaching yields improved to 78.4% when 2 g Ag/kg  $\text{CuFeS}_2$  was added<sup>lv</sup>. Fe bio-extraction from pyrite was 51.0% after 18 days in the absence of Ag but only 27.4% when 2 g Ag/kg  $\text{FeS}_2$  was added. The total Cu extracted from an ore sample containing chalcopryrite from Dexing mine, in Jiangxi, after 21 days was 29.4% in the absence of Ag but 55.7% with 0.06 g Ag/kg ore and 78.3% with 0.64 g/kg; Fe extraction was 59.6% without Ag but 19.6% with 0.32 g/kg. XRD and XPS results showed that intermediate  $\text{Ag}_2\text{S}$  formed on chalcopryrite, whereas pyrite oxidised  $\text{Ag}^+$  to metallic silver.

The electrochemical behaviour of chalcopryrite in the presence of *T.*

*ferrooxidans* has also been reported<sup>lvi</sup> and the bio-leaching of low-grade porphyry chalcopyrite has been studied at the Dexing copper mine in Jiangxi which has around 500 000 000 t of waste rocks containing 0.1-0.3% Cu<sup>lvii</sup>. Experiments have been carried out on the biological leaching of these wastes since 1979 and in 1997 a 2000 t/y cathode plant was constructed for dump leaching, solvent extraction and electrowinning. The processes are described, the results over a 10-month period presented and the overall operational flowsheet depicted.

The kinetics of electrochemical corrosion of chalcopyrite in the presence of bacteria have been studied<sup>lviii</sup>. In an uninoculated acid solution the corrosion potential was 0.255 V (vs SCE) but in solution inoculated with *Thiobacillus ferrooxidans* it was 0.308 V, while the corrosion current density was increased from 0.52 to 0.64 microamps/cm<sup>2</sup>. This showed that the bacteria enhanced the dissolution of the chalcopyrite. They also had a greater effect on cathode polarisation than on anode polarisation.

An investigation has been made into the attachment of two strains of *Thiobacillus ferrooxidans* and four strains of moderately thermophilic bacteria to pyrite, chalcopyrite/pyrite concentrate and As-containing concentrate<sup>lix</sup>. The degree of attachment of all substrate-grown cells was determined and contact angle measurements were taken for both minerals and cells, in order to evaluate the effects of growth substrate and hydrophobic interactions. The attachment of both mesophiles and moderate thermophiles was found to depend on growth substrate type and concentration and on the type of mineral studied. While sulphur-grown *T. ferrooxidans* cells showed a higher degree of hydrophobicity, both ferrous iron-grown and chalcopyrite-grown cells had a greater degree of attachment. Each moderately thermophilic strain adhered to sulphides more readily if cultured on chalcopyrite or sulphur and all showed greater adhesion to pyrite and As concentrate than to chalcopyrite.

An investigation of the attachment of *Thiobacillus ferrooxidans* to mineral sulphides using scanning electron microscopy analysis has been reported<sup>lx</sup>. Pyrite, chalcopyrite concentrate and a sample containing arsenopyrite and loellingite were mounted on resin blocks and examined for the surface erosion that would result from direct bacterial attachment and oxidation. Erosion patterns on the surface of chalcopyrite and arsenopyrite appeared to follow the crystallographic structure of the mineral species, but no erosion patterns were apparent on pyrite and elemental sulphur was found deposited on the surfaces of all three samples. Chalcopyrite was eroded in preference to pyrite, and loellingite was significantly more oxidised than arsenopyrite. The observations suggest a greater involvement of indirect oxidation by ferric ions than direct attachment.

A series of bacterial and chemical leaching tests have been conducted to clarify contradictory reports in the literature regarding the role of bacteria in the bioleaching of chalcopyrite<sup>lxi</sup>. Tests containing a high bacterial concentration showed inhibited leaching, even lower than non-inoculated controls. However when bacterial cells were washed before inoculation, it was apparent that it was not the bacterial cells but rather the chemical species introduced with them that influenced the leaching rate. In addition, the results of comparative tests with 0.1 M ferrous sulphate or ferric sulphate showed that copper was leached from the ore 2.7 times faster in leach solutions containing ferrous ion, suggesting that ferric ions inhibit chalcopyrite dissolution. The results indicated that the chalcopyrite dissolution rate is strongly dependent on the reduction potential in solution and that this parameter is far more influential than the number or activity of bacterial cells. These results imply that the role of bacteria may be only stimulatory when the prevailing electrochemical conditions are also favourable.

The role of iron-hydroxy precipitates in the passivation of chalcopyrite during bioleaching has been studied<sup>lxii</sup>. The aim of the study was to examine the role of jarosite precipitation in the bioleaching of chalcopyrite, to determine whether the moderately thermophilic bacteria *Sulphobacillus thermosulphidooxidans*, *S. acidophilus* and *Acidimicrobium ferrooxidans* could remove the iron-hydroxy precipitates from the chalcopyrite surface via the reduction of iron(III), and whether the copper leaching rates were restored to their original value by this treatment. Copper release to solution was initially rapid during bioleaching in an acidic sulphate nutrient medium by *S. thermosulphidooxidans*, but slowed significantly after about 50 hours, coinciding with significant jarosite deposition. The effect on the passivated chalcopyrite of a subsequent bioreduction phase using the three bacteria species was assessed; despite extensive bioreduction of the iron-hydroxy precipitates, it was found that jarosite was not completely removed and further biooxidation of the treated concentrate resulted in no significant increase in copper release.

Investigations of oxidative leaching of chopped copper wire scrap in sulphuric acid have been carried out by Bombach et al.<sup>lxiii</sup>. This leaching method, with reaction rates of up to 160 g Cu/l/h for copper powder and 32 g/l/h for coarse copper granules, represents an environmentally safe and attractive alternative to pyrometallurgical scrap recovery. The results are reported of experiments which indicated a strong dependence of the reaction rate on temperature, specific surface area of particles and oxygen partial pressure, while stirring speed, concentration of free sulphuric acid and the solid/liquid ratio have less influence. High concentrations of  $\text{Cu}^{2+}$  ions in solution clearly accelerated the leaching process. It was concluded that the transport of Cu ions and dissolved  $\text{O}_2$  to the copper surface is the rate-determining step.

A hydrometallurgical process for treating copper smelter flue dust has been developed

at the Shenyang smelter, in Liaoning, China<sup>lxiv</sup>. The process uses sulphuric acid leaching at 120-130°C in the absence of oxygen to remove As from the flue dust and to recover Bi and other valuable metals. The best separation of Cu and As was obtained when the leaching conditions were maintained at 1 M  $\text{H}_2\text{SO}_4$ , leaching time two hours and liquid/solid ratio five. About 90% of the As and less than 10% of the Cu dissolved into the leaching solution; most of the Cu remained in the residue as cupric sulphide. Fe and As were then removed from the solution by oxidation and precipitation as ferric arsenate. Bi was extracted from the residue in a solution containing a mixture of sulphuric acid and sodium chloride; more than 90% of the Bi was then recovered from the leaching liquors as Bi sponge, by cementation with iron powder.

A study has been made of  $\text{SO}_2/\text{O}_2$  as an oxidant in hydrometallurgy<sup>lxv</sup>. Sulphur dioxide, when combined with oxygen in the presence of certain transition metals, acts as a stronger oxidising agent than oxygen. Basic studies on the iron and manganese catalysed  $\text{SO}_2/\text{O}_2$  oxidising systems in acidic media are summarised and three processes where this system may be applied more efficiently than oxygen are examined: chalcocite leaching; oxidation and precipitation of arsenic from arsenical fume leachates; and the oxidation and precipitation of manganese impurity from nickel/cobalt solutions. The  $\text{SO}_2/\text{O}_2$  system provides a simple method of generating  $\text{H}_2\text{SO}_4$  for the autoxidation of  $\text{SO}_2$  once Fe(II) is oxidised. The system also oxidises As(III), which in the presence of Fe(III) enables a stable iron(III) arsenate compound to be precipitated. Further work on this system has been undertaken to fully describe the kinetics and mechanism<sup>lxvi</sup> of iron oxidation by  $\text{SO}_2/\text{O}_2$  in acidic media and to determine the effect of copper<sup>lxvii</sup>.

A brief summary, based on a paper presented at the ALTA 1998 copper hydrometallurgy forum, has been given of solvent extraction and electrowinning



operations in the US, Zambia, Chile, Australia, Mexico and Canada and of recent technical trends<sup>lxviii</sup>.

The impact of solvent extraction and the equipment within which the process is carried out in copper hydrometallurgy has been assessed by Casteel<sup>lxix</sup>. Solvent extraction now contributes 20% of the world's primary copper output, a success exemplified by the example of Radomiro Tomic in Chile where a fourth solvent extraction train is being added to raise cathode production to 250,000 t/y Cu. Key issues for the process are the demand for lower costs and the need to be able to adapt to process disturbances. A survey is presented of developments in solvent extraction equipment, particularly the two main types of contactor, the mixer-settler and the pulsed column. Vertical smooth flow or VSF mixer-settlers were originally designed by Outokumpu for extracting Mo, Re, Zn, Co and Ni but were installed commercially at Zaldivar Cu plant in 1994-95. The use of Lightnin axial-flow impellers greatly reduces entrainment levels.

The effect of nitrate in the copper solvent extraction circuit at the Lomas Bayas mining company has been reported<sup>lxx</sup>. When this Chilean copper plant started up in 1998, LIX 622N (a nonyl-salicyl aldoxime plus tridecanol) was initially used as extractant. After two months it became clear that the extractant had lost much of its copper transfer capacity, despite continual addition of fresh reagent. The severe degradation was traced to a high concentration of nitrates, mainly sodium nitrate, in the pregnant leach solution. Soluble nitrate salts were identified in the ore, at concentrations varying, with mining depth, from 0 to 0.5% NO<sub>3</sub>. After a number of trials, LIX 841C (a nonyl-cetoxime) was introduced with Orfom SX-12 diluent and now controls the stability of the organic and its copper transfer capacity to a large extent.

The effect of the diluent on interfacial emulsions in copper solvent extraction has been studied by Liu et al.<sup>lxxi</sup>. The organic

phase extracted from interfacial crud from the solvent extraction circuit at Dexing copper mine, Jiangxi, was analysed for its different components by combined gas chromatography and mass spectroscopy. The main impurities were found to be methyl naphthalenes and di-methyl naphthalenes originating from the commercial kerosene used as diluent. Methods are suggested for improving the properties of the diluent so as to favour disengagement of the aqueous and organic phases, preventing stable interfacial emulsions from forming.

The separation of nickel and copper from ammoniacal solutions through co-extraction and selective stripping using LIX 84 as the extractant has been reported and a flowsheet has been developed for this process<sup>lxxii</sup>.

The deportment of manganese in copper solvent extraction and electrowinning has been studied by Cheng et al.<sup>lxxiii</sup>. Transfer of Mn<sup>2+</sup> into the copper electrolyte by entrainment in the organic phase will result in oxidation of the manganese during copper electrowinning. High oxidation states of Mn causes deterioration in the phase separation characteristics of the solvent extraction system resulting in increased phase disengagement times and the formation of stable mixed phases and emulsions. During laboratory scale copper SX-EW trials it was found that the high oxidation state manganese species oxidised some organic components of the organic phase during stripping. A number of degradation products of the hydroxyoximes have been detected by a combination of gas chromatography and high performance liquid chromatography. The observed deterioration in phase separation characteristics correlated with the presence of 5-nonyl salicylic acid and a further hydroxyoxime degradation product which eluted in the most polar of three column chromatography fractions used to separate the degraded organics. Further work is in progress to verify that these more polar species do in fact inhibit phase separation processes.

The solvent extraction of copper with the reagent MOC 45 has been studied by Rao et al.<sup>lxxiv</sup>. This appears to have performed as one might expect for a hydroxyoxime reagent. The process was tested for the recovery of copper from a converter slag leach solution.

Simulation of a copper SX-EW pilot plant has been reported by Aminian et al.<sup>lxxv</sup>. Phenomenological models have been developed for both the SX and EW processes and these two models linked to make the SX-EW simulator. The simulator was used to predict the operation of the Mines Gaspé pilot plant. Results were shown to confirm the potential of the simulation in student training, process optimisation and for the assessment of control strategies.

A process based on solvent extraction to selectively recover sulphuric acid from an electrolyte bleed stream from a copper SX/EW plant has been developed. The objective was to recover up to 90% of the acid as a pure aqueous acid stream at a concentration of up to 1340 g/l that could be recycled back to the tankhouse, thus reducing both neutralisation and acid makeup costs. The extractant used was tri(2-ethylhexyl)amine (TEHA) which permitted the acidity of the bleed to be reduced from 180 g/l to as low as 18 g/l. The performance of the TEHA extractant was also compared with the trialkyl phosphine oxide extractant CYANEX 923<sup>lxxvi</sup>. In further work, the use of a pulsed perforated plate extraction column has been investigated for the recovery of sulphuric acid from copper tankhouse electrolyte bleeds<sup>lxxvii</sup>. Hydrodynamic and mass transfer information for the column have been presented and used for scale up of the operation. The results of the pilot plant experiments have demonstrated the viability of operating the acid recovery process using a pulsed perforated plate column.

The control of iron in copper electrolyte streams with a new monophosphonic/sulphonic acid resin has been described by Xue et al.<sup>lxxviii</sup>. This is a bi-

functional monophosphonic acid ion-exchange resin which strongly and selectively extracts iron(III) ion over copper and cobalt from highly acidic copper electrolyte solutions. It has superior properties to other commercially available phosphonic acid resins and is easier to prepare than Diphonix resin. The performance of the new resin was compared with that of Diphonix, Duolite C-467 and monophosphonic acid resins at Eichrom Industries. It has good selectivity for iron(III) over mono- and di-valent species, has a rapid iron uptake and high iron loading capacity (27 g/l) and can be readily regenerated. It may have potential for removing iron from nickel, cobalt and zinc processing streams.

The simulation and design of a continuous operation short-circuiter frame (MCOC) in copper electrowinning has been described by Vasquez et al. and its impact on copper electrowinning discussed with reference to pilot implementation in Chilean plants<sup>lxxix</sup>. The new short-circuiter frame allows the electrolytic cells in tankhouses to be cleaned without electric current having to be reduced, thus gaining significant advantages in production, efficiency and process optimisation. Anode life is extended, continuous cathode quality assured, the risk of rectifier failure reduced and electrical energy costs cut. Moreover, the short-circuiter frame allows the integration and complete automation of the solvent extraction and electrowinning process.

The effect of some new organic additives, such as horse-chestnut extract (HCE) and a mixture of ethoxyacetic alcohol and triethylbenzyl-ammonium chloride (IT-85) on the morphology and structure of copper deposits, as well as upon the cathode polarisation, have been investigated and compared to those exerted by thiourea and animal glue, in the case of pure, synthetic sulphate solutions<sup>lxxx</sup>. The additive IT-85 was found to be an efficient inhibitor of the copper electrocrystallisation process, leading to levelled, fine-grained cathodic deposits with a

strong [110] texture. The effects of HCE were similar to those exerted by animal glue, leading to deposits consisting of round nodules, without a clear texture, reflecting a smaller levelling effect.

The effect of electrolysis parameters on the silver content in electrorefined cathodic copper has been investigated by Burzynska<sup>lxxxii</sup>. The silver content depends on the temperature and the composition of the anodes, including the oxygen content. The silver content does not depend on the rate of recirculation of the electrolyte.

Ways of increasing space-time yields of Cu electrolysis have been investigated<sup>lxxxiii</sup> at current densities greater than 1,000 A/m<sup>2</sup>. Bipolar electrodes of PbCa<sub>0.12</sub>Sn<sub>1.4</sub> lead alloy were used in order to lower the specific energy demand. Under forced convection with varying electrolyte flow, analysis of structure and roughness showed that Cu deposition was non-uniform over the height of the electrode. However, directed agitation of the cathode surface with nitrogen via suitable nozzles led to compact deposition of Cu at low electrolyte flow and without the addition of inhibitors. During 48 hours in a pilot plant, a Cu deposit 6 mm thick was achieved on electrode strips 1,000 mm long and 100 mm wide.

The effect of anode impurities on copper electrorefining has been studied by Free and Anthian<sup>lxxxiii</sup>. Results from electrochemical, chemical, and image analysis studies indicate that arsenic is a beneficial anode impurity, improving current efficiency and reducing fine slime particles. Anode lead was found to increase significantly both voltage and fine slime generation; these fine slime particles decrease current efficiency and increase cathode impurity levels. Sulphur was also shown to decrease electrorefining performance, but bismuth seems to have a beneficial role in increasing slime particle size.

The deportment of selenium and tellurium during the electrorefining of copper has been studied by Chen and Dutrizac<sup>lxxxiv</sup>. Because Se and Te are critical elements in the overall processing flowsheet for anode slimes, a detailed mineralogical study was carried out to determine the forms present and their deportment during electrorefining of copper. In copper anodes, Se and Te occur mainly as Cu<sub>2</sub>(Se,Te); minor amounts are present in Cu-Pb-As-Sb-Bi oxides or in metastable solid solution in the Cu metal. During electrorefining, the Se and Te in the oxides and Cu solid solution dissolve, but subsequently reprecipitate as minor constituents of an oxide phase of Cu-Ag-Pb-As-S-Te-O composition, of Cu<sub>2</sub>O and of a Pb-As-Sb-Bi-S-O phase. The Cu<sub>2</sub>(Se,Te) particles are liberated and react with dissolved Ag to form Ag-rich selenide-tellurides, or with dissolved O<sub>2</sub> to form Cu<sub>3</sub>(Se,Te)<sub>2</sub> and Cu (Se, Te). Trace amounts of the Se and Te remain in the electrolyte or report to the cathode copper.

The effect of copper, acid and temperature on the diffusion coefficient of cupric ions in simulated electrorefining electrolytes has been reported by Moats et al.<sup>lxxxv</sup>. Increasing the copper and acid concentrations slightly decreased the diffusivity of copper. The diffusivity data were utilised in a simple one-dimensional finite difference model. The model indicates that saturation of copper sulphate occurs very rapidly at the high current densities (3,820 A/m<sup>2</sup>) used in accelerated passivation experiments.

Electrochemical processing of speiss has been reported by Luganov et al.<sup>lxxxvi</sup>. The main components of speiss are copper arsenide, Cu<sub>3</sub>As, and copper antimonite, Cu<sub>3</sub>Sb. A thermodynamic analysis of electrochemical speiss dissolution has shown that the main optimum parameters for transferring copper into the solution and arsenic and antimony into the slimes are solution pH between 0 and 2 and oxidation potential between 0.40 and 0.45 V. A kinetic study has indicated that anode polarisation is

mainly diffusion-controlled, as suggested by the influence of the slime formed during the process of dissolution. Electrolysis of a copper-lead speiss through a porous diaphragm under industrial conditions allows the extraction of copper into the cathode at around 95% purity and recovery. The arsenic content of the electrolyte should not exceed 0.25 g/l and arsenic in the cathode 0.002%.

## Zinc

A description of the operation of Harzer Zink's smelting reactor at Harlingerode, in Germany has been given<sup>lxxxvii</sup>, which, since 1996, has been treating secondary residues from the thermal retort process grading less than 10 wt% Zn and containing Pb, Cu, Ni, high levels of C and impurities such as As. Advantages of the process are low emissions, low off-gas volume, clean safe products, recycling of zinc, utilisation of waste heat and a clean workplace. Zn and Pb are volatilised and concentrated in mixed crude oxide, slag-forming constituents are smelted to construction materials and by-product power is generated. The 100 t/d reactor is a cylindrical, upright, steam-cooled combustion vessel, with a bottom opening through which liquid slags and gases pass into a settler with water-cooled top-blowing lances.

The direct smelting of zinc smelter residues in an electric arc furnace has been studied by O'Connor et al.<sup>lxxxviii</sup>. In particular this study was aimed at the treatment of historical wastes at the site of a closed smelter. The direct smelting tests conducted so far produced a cast iron product containing nearly 80% of the iron in the feed at a quality equivalent to that for conventional cast iron. The slag product was determined to be non-hazardous based on the EPA TCLP test. Greater than 99% of the contained zinc and lead were recovered in the smelter dust. Data on the materials balance and energy consumption in this work are given.

The production of an ultra-pure ZnO, fluorine free as well as a slag enriched in iron from EAF dust by re-engineering the Waelz kiln

process has been described<sup>lxxxix</sup>. Magnetic separation of the dust produced a phase, high in iron which was recyclable to the EAF. The technical conditions used to produce the ultra-pure ZnO are documented.

A description has been given of the Chelyabinsk electrolytic zinc works<sup>xc</sup>. The Russian plant produces electrolytic zinc as well as a hydrometallurgical indium by-product. Papers are presented on the calcining of zinc concentrates, improvement of zinc electrolysis, improvement of Waelz oxide lime washing, zinc cake pressure filtration, efficiency of zinc cake flotation, processing of lead cakes, behaviour of indium during Waelz processing of zinc cakes, extraction of indium from zinc sulphate solution, improvement of indium extraction techniques, indium cementation, electrochemical refining of indium in chloride melts, hydrolytic refining of the raffinates from indium extraction, gas cleaning during calcining, and ecological aspects of zinc production.

A heat and mass balance model of the Kokkola zinc roaster based on HSC Chemistry 4.0 software has been constructed<sup>xc<sup>i</sup></sup>. This paper describes briefly the basic principles of the calculation model and outlines the results. The calculated results were in reasonable agreement with recent process air oxygen enrichment and water feed test campaigns carried out at Kokkola in 1999.

It has been shown that zinc sulphate could be produced by leaching sphalerite with H<sub>2</sub>SO<sub>4</sub> at high O<sub>2</sub> concentration and normal pressure<sup>xc<sup>ii</sup></sup>. The effect of the leaching conditions on metal recovery was investigated. More than 95% of the zinc was leached and the sulphur from the zinc blende mostly became elemental sulphur under the following conditions: H<sub>2</sub>SO<sub>4</sub> concentration 40 mass%; liquid: solid ratio 6:1-7:1; temperature 110-120°C; soaking time two hours; O<sub>2</sub> flux per litre 40-50 cm<sup>3</sup>/min.



The results of a leaching kinetics study of low grade zinc silicate ore with sulphuric acid have been presented<sup>xciii</sup>. The results showed that about 94% of the zinc could be leached using a -200 +270 ore particle size at a reaction temperature of 70°C for 180 mins reaction time, with 10% sulphuric acid at a solid/liquid ratio of 1:20 g/ml. Leaching kinetics indicated that diffusion through the product layer was rate controlling.

A proposed expert system has been implemented at a zinc hydrometallurgical plant<sup>xciv</sup>. The system's architecture and diagnostic procedure are presented. The rule models were constructed on the basis of empirical knowledge, empirical data and the statistical results from measures taken against faults in the past. The expert reasoning strategy employs the rule models and Bayes presentation, combining forward and backward linkages. The results of actual runs showed that more than 90% of on-line diagnosis and more than 95% of off-line diagnosis was accurate.

A production process for Zn powder by alkaline treatment of an oxidised Zn ore, smithsonite, has been developed<sup>xcv</sup>. It was found that over 85% of both Zn and Pb and less than 10% of Al could be leached from the ore when the leaching operation was conducted at over 95°C using 5 M NaOH as the leaching agent. The dissolution of impurities such as Fe, Ca, etc. was negligible. Leaching of Pb is significantly improved by the addition of NaCl. Lead present in the leach liquor can be removed by addition of sodium sulphide. The Pb-free solution can then be used for the electrolysis of metallic Zn using stainless steel electrodes to produce a zinc metal powder of purity higher than 99.5%. Further information on this process is presented, including a flowsheet for production of zinc from such ores.

The bioleaching of zinc and nickel from silicates using *Aspergillus niger* cultures has been described by Castro et al.<sup>xcvi</sup>. The results obtained suggest that the type of

mineral presents a different susceptibility to the bioleaching process and also demonstrate that, depending on the situation, the presence of the fungi cells seem to improve the leaching process. Chemical leaching with citric acid gave much lower metal extraction compared to that in the presence of the *A. niger* cultures. This bioleaching process was considered to present two advantages as compared to conventional chemical leaching processes, ie a) the very low concentrations of organic compounds present in such a situation represents a lower ecological risk and b) even with a lower final yield, the cost of such a process.

A study has been carried out on the deportment of gallium during jarosite precipitation<sup>xcvii</sup>. This has shown that the molar ratio between Ga(III) and Fe(III) precipitation is approximately the same as the ratio between them in solution, with Ga<sup>3+</sup> replacing Fe<sup>3+</sup> in the jarosite structure. The relative deportment of Ga is about the same whether sodium, potassium or ammonium jarosite is precipitated. Consequently, it is virtually impossible to avoid losses of Ga in jarosite. Jarosites can be slightly enriched in Ga by precipitation at higher solution pH during the initial hours of reaction, and significantly enriched by precipitation from dilute Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> media. Solution pH exerts a major influence on the amount of jarosite formed, as does longer retention times of four-five hours, but the effect on composition is only minor.

A study has been made<sup>xcviii</sup> of the effects on Co removal and zinc dust consumption of a number of constituents of zinc sulphate solutions, such as Zn<sup>2+</sup>, Cd<sup>2+</sup> and Cl<sup>-</sup>. Without activators, the presence of zinc ions inhibits cementation but with Cu<sup>2+</sup>/Sb<sup>3+</sup> activators cementation is rapid. The addition of small amounts of Cd and Cl increases the amount of cobalt removed beyond the level achieved with Cu and Sb alone. At least one novel additive, Sn, proved as effective as Sb in terms of cobalt reduction, while zinc dust

consumption was greatly reduced in the presence of several other elements. A number of suitable combinations of activators were identified.

A study has been made of methods to decrease consumption of zinc dust during the purification of zinc solutions with antimony trioxide and the effects of temperature, amount of zinc dust, stirring velocity, dust particle size, content of cobalt in solution and pH have been determined<sup>xcix</sup>. It was found that the major influences on the purification process were temperature and amount of zinc dust. Concentration of  $\text{Co}^{2+}$  can be reduced to less than 0.50 mg/l when there is more than 1.6 g/l of zinc dust, the temperature is 85°C, the stirring velocity is greater than 300 rpm and the particle size of zinc dust is sufficiently small.

In other studies on the removal of cobalt from zinc leach liquors, the potential-pH pattern of the Co-Sb- $\text{H}_2\text{O}$  system has been determined<sup>c</sup>. This shows that the thermodynamic force driving the removal of Co by cementation with zinc dust is increased when metallic CoSb forms. Scanning electron microscopy and X-ray diffraction have revealed that Sb exists in the same forms as Ni and Co. It is clear that Co from the zinc sulphate solution combines with Sb in a metallic compound while Zn remains in the form of zinc sulphate, zinc oxide or zinc metal.

A study has been made of the products formed during cobalt cementation on zinc dust in zinc sulphate electrolytes<sup>ci</sup>. Two reactions have been identified, namely, the formation of a cobalt alloy or cobalt in solid solution and the second is the formation of basic cobalt salts. Basic cobalt salts redissolve more easily than Co alloys and this is the major reason for cobalt redissolution during the technical purification of the zinc sulphate electrolyte before zinc electrolysis. In further work on this topic<sup>cii</sup>, micro-Raman spectroscopy has been used to characterise the cemented product, and the effect of

copper and antimony on the cementation process has been examined. Raman mapping over a large area of cemented products shows that the occurrence of the peak for a basic cobalt salt or salt mixtures decreases dramatically during redissolution of cemented cobalt. The data indicate that a large fraction of the cemented  $\text{Co}^{2+}$  exists as a mixture of cobalt containing oxide and hydroxide. The influence of tartrate on cobalt cementation has also been studied using a rotating zinc disc in zinc sulphate solution<sup>ciii</sup>. These laboratory-scale experiments have shown that large amounts of tartrate in solution reduce the cementation rate of  $\text{Co}^{2+}$  significantly. Accumulation of tartrate may therefore cause problems in a zinc plant

A new approach for the removal of magnesium from zinc electrolytes has been suggested and confirmed by experimental results<sup>civ</sup>. It involves selective precipitation of magnesium fluoride from purified zinc sulphate solutions. The magnesium fluoride is then contacted with sodium hydroxide solution to convert it to magnesium hydroxide for possible sale. The resulting sodium fluoride solution can be electrolysed in a membrane cell, consisting of a zinc anode and an inert cathode, to yield zinc fluoride and sodium hydroxide for recycling to the magnesium removal process.

A study on the continuous electrowinning of zinc has been carried out using synthetic and pure zinc solutions produced from laboratory-leached oxidised zinc ores under controlled temperature and pH conditions until the least possible zinc concentration was reached<sup>cv</sup>. Conventional DC electrolysis, PC and PCR procedures were all examined. The effect of organic additives and some impurity cations were also investigated. Current efficiencies of more than 95% were obtained from acid sulphate solutions electrolysed at 45 mA/cm<sup>2</sup> and 25°C for DC and PC techniques. Electrowinning from relatively concentrated solutions (160 g/l) could be achieved with acceptable efficiencies down to about 40 g/l. Copper additives were found to decrease

current efficiency and worsen the quality of the cathode deposits. Manganese and silica were found to have limited effects on both current efficiency and deposit morphology. Iron was found to have a deleterious effect on both current efficiency and deposit morphology. Organic additives such as gelatine and thiourea have good levelling effects on the cathode deposits. Gelatine was found to improve the current efficiency—especially in the presence of a mixture of foreign cations.

A comparative study on zinc electrowinning from sulphate and chloride solutions has been made by Lupi and Pilone<sup>cv</sup>. A comparison of the results showed that a high quality zinc can be electrowon in both cases with comparable energy requirements.

A process for recovery of germanium from a zinc leach liquor by solvent extraction has been developed<sup>cvii</sup>. The main flowsheet for this recovery is presented and the parameters of the process in a commercial plant are discussed. Production capacity is 70 m<sup>3</sup>/d of feed solution containing around 0.04–0.05 g/l Ge and 120–130 g/l Zn. Recovery after three extraction stages is 95% and single-stage stripping recovery is 98%. The crude GeO<sub>2</sub> product contains around 30–40% Ge. The extractant and stripping solutions can be recycled.

Microwave treatment of electric arc furnace dust at 2.45 GHz by leaching in caustic solutions resulted in very rapid dissolution of zinc oxide<sup>cviii</sup>. Leaching was completed within minutes, whereas total dissolution of zincite took three hours for conventional caustic leaching. With microwave heating, Zn recoveries were 5–10% higher than observed with conventional heating, indicating that some zinc ferrite was being dissolved. In contrast to conventional heating, the dissolution rate in the microwave tests increased with a decrease in the solid/liquid ratio. This effect was not significant at concentrations below 60 g/l. Dissolution was both faster and more complete at higher

power levels, while the effect of caustic concentration was also significant, with 8 M the optimum for Zn recovery. More zinc was dissolved than lead, whereas in conventional leaching the reverse was the case. This was attributed to the different behaviour of Zn and Pb compounds under microwave irradiation.

The extraction of zinc from zinc ferrites by fusion with caustic soda has been studied by Zhao and Stanforth<sup>cix</sup>. Recovery of zinc from ferrites in leaching residues and steel mill EAF dusts is difficult because they are difficult to decompose chemically. A novel process to decompose zinc ferrites by fusion with sodium hydroxide at 350°C was developed. After dissolution in an alkaline leaching solution, 75–80% of the zinc was recovered by electrowinning; this increased to over 90% when ferrite was hydrolysed with water or dilute NaOH before fusion.

Hydrometallurgical routes for recycling zinc from used alkaline batteries have been reviewed<sup>cx</sup>. Some work aimed at developing a hydrometallurgical process for the dissolution of zinc and its recovery by electrolysis is also described.

### Lead

A new highly effective binder for lead-zinc sintering has been developed<sup>cx</sup>. An organic binder has been selected that raises the strength of the granules, improving sinter lumpiness. When 0.0594% of the reagent was added, the sintering lumpy rate increased from 15.4 to 17.89% and the hourly output of the blast roaster was improved by 11.6%, with considerable economic effects for the Imperial Smelting process.

The behaviour of As and Sb in Hoboken lead sinter has been studied by Evrard et al.<sup>cxii</sup>. From sinters produced over the past 15 years at the Belgian plant, arsenic and antimony have been shown to participate in the sintering reactions. Antimony is essentially found as a mixed oxide phase Ca<sub>3</sub>(Fe,Zn,Al)<sub>3</sub>(Sb,Si,Sn)<sub>2</sub>O<sub>12</sub> of garnet structure, which is among the first phases to form.

Arsenic separates during the latest steps of the sintering reactions as an apatite-type phase  $(\text{Ca,Pb})_5(\text{As,Si,S})_3\text{O}_{12}(\text{OH,Cl,F})$  intergrown with the residual high-Pb silicate. The mean level of substitution of Pb for Ca in the Pb-Ca arsenate is an indication of the amount of Si still available when the Pb silicate solidifies. High silica and lime content in the Pb-Ca arsenate is associated with high Pb and low Si content in the Pb-silicate matrix, resulting in an increase in the rate of lead oxide reduction in the blast furnace and indicating better Ca saturation of melilite. The Sb-garnet consumes only minor amounts of lime and it is not certain whether its composition indicates a deficiency or an excess of silica in the sinter.

A study has been made on the effect of mesophilic microorganisms on the electrochemical behaviour of galena<sup>cxiii</sup>. The electrochemical evolution of massive galena electrodes was investigated with and without mesophilic bacteria, using potentiometry, anodic and cathodic polarisation, and cyclic voltammetry. In the absence of bacteria, anodic dissolution was not influenced by agitation rate or nutrient content, but was significantly affected by scan rate, temperature, pH and the acid used to fix pH. A peak corresponding to sulphide oxidation was only detected in the presence of complexing Pb anions. After bioleaching at 35°C with mesophilic bacteria, major differences in the electrochemical response of the electrodes were noted. The peaks corresponding to galena oxidation decreased, while new peaks appeared during both oxidation and reduction, intensifying with time.

The recovery of lead and zinc from fly ash generated from municipal incineration plants by means of acid and/or alkaline leaching has been studied by Nagib and Inoue<sup>cxiv</sup>. The reason for this work is that such fly ash is regulated as a hazardous waste because it contains considerable amounts of heavy metals and hazardous organic materials such as dioxin. Sulphuric acid leaching is effective

where most of the zinc dissolved, and HCl or acetic acid leaching was effective where most of the Pb and Zn dissolved. However, these acids dissolved other impurities together with the Pb and Zn. Alkaline leaching suffered from low zinc solubility. In order to improve zinc solubility, the solid residue from alkaline leaching was washed with 2% or 5% HCl. This removed almost all the lead and about 68% of the zinc. A flowsheet incorporating an alkaline leach followed by a dilute HCl wash has been developed.

The recovery of lead and silver as lead concentrate and lead metal by the hydrometallurgical processing of lead-bearing materials produced at the smelters of Hindustan Zinc has been described<sup>cxv</sup>. These are lead sulphates and lead-silver-bearing residues. Two approaches have been selected, the first consisting of treating the lead sulphate residue with an aqueous solution of sodium sulphide after removal of acid soluble material to produce a high quality lead concentrate. In the second, the lead sulphate residue is treated with brine and the resulting filtrate from solid/liquid separation treated with sodium sulphide to produce a lead concentrate, or treated with aluminium scrap to produce a lead cement which was then briquetted and melted into lead metal. Alternatively, the lead cement could be roasted to litharge. Conceptual flowsheets have been developed to treat 305 t/d of lead-bearing materials.

### Nickel and Cobalt

The first of the Alta conferences held in Australia in 2000 was in May and was on nickel and cobalt and included papers on: the Ravensthorpe project; the Syerston project; the NiWest project; ramp up information on the Cawse and Bulong plants; integrated pilot-plant operation of the downstream processes including Ni EW for treatment of the liquor; from the BioNIC process; developments in Ni EW, Ni powder production by pressure hydrogen production; autoclave design and operation; problems with scale in the autoclaves; and future trends in pressure acid



leaching plant design for treatment of Ni/Co laterites<sup>cxvi</sup>.

The IMM Commodity Meeting, held in London in November 2000 was on cobalt, but unfortunately it would seem that none of the papers presented will be published.

The possibility of processing a range of ores in the shaft furnaces at the Yuzhural nickel works, in Russia, has been studied<sup>cxvii</sup>. A number of changes would allow the range of ores to be extended and their content of iron-containing components to be enlarged. Ore massifs such as hydrated iron oxides would be excluded during mining. An investigation would be carried out to determine the effects on sinter density and iron Co reducibility if converter slag were to be added to the sintering charge. The anion structural coefficient would be used in calculating the materials to be charged to sintering and shaft smelting; this would allow rapid correction of slag composition.

The technical feasibility of recovering copper, nickel and cobalt from smelting and converting slags using Ausmelt's top-submerged lancing process has been demonstrated at pilot-plant scale and in several commercial applications<sup>cxviii</sup>. Process conditions can be tailored to achieve the maximum economic recovery of valuable metals and to yield a product composition that fits downstream processing requirements. There is strong economic justification for a slag-cleaning process where the value of contained metals recovered per tonne of slag treated exceeds US\$50/t. Where this value is predominantly associated with Co recovery, the top-submerged lance system offers a relatively low-cost solution.

Microwave heating was used for chloridising roasting of a nickel-bearing garnierite ore<sup>cxix</sup>. It was demonstrated that leaching of Ni from the roasted product with dilute acid solution was more efficient when microwave heating was used than when roasting was

conventional. A decrease in the initial particle size of the ore from 0.2 mm to less than 0.1 mm, or an increase in microwave power applied from 400 to 700 W, also increased leaching efficiency, as did a moderate increase in irradiation time and the amount of FeCl<sub>3</sub> added, but efficiency was reduced if irradiation was for more than 20 min or FeCl<sub>3</sub> exceeded 28%. Under optimum conditions, leaching efficiency was 71.65%.

A cold model has been built to investigate the effects on entrainment of matte-slag interface height and skimming flow rate, during the skimming of iron oxide and silica slags from copper, nickel and iron sulphide mattes<sup>cxx</sup>. Oil was passed continuously through a laboratory-scale cell in which a stratified oil/water system was maintained. The exit flow of oil was found to entrain a small proportion of water, which depended on the distance of the interface below the centre of the exit duct. In most cases, the entrainment occurred when the interface was significantly below the bottom of the exit duct. The threshold interface level for entrainment was measured for several exit duct configurations as a function of oil flow rate and compared with a hydrodynamic prediction. This threshold and the rates of entrainment were strongly affected by the configuration of the exit duct. Scale-up calculations indicate that surface phenomena are unlikely to have much effect in an Inco flash furnace, but hydrodynamic entrainment could occur near the start of skimming.

The different routes for autoclave treatment of oxidised Ni-Co ores have been reviewed and main features of autoclave sulphuric acid leaching outlined<sup>cxxi</sup>. Data are listed for projects in Australia, Indonesia, Papua New Guinea, New Caledonia and the Philippines, including reserves, ore grade, tonnage and grade of material being treated by pressure acid leaching, Ni and Co recovery, capital investment, start-up date (actual or projected) and cost per tonne of nickel. Details are also given of the ore types and geochemistry and the process parameters for the technology

being put into use at the Bulong, Cawse and Murrin Murrin plants in Australia.

The three innovative high-pressure acid leaching nickel laterite projects have encountered a number of serious problems, which can be traced back to mechanics, basic design faults and the use of materials that could not cope with the highly corrosive conditions. Cawse is now operating at design capacity<sup>cxix</sup>. Murrin Murrin also has a positive cash flow and is producing about 1,200 t/month Ni, still only a third of design capacity; its capital costs have surpassed A\$1 billion and are still rising. The Bulong project has cost overruns of A\$200 million-A\$300 million, similar to those at Cawse, but is still some way from a positive cash flow. However, the lessons learnt should make any second-phase projects more viable.

A very brief description of Reminex's cobalt plant in Morocco has been given<sup>cxix</sup>. This plant treats the residues and concentrates from the Bou Azzer mine. The concentrates are first roasted to remove and recover arsenic as 99.9% pure  $\text{As}_2\text{O}_3$ , the roaster calcine is then leached with sulphuric acid, ferric arsenate precipitated and cobalt then recovered by solvent extraction and electrowinning. The annual output of cobalt cathode in Morocco is now ~1,000 t/y.

The development of the process for nickel and cobalt recovery from the Goro laterite ore in New Caledonia has been discussed by Mihaylov et al.<sup>cxix</sup>. This novel process involves the recovery of Ni and Co by solvent extraction directly from the partially neutralised leach solution with Cyanex 301. Ni, Co and Zn are selectively extracted without the addition of a neutralising agent. Phase separation is excellent and organic losses are very low. Stripping with hydrochloric acid produces a solution about 20 times more concentrated, allowing for ready removal of Zn by ion exchange and recovery of Co by amine solvent extraction in much smaller circuits. A high-purity nickel oxide product is then recovered from the

raffinate by pyrohydrolysis, while co-produced HCl is recycled. Reagent and energy costs are low.

A universal kinetic equation for the rate of nickel dissolution by sulphuric acid pressure leaching of limonites and limonitic/saprolitic blends has been derived by Rubisov et al.<sup>cxix</sup>. This universal equation has been successfully tested against various feeds containing from 12% to 1.9% Ni and up to 3.85% Mg at temperatures from 230°C to 270°C, acid to ore ratios from 0.15 to 0.5 and at pulp densities of up to 30%. Further work<sup>cxix</sup> has addressed the speciation and prediction of metal solubilities at temperature and these have been determined from a simple speciation programme that assumes the presence of only one dominant complex for each metal. The thermodynamic data for the precipitation reactions have been extracted from high temperature experiments on monometallic systems published previously. The validity of this approach was then tested on mixed bimetallic systems and finally applied to calculate the solubility of aluminium, iron and magnesium in laterite leach liquors at temperature. In both cases of limonitic feed and limonitic/saprolitic blends, the predictions closely follow the experimentally measured metal solubilities. Following on from the above these workers have developed a comprehensive model of a continuous autoclave for sulphuric acid pressure leaching of laterites<sup>cxix</sup>. This combines the kinetic, speciation and solubility data determined in the earlier work. The resulting model is capable of predicting nickel extraction and concentrations of the major impurities during autoclave operation for a wide variety of process conditions and feed compositions. The results from the model have been compared with continuous mini-plant acid pressure leaching data provided by Inco Technical Services during process development campaigns.

The effect of acidity at temperature on the morphology of precipitates and scale during sulphuric acid pressure leaching of nickel

laterites has been studied by Rubisov and Papangelakis<sup>cxxviii</sup>. The variable Fe and Mg contents of the laterites influence the acidity levels required for effective leaching, and lead to the rejection of Fe as haematite during leaching. Classical solid/liquid separation is performed via a countercurrent decantation circuit, the performance of which depends on the size and shape of precipitated particles. Precipitates obtained by acid leaching of various lateritic feeds at 270°C have been characterised using SEM/EDX and laser particle size analysis. As acidity increased, the shape of the precipitates gradually changed from platelets to spheres, thus improving the solid/liquid separation properties of the residue. The use of hydrogen ion concentration at temperature, calculated from a speciation analysis, allows the explanation of this change of morphology independently of the type of ore feed. The possibility of precipitating Mg sulphate is also discussed.

Experiments, designed to optimise the sulphatisation of a mechanical mixture of chemically pure nickel and iron oxide and a lateritic ore using sulphuric acid have been carried out by Kar et al.<sup>cxxix</sup>. The significance of various parameters has been established. Regression equations have been formulated for both systems and the extraction has been represented as a function of response variables. The accuracy of the equation has been verified by Fisher's adequacy test.

An increase in efficiency of autoclave disintegration of nickel-bearing sulphide concentrates has been reported by Naftal et al.<sup>cxxx</sup>. In the hydrometallurgical processing of nickel-pyrrhotite concentrates at Norilsk's Nadezhdinsk plant, in Russia, autoclaving at 125-130°C requires the addition of a hydrophilisator reagent. The reactions with  $\text{Ca}(\text{OH})_2$  are discussed and the results are reported of an investigation into the effects of adding varying amounts of an active mineral additive to inhibit sulphidation of oxide iron. Acceptable materials for use as an additive include natural silica-containing rocks and

man-made products such as nepheline slimes from alumina production and blast-furnace slags. The resulting decomposition conditions substantially reduce the consumption of hydrophilisator reagent and halve losses of elemental sulphur.

The kinetics and mechanism of pentlandite leaching in aerated acidic chloride/sulphate solutions have been studied using electrochemical and chemical techniques<sup>cxxxi</sup>. The electrochemical experiments showed that pentlandite experiences passivation at low overpotentials. However the addition of chloride ions was found to increase the leaching rate and it is believed that the role of chloride is to allow formation of a more porous sulphur product. Both temperature and oxygen partial pressure had a substantial effect on the leaching rate with optimum leaching kinetics being obtained at 85°C and an oxygen pressure of one atmosphere. Under such conditions, 96% nickel extraction could be achieved during leaching in the presence of chloride ions.

The effect of mechanical activation by attritor grinding of a pentlandite concentrate on its leaching behaviour has been reported by Balaz et al.<sup>cxxxii</sup>. The mechanical activation increases the specific surface area and a decrease in the crystalline content of the mineral components. These transformations are accompanied by mechano-chemical surface oxidation of individual minerals and the formation of water soluble Ni, Cu and Co compounds. In subsequent leaching tests with acid ferric sulphate, the mechanical activation was shown to affect the selectivity of extraction of individual minerals.

The behaviour of Co and Ni during aqueous sulphur dioxide leaching of nickel smelter slag from Inco has been studied<sup>cxxxiii</sup>. Using different leaching conditions in a batch reactor the maximum extraction of Co and Ni after three hours were 77% and 35% respectively. The shrinking core model was used to explain the behaviour of cobalt and nickel. Co extraction was limited by both ash

layer diffusion and surface chemical reaction while Ni extraction was limited only by ash layer diffusion.

The recovery of cobalt from cobalt cements produced in the purification of zinc electrolytes has been studied<sup>cxxxiv</sup>. The metals present in fresh cobalt cement can be leached with sulphuric acid under strict pH control and a precipitate containing 6-12% can be obtained compared to 0.6-1% cobalt in the original cement. It is claimed that this can now be worked up to produce a variety of cobalt salts and pigments.

The leaching kinetics of nickel and cobalt from spent cadmium-nickel batteries have been studied, using samples containing 46.76% Cd, 40.34% Ni, 2.38% Co and 1.60% Fe which had been crushed and roasted to convert Ni and Cd to their oxides<sup>cxxxv</sup>. The effects of H<sub>2</sub>SO<sub>4</sub> concentration, leaching temperature, roasting parameters and oxidising agents on the leaching processes were investigated. The experimental results showed that the leaching of Ni and Co is controlled by surface chemical reaction. The percentage leached can be markedly increased by roasting in oxygen and the addition of an oxidant can also enhance the leaching of Ni, though it decreases the percentage of Co leached.

Process simulation has been used in the commissioning of the Kasese cobalt bioleach plant in Uganda<sup>cxxxvi</sup>. The development of new processes has to follow best-practice rules in order to be technically and economically as efficient as possible. However, innovations, new process routes and new rules are continuously emerging to minimise financial risk and maximise environmental compliance. Process simulation, which offers a complete overview of the flowsheet, makes it possible to cope with the new challenge of minimising waste production and water consumption. Simulation also provides an estimate, at an early stage, of the cost of alternative technical routes.

Radio Hill in Australia is undertaking the world's first trial of bacterial heap leaching of pentlandite ores, a process which, if successful, will improve the outlook for many low-grade orebodies in Australia and elsewhere<sup>cxxxvii</sup>. The trial will investigate the bacterial recovery of Ni, Cu and Co from disseminated ores overlying the Radio Hill massive sulphides and from substantial resources of similar material at Mount Sholl. Preliminary economic studies indicate the potential for cash costs well below A\$1.00/lb Ni. This development is also discussed in another paper<sup>cxxxviii</sup>.

A study on the effects of Ni<sup>2+</sup> and Co<sup>2+</sup> on *T. ferrooxidans* on the bacterial leaching of nickel and cobalt from low-grade Ni ore from Jinchuan, in Gansu has been reported<sup>cxxxix</sup>. Experimental results showed that both Ni<sup>2+</sup> and Co<sup>2+</sup> considerably reduced the oxidation of Fe<sup>2+</sup> by wild strains of *T. ferrooxidans* under the common bioleaching conditions of 30°C and pH 2.0. Tolerance of *T. ferrooxidans* to 40 g/l concentration of Ni<sup>2+</sup> and 30 g/l Co<sup>2+</sup> was achieved after a long period of adaptation by repeated subculturing in a medium containing certain concentrations of Ni<sup>2+</sup> and Co<sup>2+</sup>. The *T. ferrooxidans* obtained had a stronger capacity for oxidising Fe<sup>2+</sup>.

A review has been presented of possible biological factors in the genesis of manganese nodules and of the potential for using biological leaching to extract Mn, Cu, Co and Ni from them<sup>cxl</sup>. It has been suggested that Fe and Mn(IV) oxides may be deposited on the surface of the nodules in thin bacterial films or that Mn is first sorbed by nodules in the form of Mn<sup>2+</sup> and subsequently oxidised by bacteria. Mn and other metals may originate in sediments or be carried by ocean currents from distant hydrothermal vents. To use the naturally present Mn(IV)-reducing bacteria to solubilise the base metals it appears that sea water would be needed, but Mn leaching by a variety of soil and fresh-water species has



been studied in the laboratory and a process design has been proposed.

The purification of synthetic laterite leach liquors by solvent extraction with D2EHPA has been reported by Cheng<sup>cxli</sup>. Basically this uses the solvent extraction process to remove Zn, Ca, Mn and Cu from cobalt and nickel.

The separation of zinc and cadmium from nickel and cobalt by solvent extraction in either the chloride or thiocyanate form of Aliquat 336 has been studied by Wassink et al.<sup>cxlii</sup>. With NaCl solutions, good separation was achieved and separation improved with decreasing NaCl concentration but was still effective at 200 g/l NaCl. Separation with the thiocyanate form of Aliquat 336 was studied with NaCl, Na NO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> solutions. Zinc extraction was favoured over Cd in every case. Because of this, separation of zinc from both cobalt and nickel was good but separation of Cd from Co was only moderate at best. Ammonia stripping of zinc and cadmium loaded Aliquat 336 was found to be effective.

The effects of modifiers on the solvent extraction of Co(II), Fe(II) and Mn(II) have been investigated<sup>cxliii</sup>. It was found that the modifier HB reduced the extraction of all three metals and also changed the properties of the Fe extracted, so that it could not be stripped with water but only with dilute acid. Co, Fe and Mn could be separated by scrubbing and stripping. The concentration of Co in the raffinate was less than 0.03 g/l and Co recovery was 98%. The Co:Fe and Co:Mn mass ratios in the cobalt chloride product were both greater than 300, meeting the standard for high-quality cobalt chloride.

The solvent extraction of Co(II) and Mn(II) from a waste solution saturated with sodium chloride has been investigated<sup>cxliv</sup>. The experimental results showed that quaternary ammonium chloride, with iso-octanol as modifier and kerosene as diluent, is suitable for separating the two metals. Although 15-

20% of Mn was co-extracted with cobalt, Mn in the loaded organic phase was reduced from 0.4 to 0.02 g/l in one stage by scrubbing with a saturated NaCl solution. Four-stage countercurrent extraction and three-stage scrubbing of a feed solution containing 0.6 g/l Mn and 1.5 g/l Co recovered 98% of the cobalt and achieved a Co/Mn ratio greater than 300.

A laboratory-scale contactor was used to obtain fundamental data on hydrodynamics and mass transfer kinetics in the solvent extraction separation of cobalt from nickel<sup>cxlv</sup>. Electrostatic fields can be used to enhance either coalescence or dispersion in solvent extraction. It was found that an increase in applied field intensity from 0 to 4.6 kV/cm increased the hold-up of the dispersed phase from 0.43% to 0.94% at an electrode insulation thickness of 0.5 mm, while mean drop size decreased with an increase from 2.5 to 4.4 kV/cm. Co extraction from Ni, using CYANEX 272 in Shellsol 2046, doubled from 44% to 88% when applied field intensity increased from 3.6 to 4.0 kV/cm; this increase in mass transfer is attributed to the smaller dispersed droplets produced and their associated vibrating and turning movements.

The extraction and separation of cobalt and nickel from aqueous sulphate solutions using CYANEX 272 pre-neutralised with ammonia has been studied<sup>cxlvi</sup>. The extraction experiments were carried out in a vigorously agitated co-current column reactor with fast phase separation in which the contact time could be varied between 2 and 90 seconds. About 90% of the metals were extracted in the first 10 seconds. At the shortest contact times the organic phase contained reverse micelles enclosing water, metal ions and ammonia. With increasing cobalt loading these micelles broke up. To achieve a high Co/Ni separation, the cobalt/extractant ratio should be 1:4 when the degree of neutralisation of the CYANEX 272 is about 50%.

Nickel extraction with carboxylic acids is currently of interest, not least because of its use at Bulong. The characterisation of the organic phase species in the extraction of nickel with pre-neutralised Versatic 10 has been reported by Jaaskelainen and Paatero<sup>cxlvii</sup>. The extraction of nickel was studied using two different techniques to adjust the equilibrium pH by a) addition of aqueous ammonia to the mixer cell or b) by neutralisation of the feed organic solution with concentrated ammonia prior to phase contact. Although these two techniques resulted in the same final equilibrium under equal conditions, the phase behaviour and kinetics were quite different. When using the pre-neutralised extractant, the structure of the nickel carboxylate complex depended on the degree of pre-neutralisation relative to the amount of nickel in the feed and the extraction concentration. If the degree of pre-neutralisation was too high for the extractable amount of nickel, the organic phase remained micellar and both water and ammonia were found in the organic phase.

The separation of nickel and calcium by solvent extraction using mixtures of carboxylic acids and alkylpyridines has been studied by Preston and du Preez<sup>cxlviii</sup>. The dependence of the synergistic shift of the  $pH_{50}$  value in this mixed extractant system and the Ni/Ca separation depends on the identities of the carboxylic acid, the alkylpyridine and the organic diluent. Large synergistic shifts were found for nickel, whereas antagonistic shifts were found for calcium, resulting on a marked enhancement of the Ni-Ca separation, e.g. from 1.04 pH units for Versatic 10 (0.5 M in an aliphatic diluent) to 3.48 units for its mixture with 4-(5-nonyl)pyridine (0.5 M). The selectivity series for this extractant mixture shows that in the recovery of nickel from laterite leach liquors, the early rejection of manganese, ferrous iron, calcium and magnesium to the raffinate would be achieved, while the more valuable impurity metals, namely copper, cobalt and zinc, would report to the nickel strip liquor,

from which they could subsequently be recovered.

The electrochemical behaviour of cathodic Ni reduction has been studied by measuring polarisation curves<sup>cxlix</sup>. The effects of total Ni,  $NH_4Cl$ ,  $NaCl$  and boric acid concentrations in the electrolyte, as well as pH value and temperature, were investigated systematically and the results analysed. The findings have much significance for the electrowinning of Ni powders from chloride solution.

The electrolytic parameters affecting the electrowinning of nickel from sulphate electrolytes have been studied by Holm and O'Keefe<sup>cl</sup>. Nickel deposits were electrowon from acid sulphate electrolytes to determine the effects of various parameters when buffering agents were not present. The nickel concentration, pH and temperature of the electrolyte were varied over a relatively broad range to evaluate changes in cathode morphology and current efficiency. Both good-quality deposits, which were flat, smooth and ductile, and degraded deposits, characterised by cracking, curling, pitting and brittleness, were obtained according to the conditions chosen for the three variables. Good deposit morphology and high current efficiency were favoured by high nickel concentrations and electrolyte temperatures. Deposit morphology improved at lower pH, but current efficiency decreased. Deposit orientations were determined, but no specific trends were evident. Cyclic voltammetry tests did show some correlation with deposit morphology but not with current efficiency.

Willis and Von Essen<sup>cli</sup> have shown that precipitation performance of nickel by hydrogen reduction can be improved by increasing the seed surface area, which in turn requires two key strategies: ensuring the discharge dip-pipe height is such that enough seed particles will be contained in the autoclave heel, and ensuring the agitators will keep all the seed particles in suspension even when they have grown. Recommendations for agitator design are

made with regard to dual- pitched blade turbines, Froude number, lower impeller torque and 50% larger blade width, separation of impellers and constant fluid level.

A rotating electrochemical quartz crystal microbalance was used to study the effect of experimental variables on the efficiency of cobalt electrowinning<sup>clii</sup>. The technique provided a useful means of differentiating between the cobalt deposition and hydrogen evolution reactions, which cannot be achieved using conventional methods. The major effects on the deposition reaction were found to be pH, temperature and Co concentration, whilst for H<sub>2</sub> evolution temperature and pH were important. It was shown that current efficiency is highest at high pH values, due to a combination of inhibited H<sub>2</sub> evolution and enhanced Co deposition. Of additives and impurities, Zn did affect Co deposition but only when present at more than 100 ppm.

A process for the recovery of nickel and cobalt from NIMH batteries has been developed and described by Lupi et al.<sup>cliii</sup>. A new plant, located in southern Italy, is now able to treat both individual cells and plastic

power packs based on the developed technology, which consists of crushing, elutriation to separate plastics, metallics etc., acid leaching, rare earth separation, multistage precipitation of Ni, Co and Fe, and finally solvent extraction on redissolved nickel and cobalt salts.

The reprocessing of lithium-ion battery scrap at a plant in the Philippines has also been described<sup>cliv</sup>. Commercial production began at the end of June 1999. Here the battery scrap, which originates from Japan, is received as a moist powder produced from the incineration and granulation of reject and used batteries. Using a batchwise treatment, the powder is dissolved in sulphuric acid with a small addition of hydrogen peroxide. The pH of the leach liquor is adjusted to 5.7 to precipitate iron, aluminium and some copper. The solution is then treated by solvent extraction with a mixture of CYANEX 272 and a hydroxyoxime to coextract the remaining copper, zinc and ferric iron. CYANEX 302 is then used to extract selectively cobalt from nickel and manganese. Various cobalt products are produced from the SX strip liquor. The extraction raffinate is passed to the waste treatment plant.

---

<sup>i</sup> Flett, D. S. and Anthony, M. T. Pressure hydrometallurgy: a review. The Mineral Industry Research Organisation, ed. N. J. Roberts, 2000, pp.163.

<sup>ii</sup> Bonney, C. F. The use of micro-organisms in the minerals and metals industries, Technical Review Series No. 6, The Mineral Industry Research Organisation, 2000.

<sup>iii</sup> EPD Congress 2000, ed P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p397-514, 549-605.

<sup>iv</sup> Lead-Zinc 2000, eds. J. E. Dutrizac, J. A. Gonzalez, D. M. Henke, S. E. James and A. H.-J. Siegmund, The Minerals, Metals & Materials Society, Warrendale, Pa., 2000.

<sup>v</sup> Fundamentals of Metallurgical Processing, Proc. James M. Toguri Symposium, 39<sup>th</sup> Annual Conference of Metallurgists, CIM, eds. G. Kaiura, C. Pickles, T. Utigard and A. Vahed, Canadian Institute of Mining, Metallurgy and Petroleum, 2000.

<sup>vi</sup> 65th anniversary to Norilsk integrated works. Tsvetnye Metally, no.6, June 2000, whole issue, 31 papers.

- vii Merry J., Sarvinis J. and Voermann N. Designing modern furnace cooling systems. *J. Metals*, vol.52, no.2, Feb. 2000, p.62-64.
- viii Mazuelos, A.; Carranza, F.; Palencia, I. and Romero, R. High efficiency reactor for the biooxidation of ferrous iron. *Hydrometallurgy*, vol. 58, no. 3, 2000, p.269-275.
- ix Blight, K.; Ralph, D. E. and Thurgate, S. Pyrite surfaces after bioleaching: a mechanism for biooxidation. *Hydrometallurgy*, vol. 58, no. 3, 2000, p.227-237.
- x Ivanov, I.; Stefanov, Y.; Noncheva, Z.; Petrova, M.; Dobrev, Ts.; Mirkova, L.; Vermeersch, R. and Demaerel, J.-P. Insoluble anodes used in hydrometallurgy, Part I. Corrosion resistance of lead and lead alloys. *Hydrometallurgy*, vol. 57, no. 2, 2000, p.109-124.
- xi Ivanov, I.; Stefanov, Y.; Noncheva, Z.; Petrova, M.; Dobrev, Ts.; Mirkova, L.; Vermeersch, R. and Demaerel, J.-P. Insoluble anodes used in hydrometallurgy, Part II. Anodic behaviour of lead and lead alloys. *Hydrometallurgy*, vol. 57, no. 2, 2000, p.125-139.
- xii ALTA 2000 Copper-6. 2-3 October 2000, Perth. Western Australia, ALTA Metallurgical Services, Blackburn South, Victoria 3130, Australia, avail. ALTA Conference Secretariat, 4 Newbury Close, Lower Templestowe, Victoria 3107, Australia.
- xiii ALTA 2000 SX/IX - 1. 4-5 October 2000, Adelaide, South Australia, ALTA Metallurgical Services, Blackburn, South, Victoria 3130, Australia, avail. ALTA Conference Secretariat, 4 Newbury Close, Lower Templestowe, Victoria 3107, Australia.
- xiv Kojo I.V., Jokilaakso A. and Hanniala P. Flash smelting and converting furnaces: a 50 year retrospect. *J. Metals*, vol.52, no.2, Feb. 2000, p.57-61.
- xv Mori G., Kippenberger C. and Paschen P. Materials' flow and energy requirement in copper metallurgy. *BHM Berg- u. Huttenm. Mh.*, vol.145, no.3, 2000, p.112-120.
- xvi Isaksson O. and Lehner T. The Ronnskar smelter project: production, expansion and start-up. *J. Metals*, vol.52, no.8, Aug. 2000, p.26-29.
- xvii Demetrio S., Ahumada J., Angel Duran M., Mast E., Rojas U., Sanhueza J., Reyes P. and Morales E. Slag cleaning: the Chilean copper smelter experience. *J. Metals*, vol.52, no.8, Aug. 2000, p.20-25.
- xviii Van Os J. Ausmelt takes to the Orient. *Metal Bull. Mon.*, no.354, June 2000, copper supp., p.26-27.
- xix Hughes S. Applying Ausmelt technology to recover Cu, Ni and Co from slags. *J. Metals*, vol.52, no.8, Aug. 2000, p.30-33.
- xx Li Yuhuang. Study and practice of reducing copper content in electric furnace slags in Guixi smelter. *Nonferrous Met. Chin. Soc. Met.*, vol.52, no.2, May 2000, p.49-52,56.



- <sup>xxi</sup> Safe, P. and Stephens, R. L. Peirce-Smith converter hood design analysis using computational fluid dynamics modelling. EPD Congress 200, ed. P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p.51-61.
- <sup>xxii</sup> Leary, R. M. and Siraa, M. A. Process control improvements at the Kennecott Utah copper smelter. EPD Congress 200, ed. P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p.63-75.
- <sup>xxiii</sup> Wesely, R. J. The case for the copper mini smelter. EPD Congress 200, ed. P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p.77-82.
- <sup>xxiv</sup> Liu Zhen, Miu Xingyi, Zhang Juan, Wang Yong, Yang Huizhen, Guo Senkui, Zhu Zuze and He Aiping. Corrosion mechanism of lining near tuyere zone by oxygen-enriched blow. Nonferrous Met. Chin. Soc. Met., vol.52, no.2, May 2000, p.53-56.
- <sup>xxv</sup> Thomas A., Grace J.R. and Samarasekera I.V. Combustion of copper concentrate particles in a stagnant gas furnace. Can. Metall. Q., vol.39, no.2, Apr. 2000, p.187-193.
- <sup>xxvi</sup> Peuraneimi, E. J. and Jokitaakso, A. Reaction sequences in sulphide particle oxidation. EPD Congress 200, ed. P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p.173-187.
- <sup>xxvii</sup> Mei Chi, Yao Jun-feng, Hu Jun, Shi Ming and Zhao Wei. The dynamic pre-estimating model of the grade of copper matte in the course of raw copper metallurgy: the best combined approach of auto-regressive and exponential smoothing. J. Cent. South Univ. Technol. China (Nat. Sci.), vol.31, no.1, Feb. 2000, p.34-36.
- <sup>xxviii</sup> Reddy R.G. Recovery of pollution-causing elements from copper slags. Minor elements 2000, processing and environmental aspects of As, Sb, Se, Te and Bi. ed. C.Young. Littleton, Colorado: Society for Mining, Metallurgy and Exploration, 2000. (Proceedings of a symposium held in conjunction with the SME annual meeting in Salt Lake City, 28 February-1 March 2000.) p.239-249.
- <sup>xxix</sup> Degterov S.A., Dessureault Y. and Pelton A.D. Thermodynamic modelling of zinc distribution among matte, slag and liquid copper. Can. Metall. Q., vol.39, no.1, Jan. 2000, p.43-54.
- <sup>xxx</sup> Bergh L.G., Yianatos J.B. and Chacana P.B. Intelligent sensor for coal powder rate injection in a slag cleaning furnace. Miner. Engng., vol.13, no.7, July 2000, p.777-781.
- <sup>xxxi</sup> Zakeri A., Hino M. and Itagaki K. Silver activity in matte and copper two-phase region of Cu-Fe-S system. Metall. Rev. MMIJ, vol.17, no.1, July 2000, p.43-60.
- <sup>xxxii</sup> Vadasz P., Havlik M. and Danek V. Density and surface tension of calcium-ferritic slags, I: the systems CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>. Can. Metall. Q., vol.39, no.2, Apr. 2000, p.143-151.
- <sup>xxxiii</sup> Shahbazian, F.; Sichen, D. and Seetharaman, S. Viscosities of some binary and ternary slags in the system CaO-FeO-SiO<sub>2</sub> with CaF<sub>2</sub> additions. EPD Congress 200, ed. P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p.121-130.

<sup>xxxiv</sup> Crites M.D., Karakus M., Schlesinger M.E., Somerville M.A. and Sun Shouyi. Interaction of chrome-free refractories with copper smelting and converting slags. *Can. Metall. Q.*, vol.39, no.2, Apr. 2000, p.129-133.

<sup>xxxv</sup> Zhong T. and Lynch D.C. Henrian activity coefficient of Bi in Cu-Fe mattes and white metal. *Can. Metall. Q.*, vol.39, no.1, Jan. 2000, p.23-35.

<sup>xxxvi</sup> Villarroel D. Design of a furnace for refining copper prior to fusion. *Miner. Engng.*, vol.13, no.1, Jan. 2000, p.95-103.

<sup>xxxvii</sup> Vracar R. and Cerovic K. The study of kinetics and mechanism of chlorination of copper (I) sulphide by chlorine in the presence of oxygen. *Can. Metall. Q.*, vol.39, no.2, Apr. 2000, p.163-173.

<sup>xxxviii</sup> Tamagawa T., Fu N.S., Kobayashi M. and Iwasaki I. Extraction metallurgy of copper from chalcopryite concentrates without sulfuric acid generation via chlorination: III. Integration of gaseous chlorination and selective oxidation. *Prepr. Soc. Min. Metall. Explor.*, no.00-118, 2000, 11pp. on CD, 9 refs. (Paper presented at the SME annual meeting held in Salt Lake City, Utah, 28 February-1 March 2000: New frontiers in mining - meeting 21st century challenges.)

<sup>xxxix</sup> Miroevskii G.P., Golov A.N., Tsemekhman L.S., Arefev K.M., Stepanov V.V. and Talalov V.A. Analysis of processing possibility for remainder of chlorine leaching of nickel concentrate in autogenous melting unit. *Tsvetnye Metally*, no.3, Mar. 2000, p.18-21.

<sup>xl</sup> Giurco D.P., Stewart M. and Petrie J.G. The role of LCA in performance assessment in minerals processing - a copper case study. *Environmental issues and management of waste in energy and mineral production. Proceedings of the sixth international conference, SWEMP 2000, Calgary, Alberta, Canada, May 30-June 2, 2000. Rotterdam: A.A.Balkema, 2000. p.267-273.*

<sup>xli</sup> McNaughton K. and Schlitt W.J. Winter field test for heap leaching Carmacks copper ore in Canada's Yukon territory. *Miner. Metall. Process.*, vol.17, no.3, Aug. 2000, p.186-193.

<sup>xlii</sup> Dixon, D. G. Analysis of heat conservation during copper sulphide heap leaching. *Hydrometallurgy*, vol. 58, no. 1, 2000, p.27-41.

<sup>xliii</sup> Ornelas Tabares J. Leaching as a part of mineral concentration. *Geomimet*, vol.27, no.224, Mar.-Apr. 2000, p.42-62.

<sup>xliv</sup> Kobayashi M. Current research projects for the development of hydrometallurgical process to refine chalcopryite. *J. Min. Mater. Process. Inst. Jpn.*, vol.116, no.1, Jan. 2000, p.1-6.

<sup>xl</sup> Su Yongqing and Liu Chunpeng. Kinetics of sulphuric acid leaching chalcopryite by microwave heating. *Nonferrous Met. Chin. Soc. Met.*, vol.52, no.1, Feb. 2000, p.62-65,68.

<sup>xlvi</sup> Stiksma J., Collins M.J., Holloway P., Masters I.M. and Desroches G.J. Process development studies by Dynatec for the pressure leaching of HBMS copper sulphide concentrates. *CIM Bull.*, vol.93, no.1041, June 2000, p.118-123.

<sup>xlvii</sup> Hiroyoshi, N.; Hajime, M.; Hirajima, T. and Tsunekawa, M. A model for ferrous-promoted chalcopyrite leaching. *Hydrometallurgy*, vol. 57, no. 1, 2000, p.31-38.

<sup>xlviii</sup> Puvvada, G. V. K. and Murthy, D. S. R. Selective precious metals leaching from a chalcopyrite concentrate using chloride/hypochlorite media. *Hydrometallurgy*, vol. 58, no. 3, 2000, p.185-191.

<sup>xlix</sup> Vracar, R. Z. and Parezanovic, I. S. Leaching of copper(I) sulfide in calcium chloride solution. *Hydrometallurgy*, vol. 58, no. 3, 2000, p.261-267.

<sup>l</sup> Correia, M. J. N.; Carvalho, J. R. and Monhemius, A. J. The leaching of tetrahedrite in ferric chloride solutions. *Hydrometallurgy*, vol. 57, no. 2, 2000, p.167-179.

<sup>li</sup> Devi, N. B.; Madhuchhanda, M.; Rao, K. S.; Rath, P. C. and Paramguru, R. K. Oxidation of chalcopyrite in the presence of manganese dioxide in hydrochloric acid medium. *Hydrometallurgy*, vol. 57, no. 1, 2000, p.57-76.

<sup>lii</sup> Lu, Z. Y.; Jeffrey, M. I. and Lawson, F. An electrochemical study of the effect of chloride ions on the dissolution of chalcopyrite in acidic solutions. *Hydrometallurgy*, vol. 56, no. 2, 2000, p.145-153.

<sup>liii</sup> Lu, Z. Y.; Jeffrey, M. I. and Lawson, F. The effect of chloride ions on the dissolution of chalcopyrite in acidic solutions. *Hydrometallurgy*, vol. 56, no. 2, 2000, p.189-202.

<sup>liv</sup> Balaz, P.; Achimovicova, M.; Bastl, Z.; Ohtani, T. and Sanchez, M. Influence of mechanical activation on the alkaline leaching of enargite concentrate. *Hydrometallurgy*, vol. 54, no. 2-3, 2000, p.205-216.

<sup>lv</sup> Wang Jun, Hu Yue-hua, Qiu Guan-zhou and Zhong Kang-nian. Mechanism of silver-influenced bacterial leaching of chalcopyrite, pyrite and a copper ore. *Trans. Nonferrous Met. Soc. China*, vol.10, special issue, June 2000, p.71-75.

<sup>lvi</sup> Qiu Guan-zhou, Liu Jian-she and Hu Yue-hua. Electrochemical behaviour of chalcopyrite in presence of *Thiobacillus ferrooxidans*. *Trans. Nonferrous Met. Soc. China*, vol.10, special issue, June 2000, p.23-25.

<sup>lvii</sup> Qiu Guan-zhou, Wang Jun, Hu Yue-hua and Zhong Kang-nian. Bio-leaching of low-grade large porphyry chalcopyrite-containing ore. *Trans. Nonferrous Met. Soc. China*, vol.10, special issue, June 2000, p.19-22.

<sup>lviii</sup> Liu Jian-she, Qiu Guan-zhou and Hu Yue-hua. Kinetics of electrochemical corrosion of chalcopyrite in presence of bacteria. *Trans. Nonferrous Met. Soc. China*, vol.10, special issue, June 2000, p.68-70.

<sup>lix</sup> Sampson M.I., Phillips C.V. and Blake R.C. Influence of the attachment of acidophilic bacteria during the oxidation of mineral sulphides. *Miner. Engng.*, vol.13, no.4, Apr. 2000, p.373-389.

- <sup>lx</sup> Sampson M.I., Phillips C.V. and Ball A.S. Investigation of the attachment of *Thiobacillus ferrooxidans* to mineral sulphides using scanning electron microscopy analysis. *Miner. Engng.*, vol.13, no.6, June 2000, p.643-656.
- <sup>lxi</sup> Third, K. A.; Cord-Ruwisch, R. and Watling. H. R. The role of iron-oxidizing bacteria in stimulation or inhibition of chalcopyrite leaching. *Hydrometallurgy*, vol. 57, no. 3, 2000, p.225-233.
- <sup>lxii</sup> Stott M.B., Watling H.R., Franzmann P.D. and Sutton D. The role of iron-hydroxy precipitates in the passivation of chalcopyrite during bioleaching. *Miner. Engng.*, vol.13, no.10-11, Sept. 2000, p.1117-1127.
- <sup>lxiii</sup> Bombach H., Khaled A.S.E. and Stelter M. Investigations of oxidative leaching of chopped copper wire scrap in sulphuric acid. *Erzmetall*, vol.53, no.4, 2000, p.222-227.
- <sup>lxiv</sup> Ke Jia-jun and Qin Rui-yun. Arsenic removal and bismuth recovery from copper smelter flue dust. *Minor elements 2000, processing and environmental aspects of As, Sb, Se, Te and Bi.* ed. C. Young. Littleton, Colorado: Society for Mining, Metallurgy and Exploration, 2000. (Proceedings of a symposium held in conjunction with the SME annual meeting in Salt Lake City, 28 February-1 March 2000.) p.293-298.
- <sup>lxv</sup> Zhang W., Singh P. and Muir D.M.  $\text{SO}_2/\text{O}_2$  as an oxidant in hydrometallurgy. *Miner. Engng.*, vol. 13, no. 13, Nov. 2000. p.1319-1328.
- <sup>lxvi</sup> Zhang, W.; Singh, P. and Muir, D. M. Iron(II) oxidation by  $\text{SO}_2/\text{O}_2$  in acidic media part 1. Kinetics and mechanism. *Hydrometallurgy*, vol. 55, no. 3, 2000, p.229-245.
- <sup>lxvii</sup> Zhang, W.; Muir, D. M. and Singh, P. Iron(II) oxidation by  $\text{SO}_2/\text{O}_2$  in acidic media part 11. Effect of copper. *Hydrometallurgy*, vol. 58, no. 2, 2000, p.117-125.
- <sup>lxviii</sup> Dicoski W. A revolution in copper recovery. *Min. Mag. Lond.*, vol.182, no.5, May 2000, p.258-262.
- <sup>lxix</sup> Casteel K. Solvent extraction: Stir crazy. *World Min. Equip.*, vol.24, no.6, July-Aug. 2000, p.18-24.
- <sup>lxx</sup> Eyzaguirre D. Effect of nitrate in solvent extraction at the Lomas Bayas mining company. *Minerales*, vol.55, no.233, May-June 2000, p.11-20.
- <sup>lxxi</sup> Liu Xiao-rong, Qiu Guan-zhou, Hu Yue-hua, Liu Jian-she and Li. Effect of diluent on interfacial emulsion in copper solvent extraction. *Trans. Nonferrous Met. Soc. China*, vol.10, special issue, June 2000, p.97-100.
- <sup>lxxii</sup> Parija, C. and Sarma, P. V. R. B. Separation of nickel and copper from ammoniacal solutions through co-extraction and selective stripping using LIX 84 as the extractant. *Hydrometallurgy*, vol. 54, no. 2-3, 2000, p.195-204.
- <sup>lxxiii</sup> Cheng, C. Y.; Hughes, C.A.; Barnard, K. R. and Larcombe, K. Manganese in copper solvent extraction and electrowinning. *Hydrometallurgy*, vol. 58, no. 2, 2000, p.135-150.



- <sup>lxxiv</sup> Rao, K. S.; Devi, N. B. and Reddy, B. R. Solvent extraction of copper from sulphate medium using MOC 45 as extractant. *Hydrometallurgy*, vol. 57, no. 3, 2000, p.269-275.
- <sup>lxxv</sup> Aminian, H.; Bazin, C.; Hodouin, D. and Jacob, C. Simulation of a SX-EW pilot plant. *Hydrometallurgy*, vol. 56, no. 1, 2000, 13-31.
- <sup>lxxvi</sup> Gottliebsen, K.; Grinbaum, B.; Chen, D. and Stevens, G. W. Recovery of sulphuric acid from copper tankhouse electrolyte bleeds. *Hydrometallurgy*, vol. 56, no. 3, 2000, p.293-307.
- <sup>lxxvii</sup> Gottliebsen, K.; Grinbaum, B.; Chen, D. and Stevens, G. W. The use of pulsed perforated plate extraction column for recovery of sulphuric acid from copper tankhouse electrolyte bleeds. *Hydrometallurgy*, vol. 58, no. 3, 2000, p.203-213.
- <sup>lxxviii</sup> Xue S.S., Gula M.J., Harvey J.T. and Horwitz E.P. Control of iron in copper electrolyte streams with a new monophosphonic/sulphonic acid resin. *Prepr. Soc. Min. Metall. Explor.*, no.00-41, 2000. Paper presented at the SME annual meeting held in Salt Lake City, Utah, 28 February-1 March 2000: New frontiers in mining - meeting 21st century challenges.)
- <sup>lxxix</sup> Vasquez J.D., Godoy O., Stocker R. and Lehuede P. Continuous operation short-circuiter frame (MCOC). *Minerales*, vol.55, no.231, Jan.-Feb. 2000, p.35-42.
- <sup>lxxx</sup> Muresan, L.; Varvara, S.; Maurin, G. and Dorneanu, S. The effect of some organic additives upon copper electrowinning from sulphate electrolytes. *Hydrometallurgy*, vol. 54, no. 2-3, 2000, p.161-169.
- <sup>lxxxi</sup> Burzynska. L. Influence of electrolysis parameters on the silver content of cathodic copper. *Hydrometallurgy*, vol. 55, no. 1, 2000, p.17-33.
- <sup>lxxxii</sup> Hein K. and Filzwieser A. Electrolytic copper extraction using bipolar electrodes and high current densities. *Erzmetall*, vol.53, no.4, 2000, p.217-221.
- <sup>lxxxiii</sup> Free M.L. and Anthian L. The effect of anode impurities on copper electrorefining. *Prepr. Soc. Min. Metall. Explor.*, no.00-62, 2000. (Paper presented at the SME annual meeting held in Salt Lake City, Utah, 28 February-1 March 2000: New frontiers in mining - meeting 21st century challenges.)
- <sup>lxxxiv</sup> Chen T.T. and Dutrizac J.E. The deportment of selenium and tellurium during the electrorefining of copper. *Minor elements 2000, processing and environmental aspects of As, Sb, Se, Te and Bi.* ed. C. Young. Littleton, Colorado: Society for Mining, Metallurgy and Exploration, 2000. (Proceedings of a symposium held in conjunction with the SME annual meeting in Salt Lake City, 28 February-1 March 2000.) p.199-212.
- <sup>lxxxv</sup> Moats, M. S.; Hiskey, J. B. and Collins, D. W. The effect of copper, acid and temperature on the diffusion coefficient of cupric ions in simulated electrorefining electrolytes. *Hydrometallurgy*, vol. 56, no. 3, 2000, p.255-268.
- <sup>lxxxvi</sup> Luganov V.A., Sajin E.N. and Chnyrenkova T.V. Electrochemical processing of speiss. *Minor elements 2000, processing and environmental aspects of As, Sb, Se, Te and Bi.* ed. C.

Young. Littleton, Colorado: Society for Mining, Metallurgy and Exploration, 2000. (Proceedings of a symposium held in conjunction with the SME annual meeting in Salt Lake City, 28 February-1 March 2000.) p.277-283.

lxxxvii Esna-Ashari M. and Kerney U. Smelting reactor for recovering zinc from industrial low-zinc-bearing residues. *Erzmetall*, vol.53, no.6, 2000, p.373-384.

lxxxviii O'Connor, W. K.; Dahlin, D. C.; Argetsinger, W. K. and Turner, P. C. Direct smelting of zinc smelter residues in the electric arc furnace. *EPD Congress 2000*, ed. P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p.323-343.

lxxxix Garcia-Carcedo, F.; Ayala, J. N.; Goicoechea, N.; Allain, E.; Hernandez, A; Ruiz-Ayucar, G. E.; Danobeitia, I. and Cornejo, N. Production of an ultra-pure fraction of ZnO by the recycling of EAF dust. *EPD Congress 2000*, ed. P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p.293-310.

xc Anon. Chelyabinsk electrolyte-zinc works. *Tsvetnye Metally*, no.5, May 2000, p.17-56,129-130.

xcI Roine, A. and Nyberg, J. Heat and material balance model of Kokkola Zn-roaster based on HSC Chemistry 4.0 software. *EPD Congress 2000*, ed. P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p.85-95.

xcII Liu Jun-feng, Yi Ping-gui and Huang Ke-long. Effects of conditions of soaking blende with sulphuric acid on rate of leaching zinc in oxygen and at normal pressure. *Chin. J. Nonferrous Met.*, vol.10, no.5, Oct. 2000, p.728-731.

xcIII Abdel-Aaal. E. A. Kinetics of sulfuric acid leaching of low-grade zinc silicate ore. *Hydrometallurgy*, vol. 55, no. 3, p.247-254.

xcIV Wu Min, Tang Zhao-hui and Gui Wei-hua. Expert fault diagnosis system for leaching progress in zinc hydrometallurgy. *Trans. Nonferrous Met. Soc. China*, vol.10, no.5, Oct. 2000, p.699-703.

xcV Zhao, Y. and Stanforth, R. Production of Zn powder by alkaline treatment of smithsonite Zn-Pb ores. *Hydrometallurgy*, vol. 56, no. 2, 2000, p.237-249.

xcVI Castro, I. M.; Fietto, J. L. R.; Viera, R. X.; Tropia, M. J. M.; Campos, L. M. M.; Pangiago, E. B. and Brandao, R. L. Bioleaching of zinc and nickel from silicates using *Aspergillus niger* cultures. *Hydrometallurgy*, vol. 57, no. 1, 2000, p.39-49.

xcVII Dutrizac J.E. and Chen T.T. The behaviour of gallium during jarosite precipitation. *Can. Metall. Q.*, vol.39, no.1, Jan. 2000, p.1-14.

xcVIII Nelson A., Demopoulos G.P. and Houlachi G. The effect of solution constituents and novel activators on cobalt cementation. *Can. Metall. Q.*, vol.39, no.2, Apr. 2000, p.175-186.

- ii<sup>c</sup> Liu Zhi-hong, Tang Chao-bo, Zhang Duo-mo, Guo Xue-yi and Chen Hui-guang. Study on the purifying processes for zinc leach solutions with antimony trioxides. *J. Cent. South Univ. Technol. China (Nat. Sci.)*, vol.31, no.3, June 2000, p.225-227.
- <sup>c</sup> Guo Zhong-cheng, Yan Jiang-feng and Yang Xian-wan. Mechanism of  $\text{Sb}_2\text{O}_3$  in removal of cobalt in zinc sulphate solution. *Chin. J. Nonferrous Met.*, vol.10, no.5, Oct. 2000, p.697-700.
- ci<sup>i</sup> Bockman, O. and Østvold, T. Products formed during cobalt cementation on zinc in zinc sulphate electrolytes. *Hydrometallurgy*, vol. 54, no. 2-3, 2000, p.65-78.
- cii<sup>i</sup> Bockman, O.; Østvold, T.; Voyiatis, G. A. and Papatheodorou, G. N. Raman spectroscopy of cemented cobalt on zinc substrates. *Hydrometallurgy*, vol. 55, no. 1, 2000, p.93-105.
- ciii<sup>i</sup> Bockman, O. and Østvold, T. The influence of tartrate on cobalt cementation on a rotating zinc disc in zinc sulphate. *Hydrometallurgy*, vol. 55, no. 1, 2000, p.107-112.
- civ<sup>i</sup> Booster J.L., Van Sandwijk A. and Reuter M.A. Magnesium removal in the electrolytic zinc industry. *Miner. Engng.*, vol.13, no.5, May 2000, p.517-526.
- cv<sup>i</sup> Saba, A. E. and Elsherief, A. E. Continuous electrowinning of zinc. *Hydrometallurgy*, vol. 54, no. 2-3, 2000, p.91-106.
- cvi<sup>i</sup> Lupi, C. and Pilone, D. Comparative study on zinc electrowinning from sulfate and chloride solutions. *EPD Congress 2000*, ed. P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p.311-320.
- cvi<sup>ii</sup> Wang Ji, Guo Pengcheng, Ma Minli, Zhou Libin, Liu Pangyou, Xie Fangyou, Yin Daixiang, Wu Weishu, Zeng Wei and Zhou Yi. Recovering germanium from zinc leaching solution by liquid-liquid extraction. *Nonferrous Met. Chin. Soc. Met.*, vol.52, no.2, May 2000, p.77-79.
- cvi<sup>iii</sup> Xia D.K. and Pickles C.A. Microwave caustic leaching of electric arc furnace dust. *Miner. Engng.*, vol.13, no.1, Jan. 2000, p.79-93.
- cix<sup>i</sup> Zhao Youcai and Stanforth R. Extraction of zinc from zinc ferrites by fusion with caustic soda. *Miner. Engng.*, vol. 13, no. 13, Nov. 2000. p.1417-1421.
- cx<sup>i</sup> De Souza, C. C. B. M. and Tenorio, J. A. S. Hydrometallurgical routes for recycling of used alkaline batteries. *EPD Congress 2000*, ed. P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p.271-279.
- cx<sup>i</sup> Li Shi-xiong, Zhang Chuan-fu, Tong Chang-dian and Lin Hong-yi. New highly effective binder for lead-zinc sintering. *Chin. J. Nonferrous Met.*, vol.10, no.4, Aug. 2000, p.569-571.
- cx<sup>ii</sup> Evrard L., Boydens E., Brouwer S. and Van Camp M. Behaviour of As and Sb in Hoboken lead sinter. *Minor elements 2000, processing and environmental aspects of As, Sb, Se, Te and Bi.* ed. C. Young. Littleton, Colorado: Society for Mining, Metallurgy and Exploration, 2000. (Proceedings of a symposium held in conjunction with the SME annual meeting in Salt Lake City, 28 February-1 March 2000.) p.251-258.

- cxiii. Gonzalez-Chavez J.L., Gonzalez F., Ballester A. and Blazquez M.L. Effect of mesophilic microorganisms on the electrochemical behaviour of galena. *Miner. Metall. Process.*, vol.17, no.2, May 2000, p.116-120.
- cxiv Nagib, S. and Inoue, K. Recovery of lead and zinc from fly ash generated from municipal incineration plants by means of acid and/or alkaline leaching. *Hydrometallurgy*, vol. 56, no. 3, 2000, p.269-292.
- cxv Raghavan, R.; Mohanan, P. K. and Swarnkar, S. R. Hydrometallurgical processing of lead-bearing materials for the recovery of lead and silver as lead concentrate and lead metal. *Hydrometallurgy*, vol. 58, no. 2, 2000, p.103-116.
- cxvi ALTA 2000 Nickel/Cobalt – 6. 15-17 May 2000, Perth. Western Australia, ALTA Metallurgical Services, Blackburn, South, Victoria 3130, Australia, avail. ALTA Conference Secretariat, 4 Newbury Close, Lower Templestowe, Victoria 3107, Australia.
- cxvii Zakharov B.N. On possibility of processing of high-ferrous kinds of oxidised nickel ores in shaft furnaces. *Tsvetnye Metally*, no.8, Aug. 2000, p.84-86.
- cxviii Hughes S. Applying Ausmelt technology to recover Cu, Ni and Co from slags. *J. Metals*, vol.52, no.8, Aug. 2000, p.30-33.
- cxix Hua Yixin, Tan Chune, Xie Aijun and Lu Hong. Microwave-aided chloridising of nickel-bearing garnierite ore with FeCl<sub>3</sub>. *Nonferrous Met. Chin. Soc. Met.*, vol.52, no.1, Feb. 2000, p.59-61,58.
- cxx Baird M.H.I., Rama Rao N.V., Diaz C.M. and Marcuson S.W. Entrainment from a flat liquid-liquid interface. *Can. Metall. Q.*, vol.39, no.1, Jan. 2000, p.113-120.
- cxxi Shneerson Y.M. Up-to-date state of hydrometallurgical processing of oxidised nickel-cobalt ores. *Tsvetnye Metally*, no.8, Aug. 2000, p.76-83.
- cxixii van Os J. The perils of pioneering. *Metal Bull. Mon.*, no.355, July 2000, p.28-31.
- cxixiii Anon. Cobalt metallurgy of Bou Azzer. *Cobalt news* October 00, no. 00/4, 2000, p.9.
- cxixiv Mihaylov I., Krause E., Colton D.F., Okita Y., Duterque J.P. and Perraud J.J. The development of a novel hydrometallurgical process for nickel and cobalt recovery from Goro laterite ore. *CIM Bull.*, vol.93, no.1041, June 2000, p.124-130.
- cxixv Rubisov D.H.; Krowinkel, J. M. and Papangelakis V.G. Sulphuric acid pressure leaching of laterites - universal kinetics of nickel dissolution for limonites and limonitic/saprolitic blends. *Hydrometallurgy*, vol. 58, no. 1, 2000, p.1-11.
- cxixvi Rubisov, D. H. and Papangelakis, V. G. Sulphuric acid pressure leaching of laterites - speciation and prediction of metal solubilities "at temperature". *Hydrometallurgy*, vol. 58, no. 1, 2000 p.13-20.



<sup>cxxvii</sup> Rubisov, D. H. and Papangelakis, V. G. Sulphuric acid pressure leaching of laterites - a comprehensive model of a continuous autoclave. *Hydrometallurgy*, vol. 58, no. 2, 2000, p.88-101.

<sup>cxxviii</sup> Rubisov D.H. and Papangelakis V.G. The effect of acidity at temperature on the morphology of precipitates and scale during sulphuric acid pressure leaching of laterites. *CIM Bull.*, vol.93, no.1041, June 2000, p.131-137.

<sup>cxxix</sup> Kar, B. B.; Swamy, Y. V. and Murthy, B. V. R. Design of experiments to study the extraction of nickel from lateritic ore by sulphatization using sulphuric acid. *Hydrometallurgy*, vol. 56, no. 3, 2000, p.387-394.

<sup>cxix</sup> Naftal M.N., Markov Y.F., Zhelezova T.M., Rozenberg Z.I. and Sukhobaevskii Y.Y. Efficiency increase of autoclave disintegration of sulphur-sulphide concentrates. *Tsvetnye Metally*, no.4, Apr. 2000, p.87-91.

<sup>cxixi</sup> Lu, Z. Y.; Jeffrey, M. I.; Zhu, Y. and Lawson, F. Studies of pentlandite leaching in mixed oxygenated acidic chloride-sulfate solutions. *Hydrometallurgy*, vol. 56, no. 1, 2000, p.63-74.

<sup>cxixii</sup> Balaz, P.; Zarova, E. B.; Achimaviceva, M. and Kammel, R. leaching and dissolution of a pentlandite concentrate pretreated by mechanical activation. *Hydrometallurgy*, vol. 57, no. 1, 2000, p.85-90.

<sup>cxixiii</sup> Gbor, P. K.; Ahmed, J. B. and Jia, C. Q. Behaviour of Co and Ni during aqueous sulphur dioxide leaching of nickel smelter slag. *Hydrometallurgy*, vol. 57, no. 1, 2000, p.13-22.

<sup>cxixiv</sup> Stanojevic, D.; Nokolic, B. and Todorovic, M. Evaluation of cobalt from cobaltic waste products from the production of electrolytic zinc and cadmium. *Hydrometallurgy*, vol. 54, no. 2-3, 2000, p.151-160.

<sup>cxixv</sup> Xu Chengkun, Tian Yanwen, Zhang Lijun and Zhai Yuchun. Selective leaching of cadmium in spent cadmium-nickel batteries. *Nonferrous Met. Chin. Soc. Met.*, vol.52, no.3, Aug. 2000, p.70-73.

<sup>cxixvi</sup> Brochot S., Durance M.V., Foucher S., Guillaneau J.C., Morin D. and Villeneuve J. Process simulation to enhance complex flowsheet development: examples in biotechnology. *Control 2000: mineral and metallurgical processing*. ed. J.A. Herbst. Littleton, Colorado: Society for Mining, Metallurgy and Exploration, 2000. p.215-222.

<sup>cxixvii</sup> Clifford D. Innovation at Radio Hill. *Min. Mag. Lond.*, vol.182, no.5, May 2000, p.250-252.

<sup>cxixviii</sup> McLean P. Titan Resources. *Aust. Miner. Gaz.*, vol.2, no.31, May 2000, p.15-19.

<sup>cxixix</sup> Li Hongmei and Ke Jiajun. Effect of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  on activity of *Thiobacillus ferrooxidans*. *Nonferrous Met. Chin. Soc. Met.*, vol.52, no.1, Feb. 2000, p.49-51,54.

<sup>cx</sup> Ehrlich H.L. Ocean manganese nodules: biogenesis and bioleaching possibilities. *Miner. Metall. Process.*, vol.17, no.2, May 2000, p.121-128.

- <sup>cxli</sup> Cheng, C. Y. Purification of synthetic laterite leach solution by solvent extraction using D2EHPA. *Hydrometallurgy*, vol. 56, no. 3, 2000, p.369-386.
- <sup>cxlii</sup> Wassink, B.; Dreisinger, D. and Howard, J. Solvent extraction separation of zinc and cadmium from nickel and cobalt using Aliquat 336, a strong base anion exchanger, in the chloride and thiocyanate forms. *Hydrometallurgy*, vol. 57, no. 3, 2000, p.235-252.
- <sup>cxliii</sup> Zhou Xue-xi, Wang Huan-qing, Xia Yun-long and Zhu Tun. Solvent extractive separation of cobalt, iron and manganese with quaternary ammonium chloride. *Chin. J. Nonferrous Met.*, vol.10, no.5, Oct. 2000, p.723-727.
- <sup>cxliv</sup> Zhou Xue-xi, Xu Xin, Ma Chi-cheng and Zhu Tun. Extractive separation of cobalt(II) and manganese(II) with quaternary ammonium chloride. *Chin. J. Nonferrous Met.*, vol.10, no.4, Aug. 2000, p.542-545.
- <sup>cxlv</sup> Briggs M.K., Cheng C.Y. and Ibana D.C. An electrostatic solvent extraction contactor for nickel-cobalt recovery. *Miner. Engng.*, vol.13, no.12, Oct. 2000, p.1281-1288.
- <sup>cxlvi</sup> Lindell, E.; Jaaskelainen, E.; Paatero, E. and Nyman, B. Effect of reversed micelles in Co/Ni separation by Cyanex 272. *Hydrometallurgy*, vol. 56, no. 3, 2000, p.337-357.
- <sup>cxlvii</sup> Jaaskelainen, E. and Paatero, E. Characterisation of organic phase species in the extraction of nickel by pre-neutralised Versatic 10. *Hydrometallurgy*, vol. 55, no. 2, 2000, p.181-200.
- <sup>cxlviii</sup> Preston, J. S. and du Preez, A. C. Separation of nickel and calcium by solvent extraction using mixtures of carboxylic acids and alkyl pyridines. *Hydrometallurgy*, vol. 58, no. 3, 2000, p.239-250.
- <sup>cxlix</sup> Guo Xueyi, Huang Kai, Liu Zhihong, Zhang Duomo and Chen Huiguang. Electrochemical behaviour of nickel cathode reduction in chloride solution under different conditions. *Nonferrous Met. Chin. Soc. Met.*, vol.52, no.1, Feb. 2000, p.55-58.
- <sup>cl</sup> Holm M. and O'Keefe T.J. Electrolyte parameter effects in the electrowinning of nickel from sulphate electrolytes. *Miner. Engng.*, vol.13, no.2, Feb. 2000, p.193-204.
- <sup>cli</sup> Willis B. and Von Essen J. Autoclaves and agitators. *Min. Mag. Lond.*, vol.183, no.1, July 2000, p.20-28.
- <sup>clii</sup> Jeffrey M.I., Choo W.L. and Breuer P.L. The effect of additives and impurities on the cobalt electrowinning process. *Miner. Engng.*, vol.13, no.12, Oct. 2000, p.1231-1241.
- <sup>cliii</sup> Lupi, C.; Pilone, D.; Cannavale, G. and Pescetelli, A. Metal recovery from NIMH batteries. *EPD Congress 2000*, ed. P. R. Taylor, The Minerals, Metals & Materials Society, 2000, p.257-270.
- <sup>cliv</sup> Anon, Reprocessing of lithium-ion battery scrap. *Cobalt News*, October 00, no. 00/4, 2000, p.5-6.