

TUESDAY, AUGUST 26, 2003, P.M.

SESSION 24: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN
HONOUR OF PROFESSOR IAN RITCHIE

SOLUTION PURIFICATION I: SOLVENT EXTRACTION II

Sponsors: Hydrometallurgy Section of the The Metallurgical Society of CIM (MetSoc), Extraction and Processing Division, The Minerals, Metals & Materials Society (TMS), and the Society for Mining, Metallurgy and Exploration (SME).

Room: Pavillion Ballroom A

Chairmen: C. MAES, CYTEC, Tempe, AZ, USA

J. HARLAMOVS, Teck Cominco Metals, Trail, BC, Canada

PAPER 24.1 — 14:00

EXTRACTION OF NICKEL AND CALCIUM FROM HYPERSALINE SOLUTIONS USING VERSATIC 10.

D. HELM, D. IBANA, WASM-Parker Centre for Hydrometallurgy, Curtin University of Technology, Perth, West Australia, Australia, and

E. PAATERO, Department of Chemistry and Technology, Lappeenranta University of Technology, Lappeenranta, Finland

The solvent extraction of nickel using carboxylic acid- based extractants such as Versatic 10 is well established but its recent application in the direct solvent extraction of nickel has highlighted the need to investigate its performance with hypersaline feed solutions. Direct solvent extraction (DSX) of nickel involves the separation of nickel and cobalt directly from the pregnant liquor stream (PLS) by solvent extraction, avoiding intermediate precipitation and re-leach stages. The result is a feed solution to the solvent extraction circuits containing high concentrations of soluble metal ions such as calcium and magnesium, resulting in some precipitations. The problem is exacerbated by the use of hypersaline process water such as those in Western Australia, which hosts many nickel laterite deposits. The effect of high calcium concentration is of particular interest because its presence in the PLS is unavoidable even in operations with access to good quality process water, as lime and limestone remain the preferred choices as neutralizing agents. This paper discusses the results of an investigation on the extraction behaviour of nickel and calcium from hypersaline solutions — both synthetic and actual plant solutions — using Versatic 10. It includes studies on the kinetics of nickel and calcium extraction.

PAPER 24.2 — 14:25

APPLICATION OF SOLVENT EXTRACTION FOR THE SEPARATION OF MOLYBDENUM FROM NANO-CRYSTALLINE COBALT ELECTRODEPOSITION EFFLUENTS.

M. OLIAZADEH, Department of Mining Engineering, The University of Tehran, Tehran, Iran,

R. WU, J.H. HUANG and A.M. ALFANTAZI, Department of Metals and Materials Engineering, The University of British Columbia, Vancouver, British Columbia, Canada

The present study was performed to develop a novel process for solvent extraction of molybdenum and cobalt from an acidic solution generated by a new electrodeposition process of nanocrystalline cobalt alloys. Solvent extraction is a common practice in hydrometallurgical and refining processes to produce metals, however, its application for separation of molybdenum and cobalt from this specific solution is new because molybdenum and cobalt are not commonly associated together in nature. Five commercial organic extractants were examined for extraction of cobalt and molybdenum from synthetic acidic solutions with pH range from 1 to 5. Preliminary results showed that at pH 2, any of the Cyanex 923, Alamine 336, Aliquat 336 and Hostarex A327 could be used to extract 99% of molybdenum from solutions, while from pH 3 to 5, Aliquat was able to extract about 100% of Mo. Cobalt extraction, on the other hand, varied from 15% to 23% at pH 3 and 30% to 53% at pH 2 using different extractants. Comparison of results revealed that Aliquat 336 and Cyanex 923 could act more effectively than others, thus, the effect of metal concentration was further considered with these two extractants. Based on results obtained, Aliquat 336 was applied on a mixed solutions of cobalt and molybdenum at various pHs. The results showed that molybdenum could be extracted as much as 99% from a mixture of Mo and Co at acidic pHs, while less than 1% of cobalt was separated at pH 2 to 4 simultaneously. The cobalt extraction was about 4.5% at pH 1.

PAPER 24.3 — 14:50

RECOVERY OF PHOSPHORIC ACID IN WASTE ACID MIXTURE DISCHARGED FROM THE LIQUID CRYSTAL INDUSTRY BY SOLVENT EXTRACTION.

J. SHIBATA, M. MORIKAWA, N. YOSHIKAWA, N. MURAYAMA and H. YAMAMOTO, Departement of Chemical Engineering, Kansai University, Suitashi, Osaka, Japan

The waste acid mixture whose main component is phosphoric acid, is discharged from the etching process in liquid crystal production industry. In order to separate impurity acids from the phosphoric acid, trioctyl phosphate (TOP) is used as an extractant. TOP can extract acetic and nitric acids selectivity. The extraction and stripping operations are carried out for the acid mixture by beaker scale experiments and countercurrent multi-stages operations with a mixer-settler equipment. TOP selectively extracts the acetic and nitric acids in the acid mixture. From the results of McCabe-Thiele analysis obtained by beaker scale tests, the extractions for acetic and nitric acids are approximately 100%, respectively, by sixstage extractions with the phase ratio (A/O) of 0.4. On the other hand, almost all of acetic and nitric acids are stripped with water from the organic phase by four-stage strippings with the phase ratio (A/O) of 1.0. About 95% of acetic and 98% of nitric acids can be removed from the acid mixture without extracting phosphoric acid in case of the mixer-settler equipment operation.

COFFEE BREAK — 15:15 – 15:30

PAPER 24.4 — 15:30

PHOSPHORIC ACID EXTRACTION FROM AN URANIUM-PHOSPHOROUS LIQUOR.

J.S. BENEDETTO and C.A. MORAIS, Cidade Universitária-Pampulha, Belo Horizonte, Brasil

The physical and chemical upgrading process developed for the phosphoro-uraniferous orebody, located in the state of Ceará-Brazil, consists of three basic steps: concentration of the phosphate-bearing uranium by flotation, chemical dissolution of the concentrate by wet phosphoric acid route, and extraction of uranium by solvent. In this process two products are obtained — uranium and phosphoric acid. The purpose of this work is to develop technological know-how by phosphoric acid purification through an extraction of P_2O_5 by solvents, in order to supply the regional market with this product. Two lines of research were investigated: 1) the uranium was extracted before the phosphoric acid purification; and 2) the phosphoric acid was extracted before uranium recovery. A comparison of the two processes is shown. Experimental work has been developed in laboratory scale to select and optimize the process conditions and variables. Following that, a complete research of extraction and stripping in pulsed perforated-plate columns made of glass in pilot scale has been carried in order to investigate the main operational and process variables such as phase relation, residence time, and the hold-up. The first experiments showed good results of phosphoric acid extraction using a raffinate sample obtained from the uranium extraction process. It was possible to obtain a high-purity phosphoric acid that can be used in animal food or other applications.

PAPER 24.5 — 15:55

INDIUM RECOVERY FROM SULPHURIC SOLUTIONS: A COMPARATIVE STUDY INVOLVING ACIDIC ORGANOPHOSPHORUS EXTRACTANTS.

P.M. ROSÁRIO, P.J. MARTINS and A.P. PAIVA, Faculdade de Ciências da Universidade de Lisboa, Lisboa, Portugal

Indium is industrially produced using leaching, cementation and electrorefining, and solvent extraction is often used to recover it from leach residues. The most common organophosphorus acids are widely applied to indium recovery from aqueous solutions, but the information available in the literature is often difficult to correlate. This paper compares the extraction performance exhibited by phosphoric (D2EHPA), phosphonic (Ionquest 801), phosphinic (Cyanex 272), and dithiophosphinic (Cyanex 301) acid derivatives toward In(III) recovery from a diluted sulphuric solution. Equilibrium extraction isotherms were obtained. Plots of %E vs pH were established for D2EHPA, Ionquest 801, and Cyanex 301, denoting their behaviour toward the extraction of similar concentrations of In(III), Fe(III), Fe(II), and Zn(II). Cyanex 301 is the least selective toward In(III), whereas, D2EHPA and Ionquest 801, both for a pH = 0.5, do not extract Zn(II) at all. Stripping of In(III) has also been studied using sulphuric and hydrochloric acid, showing that the metal ion can be efficiently stripped from Ionquest 801 and D2EHPA. In(III) from Cyanex 301 is very difficult to strip. The plots of log D vs log [extractant] or vs pH allowed the evaluation of the approximate stoichiometry of the In(III) extracted species by the four ligands.

PAPER 24.6 — 16:15

GOLD SOLVENT EXTRACTION FROM ALKALINE CYANIDE SOLUTIONS USING LIX 79 EXTRACTANT.

J.L. VALENZUELA, S. AGUAYO, University of Sonora, Hermosillo, Sonora, México,

J.R. PARGA, Institute Technology of Saltillo, Saltillo, Coahuila, México, and

R.G. LEWIS, Cognis Corporation, Tucson, Arizona, U.S.A.

The solvent extraction for gold from alkaline cyanide solutions has been investigated using LIX 79 guanidine extractant. Different variables that could affect the extraction system were evaluated: time, aqueous pH, extractant and modifier concentrations, among others. From the pH isotherms it was found that aurocyanide can be extracted in alkaline media. The extraction isotherms for the aurocyanide and other cyanoanions complexes were compared and the selectivity was in the order $Au > Ag > Cu > Zn >> Fe$. The best separation with respect to other cyanoanions was found in the pH range of 10.5 to 11.2. The highest selectivity was obtained at 10 vol.% LIX 79 and 5 vol.% tridecanol. Stripping of gold from loaded organic phases was carried out at pH greater than 12, using NaOH and NaCN solutions. These results were evaluated in a continuous circuit using an actual cyanide pregnant solution showing that solvent extraction is a viable alternative procedure for recovering precious metals.

SESSION 25: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

SOLUTION PURIFICATION II: PRECIPITATION III AND ELECTROWINNING I

Sponsors: Hydrometallurgy Section of the The Metallurgical Society of CIM (MetSoc), Extraction and Processing Division, The Minerals, Metals and Materials Society (TMS), and the Society for Mining, Metallurgy and Exploration (SME).

Room: Pavillion Ballroom B

Chairmen: P. GUERNEY, JKTech – JKMRRC, University of Queensland, Indooroopilly, QLD, Australia
T. ROBINSON, Phelps Dodge Process Technology Center, Safford, AZ, USA

PAPER 25.1 — 14:00

SELECTIVE PRECIPITATION OF COBALT FROM AMMONIA LEACH SOLUTIONS, RECENT EXPERIENCE AT THE COREFCO REFINERY IN FORT SASKATCHEWAN.

G.K.W. FREEMAN, Sherritt International Corporation, Calgary, Alberta, Canada

The efficient separation of cobalt from nickel (and other impurities) is a fundamental objective in the refining of cobalt. Based on recent experience at the Fort Saskatchewan refinery, the identification of a novel process for the selective precipitation of cobalt from an aqueous ammonia leach was discovered. The addition of calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), to an aqueous solution containing cobalt(II)hexammine sulphate, $[\text{Co}(\text{NH}_3)_6]2(\text{SO}_4)_3$, will result in the precipitation of a sparingly soluble double salt having the stoichiometry, $[\text{Co}(\text{NH}_3)_6]2(\text{SO}_4)_3 \cdot 2\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ where $x = 4$ or 6. Leach residues, which may contain a significant quantity of cobalt associated with the cobalt calcium double salt, can be washed with process solutions that contain ammonium carbonate to recover the contained cobalt. The simplicity of this elemental separation and its high selectivity for cobalt, as well as its demonstrated usefulness in improving cobalt recoveries, are the basis for the potential applications of this process.

PAPER 25.2 — 14:25

SELECTIVE PRECIPITATION FOR COBALT AND MOLYBDENUM RECOVERY FROM A SYNTHETIC INDUSTRIAL WASTE EFFLUENT.

J.H. HUANG, C. KARGL-SIMARD, A.M. ALFANTAZI, Department of Metals and Materials Engineering, The University of British Columbia, Vancouver, British Columbia, Canada, and

M. OLIAZADEH, Department of Mining Engineers, The University of Tehran, Tehran, Iran

In this investigation, the selective precipitation of cobalt and molybdenum from Co-Mo aqueous solutions was studied in order to recover efficiently valuable elements from industrial effluents generated from a novel electrodeposition of nanocrystalline Co-based alloys and reduce the effluent impact on environment. It was found that the behaviour of cobalt in aqueous solution was substantially affected with the presence of molybdenum. When adding 11.6 to 46.6 g/L molybdenum to a 50 g/L cobalt solution, the co-precipitation of molybdate and cobalt occurred when pH was increased to less than 4. However, without the presence of molybdenum, cobalt could only be precipitated out from the solution at about pH 6. Most of the molybdenum was found in the solid phase when the pH reached 5. After further increasing pH to greater than 7, the molybdenum dissolved back into solution. Cobalt kept precipitating as the pH increased. When pH was greater than 7, most of the cobalt was present in the solid phase. The chemical and physical characteristics of the precipitated materials were investigated by SEM, XRD, AAS, and EDX. It was revealed that the precipitate was initially present as cobalt molybdate oxide hydrate and subsequently transformed as sodium cobalt molybdenum oxide. With further increasing solution pH, the precipitate was changed into cobalt hydroxide. Further investigation implied that most of molybdenum was chemically tied to the precipitate produced at the low pH, yet at the same time, physically entrapped at the high pH. This paper also presents the influence of reaction temperature and time on the precipitation process and kinetics.

PAPER 25.3 — 14:50

ELECTROLYTIC COPPER ELECTROWINNING — AN HISTORICAL PERSPECTIVE.

T. ROBINSON, Phelps Dodge Mining Company, Safford, Arizona, U.S.A.

Commercial electrowinning of cathode copper from sulphate electrolytes and leach solutions has been practiced in the southwestern United States and South America since the early 1900s. This paper reports on the process technology developments in copper electrowinning from this latter time period to present day. These process technology components include operating parameters, mist suppression methods, and design of electrodes, cells and material handling. Over the past century, these developments have resulted in improved cathode purity and tank house productivity.

COFFEE BREAK — 15:15 – 15:30

PAPER 25.4 — 15:30

EFFECT OF IMPURITY PRESENCE IN ZINC CHLORIDE ELECTROWINNING.

C. LUPI, D. PILONE, Università di Roma, Roma, Italy, and

E. BELTOWSKA-LEHMAN, Polish Academy of Sciences, Krakow, Poland

Zinc chloride electrowinning presents difficulties in obtaining smooth, compact, and dendrite-free deposits with a high current efficiency. The main reason for this is the presence in the electrolyte of undesirable metal ions, more electropositive than zinc. However, it is hard to define a level of impurities tolerable in zinc deposition, and in spite of several works in this field, the undesirable metal ion action mechanism is still not clearly understood. The influence of the above mentioned metal ions as well as their synergic effect on zinc deposition process from chloride electrolyte and on the obtained deposit morphology has been studied. The addition of organic additives that can reduce the harmful effect of such impurities on the zinc reduction has also been investigated.

PAPER 25.5 — 15:55

THE EFFECTS OF ORGANIC AND INORGANIC IMPURITIES ON THE PHYSICAL PROPERTIES OF NICKEL CATHODES.

D. KITTELTY and M. NICOL, A J Parker Centre for Hydrometallurgy, Murdoch University, Murdoch, Western Australia

A fully instrumented laboratory electrowinning cell has been used to produce nickel cathodes from synthetic solutions containing various impurities in order to evaluate the effects of both metallic ions and organic reagents (from prior solvent extraction processes) on the quality of the electrodeposited nickel. The conditions used were typical of those employed in industrial electrowinning operations. The impurities were found to alter crystal size and shape, the development of hydrogen pits on the deposit surface, the incorporation of metal hydroxides in the deposit, the internal stress, and the current efficiency. In particular, an increasing concentration of aluminum ions resulted in an initial highly deleterious effect which was replaced by a positive influence at higher concentrations. A model which involves the buffering effect of the aluminum on the pH at the cathode surface has been proposed.

PAPER 25.6 — 16:20

EFFECT OF SOME POLYOLS AND ORGANIC ACIDS ON THE CURRENT EFFICIENCY AND THE CELL VOLTAGE DURING ZINC ELECTROWINNING.

S. JIN, E. GHALI, Laval University, Sainte Foy, Québec, Canada,

G. ST-AMANT and G. HOULACHI, Hydro-Québec, Shawinigan, Québec, Canada

Effect of four polyols, namely ethylene glycol (EGL), glycerol (GCL), propanediol (PDL), butanediol (BDL) and three organic acids, namely, oxalic acid (OA), malonic acid (MA) and succinic acid (SA) on the current efficiency (CE) and the cell voltage during zinc electrowinning was studied. Galvanostatic polarization was conducted in a supporting electrolyte (SE) containing $180 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$, $60 \text{ g dm}^{-3} \text{ Zn}^{2+}$, and $8 \text{ g dm}^{-3} \text{ Mn}^{2+}$ at 38°C with magnetic stirring. The imposed current density was 50 mA cm^{-2} . The anodes were made of a Pb-Ag alloy and the cathodes were made of an aluminum alloy. The results showed that all the polyols tested in this study decreased the current efficiency and the cell voltage, but the decrease of the cell voltage was not important. Oxalic and succinic acids decreased the current efficiency to a less extent than the polyols, but did not decrease the cell voltage much. The only compound that increased the current efficiency was malonic acid, and its capacity of decreasing the cell voltage was the highest within the seven tested organic compounds.

PAPER 25.7 — 16:45

DETERMINATION OF CRYSTALLITE SIZE AND SURFACE ROUGHNESS OF COPPER DEPOSITS FOR ELECTROWINNING IN THE PRESENCE OF ADDITIVES.

C. FABIAN, G. GRIFFIN, James Cook University, Townsville, Queensland, Australia,

S. NESS, Advanced Analytical Centre, James Cook University, Townsville, Queensland, Australia,

M. RIDD, James Cook University, Townsville, Queensland, Australia, and

T. LANCASTER, Western Metals Copper Limited, Mount Isa, Queensland, Australia

The crystallite size of copper electrodeposits was determined using X-ray powder diffraction analysis. Crystallite size was calculated for 4 h and deposition thin films had been electrodeposited on a 316 stainless steel rotating cylinder electrode (RCE) in the presence and absence of additives. The profiles of crystallite size and surface roughness are related to the additive system. This technique forms part of electrochemical characterization techniques used to select/optimize an additive system for copper electrowinning and electrorefining to eliminate/reduce dendrite growth.

SESSION 26: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

TECHNOLOGY APPLICATION: ENVIRONMENT

Sponsors: Hydrometallurgy Section of the The Metallurgical Society of CIM (MetSoc), Extraction and Processing Division, The Minerals, Metals & Materials Society (TMS), and the Society for Mining, Metallurgy and Exploration (SME).

Room: Junior Ballroom C

Chairmen: D. ALEXANDER, Anglo American Research, Laboratories (Pty) Ltd, Johannesburg, South Africa

B. HISKEY, Materials Science & Engineering, University of Arizona, Tucson, AZ, USA

PAPER 26.1 — 14:00

BIOSORPTION OF TOXIC METALS FROM WASTEWATER BY STREPTOMYCES VIRIDOSPORUS.

R.K. AMANKWAH and W.T. YEN, Mining Engineering, Queen's University, Goodwin Hall, Kingston, Ontario, Canada

Currently, metal polluted effluents are mostly treated by chemical methods that tend to be expensive especially in the treatment of dilute solutions. The alternative use of biomass for metal removal has been investigated extensively in recent times. This paper looks at the use of the biomass of *Streptomyces Viridosporus* in the removal of lead, copper, nickel, antimony, and zinc from wastewater. Investigations revealed that over 90% of lead and copper ions were sorbed from wastewater at a concentration of 10 ppm within 30 minutes. Sorption of antimony was 63% and that of nickel and zinc below 50%.

PAPER 26.2 — 14:25

METAL WASTE PREVENTION BY SLM.

I. VAN DE VOORDE, J. VANDER LINDEN, S. VANDERKERKEN, H. DHANENS and R.F. DE KETELAERE, Chemical and Biochemical Research Centre KaHo Sint-Lieven (CBOK), Ghent, Belgium

In this paper, results are presented concerning the search to implement Supported Liquid Membranes (SLM) for the recovery of copper, nickel, and zinc (ROPE, SERENI and SEREMET European projects) from effluents and also prevent metal waste. A study of the influence of the individual parameters and of their combined on mass transfer in small scale laboratory equipment has been performed, enabling to set forward the appropriate operating conditions for a pilot plant installation. For SLM the pilot plant has been tested extensively, including short- and long-term runs, with different real process solutions. It was demonstrated that the SLM technology is applicable for solutions containing 700 ppm of metal and also to the treatment of solutions with low metal content of origins other than plating shops.

PAPER 26.3 — 14:50

THE SO₂/O₂ SYSTEM AS A NOVEL TECHNOLOGY FOR THE REMEDIATION OF CONTAMINATED SEDIMENTS.

M.M. BERTINI and P.F. DUBY, Henry Krum School of Mines, Columbia University, New York, New York, U.S.A.

Successful treatment of contaminated sediments was achieved by sparging either 0.5 M NaOH solutions or distilled water with the SO₂/O₂ gas mixture. Metals such as Cu, Pb, Cr, and Cd were successfully removed in a relatively short time. The effect of temperature and pH was investigated. Higher temperatures produced faster and higher recoveries, with Pb and Cr more affected to temperature increase than Cu and Cd. The removal of copper, up to 50%, was achieved in alkaline solutions through the formation of copper sulphite complexes. The complete removal of metals such as Cu, Pb, Cr, and Cd required that part of the treatment be carried out in acidic solutions. A preliminary cost analysis was carried out.

COFFEE BREAK — 15:15 – 15:30

PAPER 26.4 — 15:30

SEPARATION OF CU-CO AND NI FROM SULPHURIC ACID AND CHLORIDE SOLUTIONS BY SOLVENT EXTRACTION.

Y. JIAOYONG, Beijing Extract Metallurgy and Technology Development Company Ltd., China,
L. JUNPING and Z. YONGGONG, Chengdu Shuangliu Nonferrous Metal Smelter, China

This paper will discuss a process that includes extraction of copper-cobalt and nickel from smelting slags in non-ferrous metal metallurgy. Production of pure chemicals of corresponding metallic salts is also presented. The slag is leached with sulphuric acid and chloride solutions, resulting in leach solutions with high contents of valuable metals and several impurities. The purification and enrichment of the valuable metals are achieved by a series of processes, consisted of extracting copper from the leach solution with Acorga M5640, purification with D2RHPA, and separating nickel and cobalt with PC88. The control of technological parameters and equipment arrangement in solvent extraction are emphasized. Finally, production of CuSO₄, CoSO₄, and NiSO₄, and their qualities are briefly described.

PAPER 26.5 — 15:55

RECLAMATION OF COBALT AND COPPER FROM COPPER CONVERTER SLAGS.

T. DENG and Y. LING, Chinese Academy of Sciences, Beijing, China

Clean processing of copper converter slags for reclaiming cobalt and copper could be a challenge. An innovative and environmentally benign approach for recovering metal values from such a slag was proposed in the present work. Curing the slag with sulphuric acid, without re-smelting or roasting as practiced currently in industry, made it amenable to leaching and more than 95% of cobalt and up to 90% of copper was extracted together with iron by water leaching, leaving silica behind in a residue. Copper in the leach liquor was recovered by cementation with iron and the dissolved iron crystallized as monohydrated ferrous sulphate. Cobalt in the pregnant solution rich in iron was recovered by either cementation or sulphide precipitation. Chemical and mineralogical characterizations of the slag and its processed products were examined and compared to ascertain the nature of changes during curing and leaching. Operation variables were also investigated and optimized.

PAPER 26.6 — 16:20

USE OF LEAD ISOTOPES TO DETERMINE SOURCES AND TRANSPORT OF LEAD CONTAMINATION.

J.B. HISKEY, Department of Materials Science Engineering, University of Arizona, Tucson, Arizona, U.S.A.,

O. MORFIN, M.H. CONKLIN and T.L. CORLEY, Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona, U.S.A.

There are numerous active, inactive, and abandoned metals extraction facilities in the western United States. Often located near readily-accessible surface water, such sites have contributed to pollution of an estimated 320 km of surface water in Arizona. Elevated levels of Pb, Cd, and As have been found in fish in the perennial reach of the Aravaipa Creek located near the eastern entrance of the Aravaipa wilderness area of Arizona. Several abandoned mines, piles of mine waste, and tailings from lead/zinc processing plants have been implicated as potential sources of this contamination. This study emphasizes the application of controlled sample digestion, sequential metal extraction, and lead isotope ratios as a means of differentiating between these sources. Pb isotope ratios in samples, obtained by ICP-MS analysis, describe two distinct contributors. Locations with mixed oxide/sulphide mineralization generally have lower $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ signatures, whereas, with predominantly primary mineralization (i.e., PbS), higher isotopic ratios are observed. Pb isotope ratios from perennial reach sediments are closely correlated with those obtained for the lead sulphide samples. The study concludes that Pb isotope data may successfully be reconciled to provide usefully constraints on Pb transport and its eventual fate. Importantly, this information will help identify specific targets requiring remediation and eliminate others.

SESSION 27: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

LEACHING I: THIOSULPHATE II

Sponsors: Hydrometallurgy Section of the The Metallurgical Society of CIM (MetSoc), Extraction and Processing Division, The Minerals, Metals & Materials Society (TMS), and the Society for Mining, Metallurgy and Exploration (SME).

Room: Pavillion Ballroom C

Chairmen: M. AYLMOORE, A.J. Parker Centre for Hydrometallurgy, CSIRO Minerals, Perth, WA, Australia
C. FLEMMING, Lakefield Research Limited, Lakefield, Ontario, Canada

PAPER 27.1 — 14:00

TOWARD AN UNDERSTANDING OF COPPER(I) SPECIATION AND REACTIVITY IN THE COPPER-AMMONIA-THIOSULPHATE LIXIVANT SYSTEM.

J. BLACK, L. SPICCIA, Monash University, Melbourne, Victoria, Australia, and

D.C. McPHAIL, CRC LEME and Department of Geology, The Australian National University, Canberra, Australia

Research into alternative gold leaching agents to cyanide has identified thiosulphate, in combination with a Cu(II)-ammine catalyst, as a promising, more benign alternative (Aylmore and Muir, 2001; Molleman and Dreisinger, 2002). Studies of this process highlight the need to examine the chemistry controlling thiosulphate stability, high reagent consumption impacting on viability. A Cu(II)-tetrammine acts as an electrocatalytic oxidant, increasing gold dissolution rates. Although the Cu(II)-NH₃ chemistry is well understood, the addition of thiosulphate produces radicals, Cu(I)/(II) complexes and other sulphur species, many of them poorly characterized. Since the reduction of Cu(II) to Cu(I) accompanies thiosulphate oxidation and gold leaching, an understanding of Cu(I)-ammonia-thiosulphate speciation and the mechanism by which oxygen regenerates Cu(II)-tetra-ammine is needed. With this in mind, UV-Vis. spectrophotometry was used to identify the complexes present in the Cu(I)-NH₃-S₂O₂-Cl system and to determine their thermodynamic properties. The authors are currently studying the kinetics of oxidation of Cu(I) complexes by oxygen to determine optimal conditions for regenerating the Cu(II) catalyst.

PAPER 27.2 — 14:25

THE ROLE OF CATALYSTS IN THE THIOSULPHATE LEACHING OF GOLD.

A.E. LAM and D.B. DREISINGER, Metals and Materials Engineering, The University of British Columbia, Vancouver, British Columbia, Canada

The thiosulphate leaching of gold generally requires the addition of “catalysts” such as soluble copper and ammonia in order to obtain reasonable leaching rates and gold extractions. Unfortunately, the same catalysts that accelerate gold leaching also tend to accelerate thiosulphate oxidation to tetrathionate and other species. It is therefore imperative that a detailed understanding of the role of the catalysts be obtained. It is equally important for plant application that a method of assessing the effectiveness of catalysts be developed. In this work the role of the copper and ammonia catalysts was studied using geochemical modelling for speciation prediction, thiosulphate leaching of gold ores, and chemical analysis of resulting leach solutions. Results of these studies will be presented and discussed.

PAPER 27.3 — 14:50

ALTERNATIVE COPPER(II) CATALYSTS FOR GOLD LEACHING: USE OF MULTI-DENTATE LIGANDS TO CONTROL THIOSULPHATE OXIDATION.

T. BROWN, A. FISCHMANN, L. SPICCIA, Monash University, Melbourne, Victoria, Australia, and
D.C. McPHAI, CRC LEME and Department of Geology, The Australian National University, Canberra, Australia

In the thiosulphate gold leaching process, complexation of gold with thiosulphate follows electrocatalytic oxidation by Cu(II)-ammines (Aylmore and Muir, 2001). Unfortunately, Cu(II) also catalyzes the undesirable conversion of thiosulphate to polythionates. Alternatives to ammonia, which fulfill the role of ammonia but minimize thiosulphate decomposition have been sought. These studies have involved the determination of the rate of thiosulphate oxidation by the Cu(II) complexes, from UV-visible spectral changes, and redox potentials. They are to be followed by gold leaching trials. Various ligand classes, including pyridyls, polyamines, aminocarboxylates, and picolines, have been tested and the majority found to inhibit thiosulphate decomposition. Interesting variations in reactivity with the nature and denticity of the ligand and L/M ratio will be reported. A spectrophotometric study of the oxidation of thiosulphate by a Cu(II)-tren complex [tren = tris(2-aminoethyl) amine] has indicated that several processes are occurring, two of which involve the formation and decay of a tetrathionate radical.

COFFEE BREAK — 15:15 – 15:30

PAPER 27.4 — 15:30

A NOVEL THIOSULPHATE SYSTEM FOR LEACHING GOLD WITHOUT THE USE OF COPPER AND AMMONIA.

J. JI, P.G. WEST-SELLS, Placer Dome Inc., Vancouver, British Columbia, Canada,
C.A. FLEMING, SGS Lakefield Research, Lakefield, Ontario, Canada, and
R.P. HACKL, Placer Dome Inc., Vancouver, British Columbia, Canada

The thiosulphate lixiviant system that has been under extensive investigation for nearly two decades now consists of ammonium thiosulphate, copper and ammonia. There are several challenges with this system. The occurrence of ammonia must be taken into account from a health and hygiene aspect in the work place, and also from an environmental perspective with significant levels of ammonia and copper in the tailings. Copper accelerates the leaching rate but causes excessive thiosulphate degradation. The new lixiviant consists only of sodium thiosulphate without copper and ammonia. Gold leaching is carried out in an enclosed reactor with slightly elevated oxygen overpressure and temperature. Extensive leaching experiments were carried out to minimize thiosulphate degradation while maximizing the gold extraction. For several preg-robbing carbonaceous ore samples tested, gold leaching was essentially complete within six hours and the thiosulphate consumption was lower than in the typical ammoniacal thiosulphate system. The gold thiosulphate complex in the pregnant leach solution was found to be quite stable under ambient conditions. This new leaching system has the advantages of being more environmentally friendly, has a shorter residence time, lower thiosulphate consumption, lower oxygen consumption, and is easier to control.

PAPER 27.5 — 15:55

A PROCESS FOR COUNTERACTING THE DETRIMENTAL EFFECT OF TETRATHIONATE ON RESIN GOLD ADSORPTION FROM THIOSULPHATE LEACHATES.

P.G. WEST-SELLS, J. JI, Placer Dome Inc., Vancouver, British Columbia, Canada, and
R.P. HACKL, Placer Dome Inc., Vancouver, British Columbia, Canada

Recovery of gold from thiosulphate leachates is typically accomplished by adsorption of the gold thiosulphate complex by a strong base resin. Two of the most significant impurities that can decrease this gold adsorption are tetrathionate and trithionate, which are produced as oxidation products of thiosulphate during gold leaching. This paper investigates gold adsorption on a strong base resin (Purolite A500C) as a function of the concentration of these impurities. It is shown that concentrations of tetrathionate and trithionate as low as 150 mg/L can decrease gold loading by an order of magnitude, and that of the two ions, tetrathionate has a stronger detrimental effect. The resin and solution gold concentration profiles were successfully fit using a Freundlich isotherm, which further shows the strong effect of tetrathionate. To counteract the decrease in gold adsorption by tetrathionate, a novel process was proposed. Sulphite was added to the solution to oxidize tetrathionate to trithionate, and a nitrogen blanket was added to ensure that no further oxidation of thiosulphate could take place. It is shown that by incorporating this process, gold adsorption was doubled from both synthetic and real gold thiosulphate leachates.

PAPER 27.6

AMMONIUM THIOSULPHATE HEAP LEACHING.

P.N.H. BHAKTA, Newmont Mining Corporation, Carlin, Nevada, U.S.A.

Newmont has investigated potential treatment options for low-grade refractory gold ores since 1988. After extensive R&D at Newmont's laboratories, bio-oxidation pretreatment followed by ammonium thiosulphate leaching was selected for application to sulphidic preg robbing ores. A heap bio-oxidation and ammonium thiosulphate leaching demonstration facility was constructed in 1995 to conduct large-scale pilot tests at Newmont's Carlin Operations. This paper presents Newmont's experience with the recovery of gold from preg robbing ores using ammonium thiosulphate.

SESSION 28: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

LEACHING II: FUNDAMENTALS II

Sponsors: Hydrometallurgy Section of the The Metallurgical Society of CIM (MetSoc), Extraction and Processing Division, The Minerals, Metals & Materials Society (TMS), and the Society for Mining, Metallurgy and Exploration (SME).

Room: Pavillion Ballroom D

Chairmen: J. BUDAC, Sherritt International, Fort Saskatchewan, AB, Canada
C. ANDERSON, CAMP, Montana Tech, Butte, MT, USA

PAPER 28.1 — 14:00

FLUOSILICIC ACID LEACHING OF GALENA.

P.R. TAYLOR, Y. CHOI and E.E. VIDAL, Department of Metallurgical and Mining Engineering, Colorado School of Mines, Golden, Colorado, U.S.A.

A kinetic study of the fluosilicic acid leaching of galena was performed under the presence of different oxidants. Fluosilicic acid concentration, agitation speed, concentration of solids and particle size, type and concentration of oxidant, and temperature were the variables studied. Hydrogen peroxide was found to be the most effective oxidant, its effectiveness being proportional to its concentration. As expected, an increase of leaching temperature increased the overall extraction and extraction rate. The same was found by decreasing the galena particle size. It is thought that leaching using hydrogen peroxide is controlled by fluid film mass transfer due to the calculated apparent activation energy. Reaction by-products such as sulphur and sulphur compounds retard the leaching rate. A mathematical model is proposed and compared to experimental results.

PAPER 28.2 — 14:25

USE OF ALTERNATING CURRENT FOR LEACHING OF INTERMEDIATE PRODUCTS FROM COPPER AND NICKEL PRODUCTION.

A.V. TARASOV, V.M. PARETSKY and V.A. BRYUKVIN, State Research Institute of Non-Ferrous Metals "GINTSVETMET", Moscow, Russia

In order to improve technical, economic and environmental performance of hydrometallurgical processing of intermediate products containing copper and nickel, the Gintsvetmet Institute and the IMET Institute of the Russian Academy of Sciences have conducted studies into the efficiency of the use of alternating current of industrial frequency on processes applied for hydrochemical leaching of various copper-and nickel-containing materials. It has been found that:

1. Imposition of alternating current over the process of leaching of softly reduced nickel oxide with recycled copper sulphate solutions resulted in an increase by 20% to 30% of the rate of the copper cementation process and reduced its activation energy by 20%. At the same time, the recoveries of nickel, cobalt, and iron to the leach solution increased up to 82.2%, 78.5%, and 57.1%, respectively, and that of copper to the cement precipitate up to 74%. Optimal process conditions have been identified with respect to the current density, electrode material, copper concentration in solutions and the process temperature.

2. In the process of hydroelectrochemical sulphuric acid leaching of nickel and copper sulphides, the grain size, the phase form of sulphides, the solution composition (H_2SO_4 , Cl^- , Cu^{2+} , Fe^{3+}) and the current amperage had an effect on the nickel recovery to the solution, which reached 90%, while the degree of copper transfer to solution did not exceed 20%. The process of hydroelectrochemical sulphuric acid leaching of nickel and copper sulphides with an addition of Cl^- made it possible to selectively recover nickel into the leach solution along with concentrating copper in the leach residue.

3. When subjecting samples of commercial-grade magnetic fractions of converter matte to sulphuric acid leaching, the imposition of electric current, the concentrations of sulphuric acid, and chloride ion in the solution and the duration of the reaction process had an effect on the process. The nickel recovery was 85% and that of cobalt and iron was 95% and the recoveries reached 97.5%, 98.3%, and 99.8%, as a result of repeated treatment of the primary residue under similar process conditions. Up to 75% of copper, 75% of sulphur and 99.0% to 99.5% of palladium was concentrated in the solid reach residues. The experimental data obtained indicates that the use of AC for hydroelectrochemical sulphuric acid leaching for separation of copper- and nickel-containing intermediate products has favourable prospects.

PAPER 28.3 — 14:50

THE REDUCTIVE DISSOLUTION OF MANGANESE DIOXIDE WITH IRON(II) AND SULPHUR DIOXIDE: KINETICS AND MECHANISM.

G. SENANAYAKE, Murdoch University, Murdoch, Western Australia

Iron(II) and sulphur dioxide are efficient reducing agents for manganese dioxide to produce Mn(II) solutions. The leaching of limonitic laterite and manganiferrous ores with sulphur dioxide in acid media produces Fe(II) which in turn catalyzes the leaching of manganese dioxide. Therefore, the kinetics of manganese dioxide dissolution plays an important role in the selective leaching of manganese from these materials. This paper presents a critical analysis of the reductive dissolution kinetics of synthetic manganese dioxide to compare and contrast the effect of sulphur dioxide and Fe(II) in acid media containing sulphate or perchlorate anions. Both one-electron and two-electron mechanisms are considered when sulphur dioxide is used as the reductant. The current knowledge on chemical speciation is used to modify the published Eh-pH diagrams to show the effect of anions. Heterogeneous and electrochemical reaction kinetic models are combined to propose reaction mechanisms which rationalize the dissolution kinetics.

COFFEE BREAK — 15:15 – 15:30

PAPER 28.4 — 15:30

ATMOSPHERIC CHLORIDE LEACHING: THE WAY FORWARD FOR NICKEL LATERITES:

B. HARRIS and J. MAGEE, Chesbar Resources Inc., Toronto, Ontario, Canada

Chesbar Resources Inc. is developing a nickel-cobalt laterite project in Guatemala, Central America, by applying existing atmospheric chloride technology to a known resource. The tropical laterite project has an inferred resource of 133 million tonnes grading 1.51% nickel, which represents ~20% of Chesbar's land holdings in Guatemala. Within its boundaries, the Sechol area has a measured resource of 14 million tonnes grading 1.46 % nickel and 0.08% cobalt, and an indicated resource of 23 million tonnes grading 1.34% nickel and 0.08% cobalt. Notwithstanding the impressive overall resource, the company has taken an innovative approach to a laterite project and is concentrating on El Inicio, a high-grade starter pit with five million tonnes grading 2.1% nickel and 0.08 % cobalt. The process flowsheet is based on atmospheric chloride leaching in a slightly acidic magnesium chloride brine, solution purification by recycled magnesia, precipitation of a mixed nickel/cobalt hydroxide intermediate product, and lixiviant regeneration by modified pyrohydrolysis technology. Initial results suggest that >90% of the contained nickel and cobalt in the non-magnetic fraction of the feed can be recovered, with <5% of the iron leaching. A metallurgical scoping study has established preliminary capital and operating costs for a production facility at a proposed rate of 20,000 tonnes per year of nickel as the intermediate mixed hydroxide. A preliminary assessment of producing a magnesium oxide by-product has also been carried out. This paper reports on the current development of the project and highlights the advantages of working in a chloride medium at atmospheric pressure and slightly elevated temperatures.

PAPER 28.5 — 15:55

CHLORIDE HYDROMETALLURGY: APPLICATION OF FUNDAMENTALS.

G. SENANAYAKE, Murdoch University, Murdoch, Western Australia, and

D.M. MUIR, CSIRO Minerals, Bentley, Perth, Western Australia

A good understanding of fundamentals is beneficial for the rationalization of complex chemistry in hydrometallurgical processes. Water activity decreases and proton and chloride ion activity increases with ionic strength. Thus acidic concentrated chloride solutions provide faster kinetics and selectivity in the leaching of sulphides and oxides. Activity of the metal ion in the form of the hydrated chloro complex species plays an important role in determining the redox potential and solubility of metal chloride at high ionic strengths. While the hydration theory can be used to predict and/or rationalize the changes in proton and uncomplexed or complexed metal ion activity, Pourbaix diagrams along with the measured redox potentials can be used to predict the nature of the complex ion. This paper outlines the successful outcomes and limitations of translating the fundamental knowledge of the physico-chemical behaviour of base metal ions to practical applications in chloride hydrometallurgy.

PAPER 28.6 — 16:20

MINIMIZING FUEL COSTS DURING THERMAL REGENERATION OF THE HYDROCHLORIC ACID LIXIVANT.

K. ADHAM and C. LEE, Hatch Associates Ltd., Mississauga, Ontario, Canada

Hydrochloric acid is used as lixiviant in such hydrometallurgy flowsheets as synthetic rutile and nickel production. Intermediary metal chloride is roasted to release gaseous HCl and a solid metal oxide. A large amount of fuel is required for this regeneration, mainly to vaporize the water content. Some energy recovery from the off-gas is currently achieved, but fuel consumption can further be reduced by process optimization and energy recovery from the roaster products. Here, first the existing limitations to fuel efficiency in the industrial scale HCl roasters are described. Then, for the case of a dilute feed solution, options for pre-evaporation and fuel minimization are modelled and compared. Energy recovery technologies including heat pumps, acid heat exchangers and solid waste heat boilers are described, and their potential as heat source for the pre-evaporation process is evaluated. Finally, for a representative example, the possible fuel saving from each option is quantified.