

WEDNESDAY, AUGUST 27, 2003, A.M.

SESSION 36: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

SOLUTION PURIFICATION I: SOLVENT EXTRACTION III

Sponsors: Hydrometallurgy Section of 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 A

Chairmen: K. SOLE, Anglo American Research, Laboratories (Pty) Ltd, Johannesburg, South Africa  
M. DIETZ, Chemistry Division, Argonne National Laboratory, Argonne, IL, USA

PAPER 36.1 — 8:30

PREPARATION OF ULTRAFINE SILVER PARTICLES BY SOLVENT EXTRACTION TECHNIQUES.

M.G. SÁNCHEZ-LOREDO, M.M. GONZÁLEZ-CHÁVEZ and J. LÓPEZ-MARTÍNEZ, Universidad Autónoma de San Luis Potosí, San Luis Potosí, México

Research efforts are devoted toward synthesis of silver nanoparticles due to the role played by silver in catalysis, as substrate for surface-enhanced Raman spectroscopy (SERS) and photographic processes. Particles with small size, narrow size distribution, and highest purity are chemically produced by reduction of metal complexes in organic media. The use of reducing agents was proposed as an alternative to conventional stripping in solvent extraction technology. In this paper, solvent extraction of silver by the commercial extractants TBP, Cyanex 471x, Cyanex 301 and Cyanex 302, was studied. After loading, several reagents were used to prepare silver powders by reductive stripping. Both Cyanex 471x and TBP could be stripped by aqueous solutions of ascorbic acid. Silver was recovered as fine particles, which were characterized by means of SEM, X-ray diffraction and spectroscopical techniques. The powder size and morphology were affected by the composition of the applied organic and aqueous reducing phases.

PAPER 36.2 — 8:55

EQUILIBRIUM MODIFIERS IN COPPER SOLVENT EXTRACTION REAGENTS - FRIEND OR FOE?

G.A. KORDOSKY and M.J. VIRNIG, Cognis Corporation, Tucson, Arizona, U.S.A.

Equilibrium modifiers, first introduced into copper solvent extraction reagents in the late 1960s, are widely used. Equilibrium modifiers affect the following properties of a copper solvent extraction reagent: copper extraction and stripping, copper/iron selectivity, reagent stability, crud generation and entrainment. These properties are discussed and some conclusions are drawn relating the structure of the modifier to the resulting properties of the copper solvent extraction reagent. The properties of a new highly selective, low viscosity modifier are given and discussed.

PAPER 36.3 — 9:20

THIRD PHASE FORMATION IN TBP SOLVENT EXTRACTION SYSTEMS AS A RESULT OF INTERACTION BETWEEN REVERSE MICELLES.

R. CHIARIZIA, P. THIYAGARAJAN, M.P. JENSEN, M. BORKOWSKI and K.C. LITRELL, Argonne National Laboratory, Argonne, Illinois, U.S.A.

Third phase formation, i.e., the splitting of the organic phase in two layers, is a common feature observed, under conditions of high loading, for many solvent extraction systems of both analytical and industrial interest. Although this phenomenon has been investigated in a large number of works, its structural and physico-chemical description is still lacking. In this paper, small-angle neutron scattering (SANS) data for the tri-n-butylphosphate (TBP)-n-octane,  $\text{Th}(\text{NO}_3)_4\text{-HNO}_3$  solvent extraction system have been interpreted using the Baxter model for hard-spheres with surface adhesion. The increase in scattering intensity in the low Q range, observed when increasing amounts of  $\text{HNO}_3$  and/or  $\text{Th}(\text{NO}_3)_4$  are introduced into the organic phase, has been interpreted as arising from interactions between reverse micelles containing three TBP molecules plus solutes in their polar core. This intermicellar attraction, under suitable conditions, leads to third phase formation.

PAPER 36.4 — 9:45

ROOM-TEMPERATURE IONIC LIQUIDS AS DILUENTS FOR THE LIQUID-LIQUID EXTRACTION OF METAL IONS: PROMISE AND LIMITATIONS.

M.L. DIETZ, M.P. JENSEN, J.V. BEITZ and J.A. DZIELAWA, Argonne National Laboratory, Argonne, Illinois, U.S.A.

The unique physicochemical properties of room-temperature ionic liquids (RTILs) have led to intense interest in these materials as alternatives to conventional organic solvents in a range of synthetic, catalytic, and electrochemical applications. Recently, there has been growing interest in their potential use in various separation processes, among them the liquid-liquid extraction of metal ions. Although certain RTIL-extractant combinations (e.g., crown ethers in 1-alkyl-3-methylimidazolium bis [(trifluoromethylsulphonyl)] imides) have been shown to provide extraction efficiencies far exceeding those observed with conventional solvents, recent work suggests that the utility of RTILs may be limited by solubilization losses and difficulties in recovering extracted metal ions. In this paper, the authors demonstrate that these limitations arise from differences in the mechanism of metal ion partitioning in RTIL systems versus conventional organic diluents and consider approaches by which they might be overcome.

COFFEE BREAK — 10:10 – 10:30

PAPER 36.5 — 10:30

DEVELOPMENT OF EXTRACTANTS TO TRANSPORT METAL SALTS IN BASE METAL RECOVERY PROCESSES  
S.G. GALBRAITH, D.K. HENDERSON, H.A. MILLER, P.G. PLIEGER, P.A. TASKER, K.J. SMITH and L.C. WEST,  
Department of Chemistry, University of Edinburgh, Edinburgh, United Kingdom

The authors have used the principles of supramolecular chemistry to develop reagents to transport metal salts. These have separated charged “compartments” which recognize a metal cation and its attendant anions. They are potentially simple to manufacture because they contain phenolic-imine units that are structurally related to the commercial phenolic-oxime extractants for copper. The metal salt is transported in a zwitterionic form of the ligand,  $[M(L)X]$ , leaving the pH of the aqueous feed solutions unchanged, thus removing the need for interstage neutralisation in metal recovery circuits. Stripping the loaded organic can be achieved by simple “pH-swing,” or other mechanisms. Incorporating the appropriate groups into the ligand superstructure allows the selectivity and strength to be tuned for particular metal cations or anions. In this paper, the authors will focus on how these types of reagent can be used to recover base metals from sulphate and chloride media in flowsheets in which solvent extraction achieves separation and concentration, interfacing between conventional leach and electrowin/reduction processes. Work on the development of reagents that have high selectivity for metal chloride/sulphate transport, convenient stripping protocols and appropriate hydrolytic stability will be described.

PAPER 36.6 — 10:55

APPLICATION OF COMPETITIVE COMPLEXATION/SOLVATION THEORY IN METALS SOLVENT EXTRACTION NEW OPPORTUNITIES IN PROCESS DEVELOPMENT.

V.S. KISLIK, The Hebrew University of Jerusalem, Jerusalem, Israel

Competitive complexation/solvation theory of solvent extraction constitutes a general framework for interpretation and quantification of ion-molecular interaction data in extraction systems. Depending on extracting metal-solvent affinity constant and metal concentration ratios, four possible stages of extraction behaviour and interacting mechanisms, are considered. Affinity constant ratios are easily acceptable through the independent measurements of three-component systems. Once determined and tabulated, the affinity constant ratio data may be used in any system of interest. Mathematical descriptions of the results are introduced for different interactions. Active solvent (including water) concentrations in the organic phase and temperature are included to the quantitative consideration. The theory allows to compare directly the complexing/solvating power (competition order) of various extractants, active solvents and diluents. As a result, predictions for the extraction effectiveness and selectivity are possible. Some metal extraction systems are analyzed on the base of the theory. Analysis gives a key for preliminary quantitative prediction of suitable extraction systems.

PAPER 36.7 — 11:20

SOLVENT EXTRACTION SYSTEM MODELLING USING THE PROGRAM SXFIT.

L.H. DELMAU, C.F. BAES, D.A. BOSTICK, T.J. HAVERLOCK and B.A. MOYER, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

SXFIT is the latest in a series of programs developed in our group designed to model solvent extraction systems of increasing complexity. SXFIT permits the user complete freedom to define the constituents from which the composition of each phase is to be specified in the data and from which all species of a model for a system are assumed to be formed. Activity coefficients in the non-aqueous and aqueous phases, water activity, apparent molar volumes of aqueous species, and solution density needed for the conversion of concentration from the molarity to the molality scale are all taken into account by the program. Several extraction systems relevant to nuclear-waste treatment were modelled successfully using this program. As an example, the cesium extraction efficiency of the CSSX process chosen by the U.S. DOE for cesium removal from high-level waste stored at the Savannah River site can be predicted correctly for varying feed composition.

## SESSION 37: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

SOLUTION PURIFICATION II: ELECTROWINNING II

Sponsors: Hydrometallurgy Section of 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: T. BAGSHAW, AMIRA International Limited Research, PO Box 1368, W. Perth WA, Australia  
A. SIEGMUND, RSR Technologies, Inc., Dallas, TX, USA

PAPER 37.1 — 8:30

ELECTROCRYSTALLISATION OF NICKEL: EFFECT OF CERTAIN METAL IONS.

B.C. TRIPATHY, U.S. MOHANTY, T. SUBBAIAH, S.C. DAS and V.N. MISRA, Regional Research Laboratory, Council of Scientific & Industrial Research, Bhubaneswar, Orissa, India

The effects of alkali metal ions  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and transition metal ions  $\text{Cr}^{3+}$  and  $\text{Mo}^{6+}$  on the cathodic current efficiency, deposit quality, crystallographic orientations, deposit morphology and polarization behaviour of the cathode during nickel electrocrystallization on stainless steel substrate from aqueous sulphate solutions containing boric acid were investigated. The alkali metal ions had virtually no effect on the cathodic current efficiency, deposit quality, crystallographic orientations, deposit morphology and cathodic polarization. On the other hand, there were significant variations in the current efficiency and deposit characteristics when  $\text{Cr}^{3+}$  or  $\text{Mo}^{6+}$  was present in the electrolyte. Current efficiency decreased by more than 10% even at lower concentrations. Similarly purity of the deposits was affected by the presence of either of the metal ions. In the presence of  $\text{Cr}^{3+}$  there was progressive shifting of the nucleation potential of nickel toward more -ve values, whereas, in the case of  $\text{Mo}^{6+}$  the nucleation potential shifted initially toward +ve values in the concentration range 2 to 40 mg/L but then toward -ve values when its concentration exceeded 40 mg/L.

PAPER 37.2 — 8:55

THE EFFECT OF DISSOLVED MANGANESE ON ANODE ACTIVITY IN ELECTROWINNING.

L. PAJUNEN, J. AROMAA and O. FORSÉN, Helsinki University of Technology, Helsinki, Finland

DSA-anodes are widely used in metal electrowinning. In zinc electrowinning, the electrolyte solution contains manganese ions and deposition of manganese dioxide happens on the anode. This manganese dioxide layer can not be removed without losing the active coating of the DSA-anode. Same problem can be found with hybrid anodes. In hybrid anodes mixed metal oxide coated titanium mesh is attached to lead base material. In this study, the effect of dissolved manganese on anode behaviour is studied with three different anodes. These anodes are lead anode with 0.6% silver, hybrid anode and DSA-mesh. Study of anodes includes polarization, galvanostatic and potential mapping experiments.

PAPER 37.3 — 9:20

STUDY OF ANODIC SLIME FROM CHILEAN COPPER ELECTROWINNING PLANTS.

J. IPINZA, J.P. IBANEZ and J. ARAGON, Arturo Prat University, Iquique, Chile

Impurities such as  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  in the pregnant leaching solution are transferred to copper electrowinning plants causing a series of troubles, being the slime generation the less studied one. During electrowinning, in the cathode the cupric ions are reduced and in the anode occurs a redox process: water oxidation and impurities reduction. These redox reactions are the basis for slime generation during electrowinning of copper. On the fresh Pb-Ca-Sn anode surface takes place the formation of  $\text{PbSO}_4$  at first, then, it is transformed in the conducting  $\text{PbO}_2$ , which covers the anode surface. The formation of a manganese dioxide double layer at the anode has been experimentally established; this double layer was always composed of a thick external layer of non-adhering and easily removable scales, and of a thin internal layer, which adheres relatively well to the surface of the electrode. It was found that manganese dioxides present in the slime were of a different nature: a non-adhering layer produced by electrolysis ( $-\text{MnO}_2$ ) on the  $\text{PbO}_2$  surface and a pure chemical precipitation in the solution ( $-\text{MnO}_2$ ). It was established that in the overall process of slime formation the  $-\text{MnO}_2$ -type manganese dioxide promote the detachment of the conducting combined layer of  $\text{PbO}_2$ - $\text{MnO}_2$  ( ) due to a significant increase of the layer's weight. In industrial operations this detachment is favoured by the frequent short circuit in the cells. Due to the thermodynamic conditions of the process,  $\text{PbO}_2$  is spontaneously transformed to  $\text{PbSO}_4$ . Therefore, the slimes were found to consist mainly of manganese dioxides and lead sulphate. In addition, the chemical dynamic stability of the slime is discussed.

COFFEE BREAK — 10:10 – 10:30

PAPER 37.4 — 9:45

ZINC ELECTROWINNING USING NOVEL WROUGHT Pb-Ag-Ca ANODES.

D. PRENGAMAN and A. SIEGMUND, RSR Technologies, Inc., Dallas, Texas, U.S.A.

Cast or rolled lead anodes employed in zinc electrowinning typically contain between 0.5% to 1.0% silver to decrease the overall corrosion rate. The production of cast lead-silver or lead-silver-calcium anodes often results in the formation of numerous holes, voids or laps in the anode surface that can initiate internal corrosion in localized areas. In rolled anodes, the presence of internal porosity is significantly reduced, thus resulting in extended service life. The obtained grain structure of rolled Pb-Ag anodes, however, requires a relatively long period of time to form a stable protective  $\text{PbO}_2/\text{MnO}_2$  layer that can evolve oxygen without excessive lead contamination of the cathode. Therefore, these anodes are often mechanically, chemically or electrochemically conditioned prior to being placed in the electrowinning process. RSR Technologies developed an improved anode for zinc electrowinning. The anode consists of a rolled Pb-Ag-Ca-alloy with controlled surface grain structure. The preferred calcium and silver content of the alloy is 0.05% to 0.08% and 0.3% to 0.4%, respectively. Since May 2001, industrial-scale tests are carried out at two zinc smelters in the United States in industrial electrowinning cells. The controlled grain structure of these anodes allows forming an adherent protective oxide coating within a short period of days when placed in an electrowinning cell without the necessity of being preconditioned. Anode sludge growth is evenly distributed. The anodes stay dimensional stable and no short circuits have been observed. Consequently, low corrosion rates and improved current efficiencies have been achieved.

PAPER 37.5 — 10:30

ELECTRODEPOSITION OF NICKEL-COBALT ALLOYS FROM SULPHATE ACID BATHS.

C. LUPI and D. PILONE, Università degli Studi di Roma, Rome, Italy

Ni-Co alloys, having interesting properties such as hardness, magnetic properties and high strength, have found many technological applications. The aim of this work is to directly produce these binary alloys by electrowinning from sulphate baths coming from secondary battery dissolution. Nickel-cobalt alloys were electrowon from solutions containing about 40 g/L Ni and 2 to 8 g/L Co. Experimental tests have been carried out to investigate the effect of current density, temperature and electrolyte pH on current efficiency and specific energy consumption. The effect of the addition of two buffers such as  $H_3BO_3$  and  $(NH_4)_2SO_4$  has been also investigated. Experimental results show that the process parameters affect not only current efficiency and cell voltage, but also morphology and composition of the produced alloy.

PAPER 37.6 — 10:55

EXTRACTION OF COPPER AT HIGH FEED CONCENTRATIONS.

R. MOLNAR and N. VERBAAN, SGS Lakefield Research Limited, Lakefield, Ontario, Canada

A number of flowsheets have been designed and operated, or are currently being considered, to extract copper from leach solutions having much higher concentrations of copper than the 4 g/L levels typically found in heap leach liquors. Copper concentrations of 15 to 20 g/L are encountered. Dealing with these solutions has required that the envelope for "normal" copper solvent extraction be pushed beyond the usually considered limits. This paper discusses two pilot plant circuits that were operated at Lakefield Research to produce cathode copper from such solutions. Three different extractants were tested in these two campaigns. The roles of acidity and iron as well as some other key impurities, are discussed.

PAPER 37.7 — 11:20

INVESTIGATIONS OF SPOUTED BED ELECTROWINNING FOR THE ZINC INDUSTRY.

O.M.G. NEWMAN, P.A. ADCOCK, P. FREEMAN, M.J. MEERE, Pasminco Smelter Technical Support, Boolaroo, New South Wales, Australia,

J.W. EVANS, J.C. SALAS, S. SIU and A. ROY, Department of Materials Science and Engineering, University of California-Berkeley, Berkeley, California, U.S.A.

Research into potential applications of spouted bed electrowinning (SBE) in the zinc industry was conducted in a collaboration between our two organizations. The main system investigated was zinc from acidic sulphate electrolytes. However, SBE can be extended to other electrolytes, or recovery of other elements. Electrolytic tests were carried out at the 0.01 to 0.1 m<sup>2</sup> scale. Spouting behaviour has been studied at a larger scale, approaching a size suitable for an industrial unit cell. Much of our work was carried out using a micro-porous separator (Daramic®). However, it has also been shown that ion exchange properties can have a controlling effect on the process chemistry, electrochemical efficiency, and plant flowsheet. In 0.1 m<sup>2</sup> scale electrolytic tests, problems which appeared minor at smaller scale were magnified. The authors review the major achievements, promising areas for application in the zinc industry, current status, and remaining barriers to development of SBE technology. Funding from AusIndustry, formerly Department of Industry, Technology and Regional Development (Commonwealth Grant AGR 05495), as well as the support of ILZRO (for research on alkaline SBE) is gratefully acknowledged.

## SESSION 38: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

### TECHNOLOGY APPLICATION: RECYCLING

Sponsors: Hydrometallurgy Section of 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: Junior Ballroom C

Chairmen: R. STEPHENS, Teck Cominco Metals, Trail, BC, Canada

P. QUENEAU, P.B. Queneau & Associates Inc., Golden, CO, USA

#### PAPER 38.1 — 8:30

U.S. PLANTS OPERATED SOLELY TO RECYCLE METAL-RICH WASTES — AN UPDATE.

P.B. QUENEAU, P.B. Queneau & Associates Inc., The Bear Group, Golden, Colorado, U.S.A.

Some twenty United States plants solely devoted to recovering values from metal-rich wastes have established market niches based on one or more competitive advantages: superior process technology, access to key feedstocks, unique equipment, special knowledge of markets, and an appropriate exit for outfall water. Plant methodology, competitiveness, environmental, and changing economics are examined, with particular attention to feedstocks, technologies, products, and outputs.

#### PAPER 38.2 — 8:55

COPPER RECOVERY FROM WASTE PRINTED CIRCUIT BOARD.

K. KOYAMA, M. TANAKA, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan, and

J.-C. LEE, Korea Institute of Geoscience and Resources (KIGAM), Daejeon, Korea

Leaching of copper from printed circuit board (PCB) and electrowinning of copper from cuprous solution in ammoniacal alkaline solutions were examined in order to develop an energy conservative hydrometallurgical process for copper recovery from electronic scraps. In the leaching experiments, copper in PCB was oxidized by Cu(II), and Cu(I)-ammine complex ions were formed. Copper(I)-ammine complex slightly depressed the leaching rate, while Cu(II)-ammine markedly enhanced it. In the electrowinning experiments, current efficiency of copper deposition was approximately 100% in the range of 200 to 1000 A m<sup>-2</sup> in current density. It decreased with an increase in Cu(II) concentration. Electrowinning of copper from Cu(I)-ammine complex solutions favoured the production of plates rather than powders.

#### PAPER 38.3 — 9:20

METAL RECOVERY FROM ELECTRONIC SCRAP BY LEACHING AND ELECTROWINNING IV.

D. PILONE, Università degli Studi di Roma, Rome, Italy, and

G.H. KELSALL, Imperial College, London, United Kingdom

A novel process is being developed for metal recovery from waste electrical and electronic equipment and involving a leach reactor coupled to an electrochemical reactor. Metals such as Ag, Au, Cu, Pb, Pd, Sn, etc., are dissolved from shredded electronic scrap in an acidic aqueous chloride electrolyte by oxidizing them with aqueous dissolved chlorine species. In the electrochemical reactor: (1) chlorine is generated at the anode for use as the oxidant in the leach reactor, and, simultaneously, (2) at the cathode, the dissolved metals are electrodeposited from the leach solution. Results are described for the electrowinning of dissolved metals carried out at ambient temperature in a membrane divided cell using carbon felt as cathode. The experimental results are compared with the prediction obtained by a numerical model simulating the behaviour of flow-through porous electrode systems.

#### PAPER 38.4 — 9:45

RECOVERY OF ZINC(II) FROM SPENT HYDROCHLORIC ACID SOLUTIONS FROM ZINC HOT GALVANIZING PLANTS.

M. REGEL-ROSOCKA, R. CIERPISZEWSKI, I. MIESIAC, K. ALEJSKI, J. SZYMANOWSKI, Poznan University of Technology, Poznan, Poland, and

A.M. SASTRE, Universitat Politècnica de Catalunya E.T.S.E.I.B., Barcelona, Spain

Extraction of zinc(II) from spent pickling hydrochloric acid solutions obtained in zinc hot dip galvanizing plants was studied. Tributyl phosphate and its mixtures with di(2-ethylhexyl)phosphoric acid (DEHPA), HOE F® 2562, ALIQUAT® 336, ALAMINE® 304, ALAMINE® 308, ALAMINE® 310, ALAMINE® 336 and CYANEX® 301 were used as extractants. The acidic extractants (CYANEX® 301 and DEHPA) did not extract both zinc(II) and iron(III) from 10% HCl. A precipitation occurred or stable emulsions were formed when ALAMINE® 304, ALAMINE® 308, ALAMINE® 310 were used. Each of other reagents co-extracted both zinc(II) and iron(III). The latter had to be reduced to iron(II) prior to extraction. However, iron(II) was also coextracted and transferred to the strip. The formation of reverse micelles and/or partial hydrolysis of TBP are probably responsible for that transfer. Tributyl phosphate and HOE F® 2562 showed the best extraction performance. ALAMINE® 336 and ALIQUAT® 336 induced the oxidation of iron(II) to iron(III) enhancing the co-extraction of iron. Zinc(II) could be effectively stripped from the loaded phases containing TBP and HOE F® 2562 with water. A higher efficiency of zinc(II) stripping was observed in the second stage. TBP was used for separations carried out in laboratory mixer settlers. The dynamics of extraction and stripping was studied and successfully modelled.

COFFEE BREAK — 10:10 – 10:35

PAPER 38.5 — 10:35

RECYCLING OF ZNO FLY DUST TO PRODUCE ZINC BY HYDROMETALLURGICAL ROUTES.

J. JANDOVÁ, P. DVORÁK, Prague Institute of Chemical Technology, Prague, Czech Republic, and  
V. JIRICNÝ, Institute of Chemical Process Fundamentals Academy of Science, Prague, Czech Republic

ZnO fly dust arising during zinc removal from galvanized low-alloy steel sheets was investigated on a laboratory scale to obtain electrolytic zinc. The dust, which comprised ZnO in combination with  $ZnFe_2O_4$  and  $SiO_2$  was contaminated by Mn, Pb, Al, Mg, Pb, Cu, and Ca. The dust was leached in 0.5 and 1.0 M  $H_2SO_4$  and/or in 20% and 30% NaOH at various temperatures and liquid-to-solid ratios to determine optimum conditions leading to the highest possible selectivity of the leaching and the efficiency of Zn extraction in minimum time and to reach sufficient Zn concentration for the subsequent electrowinning of zinc. The electrolysis was performed with refined zinc sulphate leach liquors and/or with untreated zinc caustic solutions. Effects of operational variables on Znelectrowinning have been studied for sulphate and caustic electrolytes.

PAPER 38.6 — 11:00

RECOVERY OF COBALT AND TUNGSTEN FROM SCRAPED CARBIDE PIECES THROUGH A HYDROMETALLURGIC ROUTE.

S.N. ASHRAFIZADEH, Iran University of Science and Technology, Tehran, Iran

Nowadays, hard carbides have found various industrial applications in the manufacture of cutting tools, drilling and metal forming devices. About 60% of the world tungsten production is consumed in the manufacture of hard carbide pieces. Regarding the high values of hard carbide components such as Ni, Co, TaC, TiC, and WC, their recovery from scraped species has attracted many interests. In the current research, metallic cobalt and tungsten were recovered from scraped cemented carbide pieces through the application of high-voltage electrolysis in nitric acid media. By the latter method, cobalt and tungsten were initially recovered as cobalt nitrate and tungstenic acid, respectively. The tungstenic acid precipitate was calcinated at 800 °C after being washed twice by distilled water. A pure tungsten oxide was obtained. The effect of current density, electrolyte concentration, speed of agitation, and the anode surface area on the efficiency of the electrolysis process were investigated. The optimum conditions including a current density of 1500 A/m<sup>2</sup>, an acid concentration of 1.5 M, and a cell temperature of 80 °C were obtained.

PAPER 38.7 — 11:25

SELECTIVE LEACHING OF PLATINUM AND PALLADIUM BY CHLORIDE SOLUTION.

K. LIU, T. FUJITA, ATSUSHI SHIBAYAMA, Akita University, Akita, Japan, and  
W.T. YEN, Department of Mining Engineering, Queen's University, Kingston, Ontario, Canada

Platinum and palladium are usually dissolved together and followed by separation. In this study, the selective leaching of platinum and palladium from a secondary resource, such as dental waste, by using chloride solution (hypochlorite and chlorate) has been developed. Results indicated that about 100% of palladium could be initially extracted by the combination of 1.34 mol/L sodium hypochlorite (NaClO) and 0.068 mol/L sodium chloride (NaCl) at pH 1.2 and 298K in 1.5 hours or the combination of 0.005 mol/L sodium chlorate (NaClO<sub>3</sub>) and 6.0 mol/L hydrochloric acid (HCl) at 298K in 0.5 hour. About 100% of platinum could be extracted from the residue by the combination of 0.47 mol/L sodium chlorate (NaClO<sub>3</sub>) and 12 mol/L hydrochloric acid (HCl) at 298K in 2 hours.

## SESSION 39: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

### LEACHING I: HEAP LEACHING I

Sponsors: Hydrometallurgy Section of 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 C

Chairmen: L. TODD, Leaching & Environmental, Phelps Dodge Process Technology Center, Safford, AZ, USA

P. BHAKTA, Newmont Mining Corporation, PO Box 669, Carlin, NV, USA

PAPER 39.1 — 8:30

MEASUREMENT AND APPLICATION OF BIO-OXIDATION KINETICS FOR HEAPS.

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

The use of microbes for sulphide oxidation was investigated as a potential treatment option for low-grade refractory gold ores at Newmont Mining Corporation. The patented technology of heap bio-oxidation relied on maximizing the oxidation rate through even distribution of microbes on the ore before placement on the heap. This paper presents data on global oxidation rates based on oxygen uptake in a 50 kg column for two ore types. The oxygen uptake data was converted to a global oxidation rate. The calculated global oxidation rate was used to determine heap cycling times for Newmont's commercial heap bio-oxidation facility.

PAPER 39.2 — 8:55

**MATHEMATICAL MODELLING OF PYRITIC REFRACTORY GOLD ORE HEAP BIO-OXIDATION: MODEL DEVELOPMENT AND ISOTHERMAL COLUMN SIMULATIONS.**

S.C. BOUFFARD and D.G. DIXON, Department of Metals and Materials Engineering, The University of British Columbia, Vancouver, British Columbia, Canada

Poor understanding of the heap bio-oxidation pretreatment of pyritic refractory gold ores prompted us to develop a mathematical model, which includes experimentally-measured and fundamentally-derived subroutines. Lateral stagnant pores, connected to vertical plug flow channels, and in contact with uniformly-distributed gas streams, constitute the model hydrodynamic structure. Results from potentiostatic stirred-tank and packed-bed tests provide the particle kinetic model. Growth of attached and planktonic iron- and sulphur-oxidizing cells is modelled over three specific temperature ranges with a dual, limiting-substrate Monod expression. Heat conduction, generation, and advection complete this unsteady-state system of non-linear partial differential equations. Isothermal column tests validate the model simulations. Excellent fits of several leaching indicators (potential, extent of sulphide oxidation, iron concentration, cell numbers) reveal the rate-limiting step to shift from particle kinetics to oxygen gas/liq uid mass transfer with increasing temperatures. The model demonstrates how faster particle kinetics, higher head grade, and lower mass transfer coefficient prolong the oxygen transfer-limited phase. According to the model simulations, large pellets, comprised of rapidly oxidizable pyrite, leach zone-wise due to the rapid consumption of dissolved oxygen within the pellet pores. This modelling tool may assist engineers in the design and operation of heaps, hopefully resulting in complete gold liberation and shorter bio-oxidation time.

PAPER 39.3 — 9:20

**HEAP LEACH MODELLING: THE CURRENT STATE OF THE ART.**

D.G. DIXON, Department of Metals and Materials Engineering, The University of British Columbia, Vancouver, British Columbia, Canada

Since the early 1970s and its first implementation for the recovery of gold from low-grade ores by cyanidation, heap leaching has developed into a key hydrometallurgical technology, in conjunction with solvent extraction and electrowinning, for the recovery of base metals, including most notably copper from both oxides and secondary sulphides, and more recently, nickel and zinc. And given recent advances in bioleaching with thermophilic microbes, the successful application of heap leaching technology to low-grade primary copper ores seems only a matter of time. However, with each new development, it becomes increasingly apparent that the successful application of heap leaching technology will ultimately depend on our having an ever more complete understanding of the fundamental processes underlying the process. Much work has been done toward the development of this understanding, on many different fronts. In this paper, a critical overview of the most important work of the last ten years is presented, and potential directions for future work are discussed.

PAPER 39.4 — 9:45

**A COMPREHENSIVE COPPER STOCKPILE LEACH MODEL: PART I. BACKGROUND AND MODEL FORMULATION.**

C.R. BENNETT, J.E. GEBHARDT, Process Engineering Resources Inc., Salt Lake City, Utah, U.S.A.,

M. CROSS, T.N. CROFT, University of Greenwich, Greenwich, London, United Kingdom, and

L. UHRIE, Phelps Dodge Mining Company, Safford, Arizona, U.S.A.

The first phase in the design, development and implementation of a comprehensive computational model of a copper stockpile leach process is presented. The model accounts for transport phenomena through the stockpile, reaction kinetics for the important mineral species, bacterial effects on the leach reactions, and heat, energy and acid balances for the overall leach process. The paper describes the formulation of the leach process model and the implementation of the model in PHYSICA+, a computational fluid dynamic (CFD) modelling software environment. The model draws on a number of phenomena to represent the competing physical and chemical features active in the process model. The phenomena are essentially represented by a three phase (solid-liquid-gas) multi-component transport system; novel algorithms and procedures are required to solve the model equations and these are described, including a methodology for dealing with multiple chemical species with different reaction rates in ore divided into multiple particle size fractions.

COFFEE BREAK — 10:10 – 10:30

PAPER 39.5 — 10:30

**ORE GEOTECHNICAL EFFECTS ON COPPER HEAP LEACH KINETICS.**

G. MILLER, University of Queensland, Brisbane, Queensland, Australia

The ore geotechnical characteristics are important in understanding the kinetics of copper heap leaching. They can indicate potential problems and be used to determine the semi-quantitative changes in field kinetics as compared with column kinetics. The application of this approach allows a more rigorous basis for scale-up than previously. The shrinking core model is a poor predictor of leach kinetics based on crushed ore size distribution. However the model itself is a useful tool to analyze leach data. Geotechnical parameters such as: bulk density-stress characteristic, limit moisture capacity and particle density are used to determine the effect of changes on the diffusion-controlled leach rate. By considering the geotechnical reaction of the ore mass the leach rate changes are related to changes in these variables. Analysis of leach data has indicated effective diffusion lengths of up to ten times the largest particle size.

PAPER 39.6 — 10:55

PROCESS IMPROVEMENTS AT MANTOVERDE HEAP LEACH OPERATION.

G.E. ZÁRATE, Empresa Minera de Mantos Blancos, Providencia, Santiago, Chile,

L.O. TRINCADO, U.I. TRONCOSO and C.A. VARGAS, Empresa Minera de Mantos Blancos, Providencia, Santiago, Chile

Mantoverde is a heap leach-solvent extraction-electrowinning plant that was commissioned in December 1995 at a production rate of 42 130 tpy of copper and an ore treatment rate of 5.4 Mtpy. Copper production has steadily increased from 40 539 t in 1996 to 56 311 t in 2001. Forecast copper production for 2003 is 60 000 t for an ore treatment rate of 8.5 Mt. Several improvements in the heap leach process, in order to reach the actual level of production have been implemented. The main process improvements are related to the optimization of operating conditions such as heap height, particle size, irrigation rate and leach cycle, in addition to a better heap drainage design and a better solution management system. A first dump leach operation was started in 1999 at an initial production rate of 1922 t of copper. A second dump leach operation was started in early 2002 at an initial production rate of 2805 t of copper. Dump leach copper production will increase over time to as much as 24 000 t of copper. The main heap leach process improvements, as compared to the original plant design, as well as the main dump leach operating conditions are discussed in this paper.

## SESSION 40: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

### LEACHING II: CHLORIDE LEACHING

Sponsors: Hydrometallurgy Section of 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 D

Chairmen: G. VAN WEERT, Metals and Materials Engineering, University of British Columbia, Vancouver, BC  
D. VERHULST, Altair Nanomaterials Inc., Reno, NV, USA

PAPER 40.1 — 8:30

SOLUTION PURIFICATION IN THE OUTOKUMPU HYDROCOPPER® PROCESS.

M. HÄMÄLÄINEN, M. JYRÄLÄ and O. HYVÄRINEN, Outokumpu Research Oy, Pori, Finland

Outokumpu has developed a new chloride leaching process, HydroCopper®, for copper concentrates. The process utilizes cupric ion as oxidant, which is able to dissolve chalcopyrite. After solution purification monovalent copper is precipitated as cuprous oxide,  $\text{Cu}_2\text{O}$ , with sodium hydroxide. Copper product is produced from  $\text{Cu}_2\text{O}$  by reduction, melting and casting. An essential part of the new process is chlor-alkali electrolysis, which regenerates the reagents used. All impurity metals are removed before  $\text{Cu}_2\text{O}$  precipitation, because otherwise they report to the copper product, impairing its quality. A multi-stage solution purification scheme has been developed consisting of firstly, chemical precipitation of impurity metals by pH increase, secondly, cementation of silver, and thirdly, removal of trace multivalent ions by ion exchange. This paper describes the characteristics of the HydroCopper® process solution purification based on the laboratory tests and pilot runs made by Outokumpu Research Oy.

PAPER 40.2 — 8:55

DIRECT HYDROCHLORIC ACID LEACHING OF AN EGYPTIAN ILMENITE ORE FOR PRODUCTION OF SYNTHETIC RUTILE.

I.A. IBRAHIM, M.H.H. MAHMOUD, A.A.I. AFIFI, Central Metallurgical Research and Development Institute, Helwan, Cairo, Egypt, and B.A. EL-SAYED, Azhar University, Helwan, Cairo, Egypt

Ilmenite in its natural form is inactive mineral from which the selective removal of iron is rather difficult. The reactivity of ilmenite so that it can be leached with dilute hydrochloric acid can be enhanced by chemical reduction in solution using a suitable metal as a reducing agent. This paper aims at evaluation of an Egyptian ilmenite for the production of synthetic rutile by direct leaching with hydrochloric acid in the presence of iron powder. In this process, the titanium and iron contents are dissolved; meanwhile the dissolved titanium is hydrolyzed and re-precipitated leaving mainly iron in solution. Leaching conditions were optimized to obtain less iron in the final solid product. Addition of sufficient amount of iron powder during leaching reduces the dissolved  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and reduces the dissolved  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ . The creation of  $\text{Ti}^{3+}$  in solution is assumed to have a role in dissolving the ferric iron and hence increase the reactivity of ilmenite ore. Synthetic rutile of about 90%  $\text{TiO}_2$  and 0.77%  $\text{Fe}_2\text{O}_3$  was obtained from ilmenite ore of grain size 100% -200 mesh using 20% HCl at boiling temperature (110 °C), with the addition of 0.11 g iron powder/g ore for 5 hours.

PAPER 40.3 — 9:20

NEW DEVELOPMENTS IN THE ALTAIR HYDROCHLORIDE  $\text{TiO}_2$  PIGMENT PROCESS.

D. VERHULST, B. SABACKY and T. SPITLER, Altair Nanomaterials Inc., Reno, Nevada, U.S.A.

The Altair process involves digesting ilmenite ore in concentrated hydrochloric acid, cooling and crystallizing to separate iron chloride, solvent extraction to concentrate Ti in a purified stream and spray hydrolysis to produce a  $\text{TiO}_2$  hydrate, followed by final calcining and milling. HCl gas is regenerated by pressure-swing distillation and reinjected in the leaching solution. Chromium compounds generally remain in the residue. Solvent extraction provides flexibility for the removal of radioactive elements (NORMs). The process was previously tested at a 5 t/d feed scale. Recent work at pilot scale (30 L reactor) led to further improvements. Digestion time is now less than 3 h, crystallization at lower temperature lowers the amount of Fe in solution to about 5 g/L and improves solvent extraction, which is now conducted in columns. Higher Ti and lower Fe concentrations in the SX eluate improve the economics. A new formula for pigment production via spray hydrolysis looks very promising.

PAPER 40.4 — 9:45

ELECTROCHEMICAL MECHANISM INVESTIGATION OF MANGANESE DIOXIDE DISSOLUTION IN ACIDIC CHLORIDE SOLUTION IN PRESENCE OF FERROUS/FERRIC IONS.

G. XUEYI, Central South University, College of Metallurgical Science and Engineering, Changsha, Hunan, China

The hydrometallurgical method is a prospective choice to extract Mn and co-existing metal values from low-grade manganese ore in land and manganese nodules in deep sea beds. In this process, the manganese dioxide dissolves with the presence of reductants, implying that leaching is essentially an electrochemical process. In this study, the electrochemical kinetic equation of manganese dioxide reduction dissolution in acidic chloride solution in the presence of ferrous/ferric ions was deduced in terms of the Butler-Volmer equation and chemical kinetics theories; thereafter a series of experiments were conducted and the results obtained were found to be consistent with the theoretical deduction. These results are useful in offering a guide for the actual leaching of manganese dioxide minerals.

COFFEE BREAK — 10:10 – 10:30

PAPER 40.5 — 10:30

THE EFFECT OF CHLORIDE IONS ON THE OXIDATION OF PYRITE UNDER PRESSURE OXIDATION CONDITIONS.

M. NICOL and J.Q. LIU, Murdoch University, A J Parker Centre for Hydrometallurgy, Murdoch, Western Australia, Australia

Pressure oxidation of refractory gold minerals such as pyrite has become one of the main pre-treatment routes prior to cyanidation for gold extraction. It has been reported from some operations that the presence of chloride is detrimental for both the oxidation of pyrite and the recovery of the gold. Electrochemical experiments have been conducted at high temperatures and pressures in order to confirm these reports and to establish possible mechanisms for the effects. Experiments on the anodic oxidation of pyrite and cathodic reduction of iron(III) were carried out using linear sweep voltammetry in sulphate solutions containing various concentrations of chloride ions in a nitrogen atmosphere at various temperatures up to 200°C and 2000 Kpa. Results indicate that an increase in temperature results in higher reactivity for both the anodic oxidation of pyrite and the cathodic reduction of iron(III). An increase in chloride concentration results in decreased reactivity for both reactions. A possible mechanism for the effect of chloride is presented.

PAPER 40.6 — 10:55

THE USE OF ORTHO-PHENYLENE-DIAMINE (OPD) AS A SURFACTANT IN THE PRESSURE OXIDATION OF PYRITE.

D.B. DREISINGER, Z. ZHENG, Metals and Materials Engineering, The University of British Columbia, Vancouver, British Columbia, Canada, and N.J. DUNLAP, Dupont Company, Wilmington, Delaware, U.S.A.

The pressure oxidation of pyrite is an important hydrometallurgical technology, especially in the total oxidation of refractory gold ores and concentrates (gold is locked in the pyrite structure). It has been noticed in some commercial applications and bench-scale studies that the leaching of pyrite may be slow and can be inhibited by the presence of molten elemental sulphur in the leach pulp. The purpose of this study was to determine whether ortho-phenylene-diamine (OPD) could be used as a surfactant or dispersant for sulphur in the pressure oxidation of pyrite. OPD has previously been shown to be useful for pressure leaching of zinc and copper sulphides at 150 °C. In this work, the interfacial chemistry of sulphur was studied at temperatures of up to 200 °C in acidic solutions in the presence of OPD and other surfactants. The contact angle between molten sulphur and pyrite was also measured and the work of adhesion calculated. Finally, the impact of OPD on the kinetics of pyrite oxidation was measured in bench-scale pressure oxidation experiments. OPD was found to be effective as a surfactant and fully degraded at high temperature in the leach tests.