

TUESDAY, AUGUST 26, 2003, A.M.

SESSION 14: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

SOLUTION PURIFICATION I: ADSORPTION AND SOLVENT EXTRACTION 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 A

Chairmen: D. IBANA, A.J. Parker Centre for Hydrometallurgy, Curtin University of Technology, Perth, WA, Australia, S. DUYVESTYN, Metallurgical Engineering, University of Utah, Salt Lake City, UT, USA

PAPER 14.1 — 8:30

THE EFFECT OF PORE SIZE DISTRIBUTION ON GOLD ADSORPTION BY MAGNETIC ACTIVATED CARBONS.

G.A. MUNOZ, S. DUYVESTYEN and J.D. MILLER, Department of Metallurgical Engineering, University of Utah, Salt Lake City, Utah, U.S.A.

Activated carbons owe their adsorption properties to their highly developed pore network structure. As a result, these adsorbents generally exhibit high specific surface areas. Currently, granular activated carbons produced from coconut shells are extensively used for gold recovery by adsorption from cyanide leaching solutions. Magnetic activated carbons (MACs) for gold recovery from cyanide solutions produced from sources other than coconut shells have been developed at the University of Utah by mixing a magnetic precursor with a carbon source, and treating the mixture under controlled conditions of temperature and gas composition. The pore size distribution of the activated carbons is dependent, among other factors, on the degree of activation. The significance of the MAC pore size distribution on gold adsorption kinetics and gold adsorption capacity is presented.

PAPER 14.2 — 8:55

MAGNETIC ADSORPTION/FILTRATION PROCESS FOR WASTEWATER TREATMENT.

J.D. NAVRATIL, Environment Engineering and Science, Clemson University, Anderson, South Carolina, U.S.A.

Magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) has been used to separate a wide variety of substances, such as dissolved metal species, particulate matter, and organic and biological materials. In the absence of an external magnetic field, activated magnetite readily adsorbs numerous metal species including actinide elements. In the presence of an external magnetic field, a synergistic effect was observed in using supported magnetite in a fixed-bed for removal of plutonium and americium from wastewater. These observations may be explained by an anolevel high gradient magnetic separation effect, as plutonium and americium are known to form colloidal particles with satisfactory magnetic properties at elevated pH. The process has been tested for the removal of other metal ions including cobalt, iron, and manganese. This paper will review results to date on testing the process for wastewater treatment and outline potential applications in hydrometallurgy.

PAPER 14.3 — 9:20

SOLVENT EXTRACTION OF HALIDES FROM METALLURGICAL SOLUTIONS.

C. MASON, J. HARLAMOVS, , Teck Cominco Metals, Trail, British Columbia, Canada,

B. GRINBAUM, IMI Institute for Research and Development, Haifa Bay, Israel, and

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

Extraction of halides (fluoride, chloride) from metallurgical solutions can reduce corrosion rates and improve hygiene from decreased anodic chlorine evolution. This is particularly true for zinc sulphate electrowinning solutions. This paper describes the chemistry of a new process for the removal of halides from such solutions by solvent extraction. In this process, the halide species are loaded directly from commercial zinc sulphate solutions and are stripped into a form suitable for disposal. The method of optimizing the solvent composition is demonstrated.

PAPER 14.4 — 9:45

PILOTING OF A HALIDE EXTRACTION PROCESS WITH MIXER SETTLERS AND BATEMAN PULSED COLUMNS.

J. KUHN, J. HARLAMOVS, C. MASON, Teck Cominco Metals, Trail, British Columbia, Canada,

M. BELL, Bateman Engineering Inc., North Vancouver, British Columbia, Canada, and

E. BUCHALTER, Bateman Advanced Technologies Ltd., Yokneam, Israel

A new solvent extraction process for the removal of halides from zinc sulphate solution was tested in pilot plants at both a 0.1 L/min. scale and at a 3 L/min. scale. Mixer settlers were used for the 0.1 L/min. pilot scale and 100 mm diameter Bateman pulsed columns for the higher rates. Pilot testing was performed with commercial zinc sulphate solutions containing variable amounts of chloride and fluoride. The deleterious halides were loaded and stripped into a form suitable for disposal. The engineering aspects and economics of this solvent extraction process for halide removal are reported.

COFFEE BREAK — 10:10 – 10:30

PAPER 14.5 — 10:30

SYNERGISTIC SOLVENT EXTRACTION AND ITS POTENTIAL APPLICATION FOR METAL RECOVERY.

C.Y. CHENG, M. URBANI, M. DAVIES and M. HOUCHEIN, Division of Minerals, CSIRO, Bentley, Western, Australia

Since commissioning, Bulong Nickel has experienced gypsum formation in its nickel solvent extraction circuit. To solve this problem, the AJ Parker Cooperative Research Centre for Hydrometallurgy/CSIRO Minerals conducted laboratory batch tests using Bulong plant solutions and Acorga DS5443A or Acorga CLX50 as synergist. The results showed that at an A/O ratio of 1.0, the pH₅₀(Ca-Ni) value increased 1.29 pH units with 20% Acorga CLX50 addition. This would largely improve the separation of nickel from calcium if synergist Acorga CLX50 is used. The nickel extraction and stripping kinetics were very fast and there was no noticeable difference in kinetics between the two organic solutions with and without Acorga CLX50 addition. The use of intermediate precipitation, solids/liquid separation and re-leach in the three WA nickel plants make these processes complicated and costly in capital and operation. The research carried out by the SX group at the AJ Parker Cooperative Research Centre for Hydrometallurgy/CSIRO Minerals has led to the development of DSX processes to recover nickel and cobalt from leach solutions using synergistic solvent extraction. By using a new synergistic organic system in semi-continuous tests with a pilot plant leach solution from a BHP-Billiton project (after iron precipitation), the metal values (Ni and Co), together with zinc and copper, were separated from the major impurities (Mn, Mg, and Ca, together with Cl) in the first SX circuit. The co-extracted manganese, magnesium, and calcium were easily scrubbed out. After stripping, the metal values (Ni and Co), together with zinc and copper, were concentrated, resulting in a much smaller second SX circuit and equipment in the down stream processes. The extraction and stripping kinetics of the metals with the new synergistic organic solution were very fast. Within 0.5 minutes, the extraction and stripping almost reached steady state.

PAPER 14.6 — 10:55

FLEXIBILITY TRENDS IN COPPER SOLVENT EXTRACTION.

H.C. HEIN, Cognis Corporation, Santiago, Chile

In its early stage of copper solvent extraction development, SX plants were designed in a series configuration and gradually the copper industry reduced SX staging for keeping capital investments reasonably low. Mixer settlers were built bigger and the number of SX trains were diminished, whenever possible, for producing copper cathodes through solvent extraction followed by electrowinning. At a later date of its development, series parallel configuration was applied in some copper SX plants, increasing copper production at limited layout space and/or economics improved particularly under circumstances of low copper tenor in pregnant leach solutions. A gap between series and series parallel configuration had been observed for years, whereby conventional SX plants did not have sufficient flexibility for maintaining designed or expected production level, whenever copper concentrations in pregnant leach solutions diminished, as parallel or series parallel flow schemes virtually require to double SX feed flows for achieving optimum results. A combined SX configuration breaks the gap and its application potentials are extensively explained.

PAPER 14.7 — 11:20

HEAT BALANCES IN COPPER SX/EW OPERATIONS.

D.J. BURKHARDT, Fluor Daniel, Vancouver, British Columbia, Canada

Newer copper SX/EW processes often incorporate hot water heating for the cell feed electrolyte to obtain the necessary plating temperatures of 40 °C to 50 °C. Heating is most necessary in oxide heap leaching, however, it may also be required in bioleaching of secondary sulphides in colder climates or higher altitudes where most of the heat gain in the heap is lost to the environment. Given that the solution flows in the leach, organic circuit and electrolyte circuit are circular in nature, and the fact that the hot lean electrolyte is often exchanged with cooler rich electrolyte, it can be difficult to access the heating requirement for the cell feed. There are energy losses in piping, tankage, raffinate, and energy gains through the PLS and electrowinning process itself; some of these are significant and others are not. This paper discusses the overall heat balance, the relative significance of the various energy gains and losses, and describes a methodology to develop a heat balance to assist the engineer in sizing the heating equipment.

SESSION 15: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

SOLUTION PURIFICATION II: PRECIPITATION 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: L. TWIDWELL, Metallurgical and Materials Engineering, Montana Tech, Butte, MT, USA

J. DUTRIZAC, CANMET, Ottawa, ON, Canada

PAPER 15.1 — 8:30

REMOVAL OF THALLIUM FROM WASTEWATER.

L.G. TWIDWELL and C. WILLIAMS-BEAM, Metallurgical and Materials Engineering, University of Montana, Butte, Montana, U.S.A.

Thallium is more toxic to humans than mercury, cadmium, lead, copper or zinc. Its chemical behaviour resembles the alkali metals (K, Rb, Cs). It occurs almost exclusively in natural waters as a monovalent cation. The solubilities of thallos compounds are relatively high so that thallium is readily transported through aqueous routes into the environment. The major sources of thallium are the base metal sulphides and precious metal bearing sulphides. Therefore, it is often present as a contaminant constituent in waters emanating from heavy metal sulphide-bearing deposits. Viable technologies for reducing thallium concentrations to less than two micrograms per litre (USEPA maximum concentration level) do not presently exist. An innovative technology has been developed at Montana Tech that does achieve lowering the thallium concentration to below the maximum concentration level. The technology is based on reductive precipitation of thallium sulphide. Effective precipitation requires a controlled solution potential/pH combination that can be achieved by utilizing a particulate iron slurry or a packed column environment. Experimental results will be presented and discussed.

PAPER 15.2 — 8:55

ADAPTATION OF DILUTE MODE LIME DUAL ALKALI SCRUBBING AT STILLWATER MINING COMPANY'S PGM SMELTER.

R.R. LUNT, D.K. MODROW, FOCIS Associates Inc., Newton, Massachusetts, U.S.A., and G.K. ROSET, Stillwater Mining Company, Columbus, Montana, U.S.A.

The Stillwater Mining Company (SMC) has operated platinum-group metals (PGM) smelter in Columbus, Montana since 1990 to process concentrates produced at its nearby mines. In 1998, SMC embarked on a two-phase project to triple smelter capacity through essentially a complete replacement of the existing facility. Dilute mode lime dual alkali (LDA) technology was selected for meeting the stringent control requirements established for both sulphur dioxide and sulphur trioxide emissions. This same technology had been used in the existing plant and had demonstrated the capability for meeting similar, difficult challenges of handling very high peak levels of sulphur dioxide and sulphur trioxide as well as wide and rapid fluctuations in gas flow and concentrations. Unlike the dilute mode LDA system in the existing facility, though, a streamlined dilute mode LDA concept was envisioned for the new facility. The approach would greatly simplify the design and at the same time significantly reduce both capital investment and operating costs, plus achieve both objectives without sacrificing environmental performance. A joint effort of SMC, the technology supplier and the engineering/design firm has resulted in the successful implementation of this new adaptation of dilute mode LDA technology. The first phase of the expansion was completed in November 1999, and the second phase in November 2001. Over this period, several operational adjustments have been undertaken to optimize process performance such that it is now meeting or achieving all performance expectations 99.5% sulphur dioxide removal and greater than 90% sulphur trioxide removal. Production of a high-purity gypsum by-product is now being sold as an agricultural soil amendment and has been qualified for use in cement manufacture.

PAPER 15.3 — 9:20

GYPSUM FOULING IN NEUTRALIZATION REACTORS AND AQUEOUS STREAMS.

J.F. ADAMS and V.G. PAPANGELAKIS, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada

Gypsum fouling is a common problem in the hydrometallurgical industry. It is a particular problem in free sulphuric acid neutralization, or iron removal operations where sulphates are removed from aqueous solutions by the addition of calcium-containing bases. Previous work revealed a strong correlation between the degree of gypsum supersaturation in the reactor and the rate of scale growth indicating that scale formation and growth are primarily controlled by chemical phenomena. However, the chemical behaviour of gypsum is variable and unpredictable with solution chemistry and temperature. Many of the "rules of thumb" that are used to predict its behaviour (and avoid fouling) are in fact based on gypsum solubility in water, rather than on real mixed metal sulphate systems. However, despite this unconventional solubility behaviour, the authors have been able to accurately model it in Ni, Mg, and Zn containing solutions over a wide range of temperature (25°C to 90°C) and solution concentration (0 m to 6 m) using the OLI simulation software. Furthermore, by studying fouling rates in a simulated continuous neutralization reactor, the relationship between process conditions and fouling rates were explained for the first time. This has led to an understanding of how techniques for minimizing gypsum fouling work.

PAPER 15.4 — 9:45

THE BEHAVIOUR OF LANTHANIDE GROUP ELEMENTS DURING JAROSITE PRECIPITATION.

J.E. DUTRIZAC, CANMET, Ottawa, Ontario, Canada

The behaviour of the lanthanide group elements La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, during the precipitation of sodium and potassium jarosites at 98°C from sulphate media was systematically investigated. Solutions of the lower atomic weight lanthanide elements (La to Gb) are characterized by the limited solubility of alkali-lanthanide sulphates, such as $\text{Na}_2\text{Gd}_4(\text{SO}_4) \cdot x\text{H}_2\text{O}$, which commonly contaminates the jarosite precipitates. Hence, single phase jarosite-type compounds were precipitated only from solutions containing <0.2 to 0.3 g/L of the La to Gd lanthanides. The heavier atomic weight lanthanide elements (Tb to Lu) have significantly higher solubilities such that solutions containing up to 10 g/L of the individual lanthanide could be investigated without the precipitation of alkali-lanthanide sulphate species. Even at the highest lanthanide concentrations, however, none of the jarosite precipitates incorporated more than 0.3 wt% of any of the lanthanide elements. Comparable levels of lanthanide incorporation were noted in both Na-jarosite and K-jarosite. Although the mass of the jarosite precipitate increased with increasing ferric sulphate concentration with increasing pH, the extent of lanthanide incorporation was not significantly affected. Clearly, the trivalent lanthanide elements do not substitute extensively for trivalent iron in the jarosite structure, and end-member lanthanide analogues of jarosite-type compounds could not be synthesized. This behaviour likely reflects the significantly lower hydrolyzability of trivalent lanthanide ions relative to ferric ions.

COFFEE BREAK — 10:10 – 10:30

PAPER 15.5 — 10:30

RECOVERY OF CERIUUM BY OXIDATION/HYDROLYSIS WITH KMnO_4 — Na_2CO_3 .

C.A. MORAIS, J.S. BENEDETTO, A.C.Q. LADEIRA, Centro de Desenvolvimento da Tecnologia Nuclear-CDTN/CNEN, Belo Horizonte, Brazil, and

V.S.T. CIMINELLI, Universidade Federal de Minas Gerais-UFGM, Belo Horizonte, Brazil

Cerium has important applications in catalysts, green phosphors and magneto alloys. The separation of this element from RE mixtures is generally based on the oxidation of Ce(III) to Ce(IV). In acid solution, only stronger oxidants, such as persulphate and bismuthate, are capable of oxidizing Ce(III) to Ce(IV). In basic medium, otherwise, the trivalent cerium is readily oxidized to the tetravalent state. The present work describes the development of a process to obtain high-grade CeO_2 . The process involves cerium oxidation and hydrolysis by addition of a mixture of KMnO_4 - Na_2CO_3 solution. The results indicated that the major parameters affecting cerium recovery are the KMnO_4 excess and the liquor acidity. In this case, cerium was precipitated as a mixture with manganese. Further purification was carried out by the dissolution of $\text{Ce}(\text{OH})_4 \cdot x\text{H}_2\text{O}$ in HCl, followed by cerium precipitation as oxalate. The final product, assaying 99.5% CeO_2 , was obtained with a recovery nearly 100%.

PAPER 15.6 — 10:55

COMPARTMENTAL MODELLING OF WELL-MIXED AND INHOMOGENEOUSLY MIXED, BATCH GIBBSITE PRECIPITATORS.

T. LI, I. LIVK, D. ILIEVSKI and G. LANE, CSIRO Minerals, Bentley, Western Australia, Australia

The behaviours of well-mixed and inhomogeneously mixed particulate phase batch gibbsite precipitators were studied in this work. The precipitation experiments were conducted at the same “chemistry”, i.e., the same temperature, initial liquor composition, seed type and charge, and mean shear rate. The inhomogeneously mixed vessel had a larger tank height to diameter ratio and a smaller impeller diameter to tank diameter ratio than the well-mixed vessel. Comparisons of the experimental precipitation responses showed that both precipitator configurations have the same desupersaturation profiles but have significantly different crystal size distribution (CSD) evolution (Li and Ilievski, 2002). The potential of compartmental modelling for describing the behaviours of well-mixed and inhomogeneously mixed gibbsite precipitators was investigated. Different compartmental configurations, comprising various combinations of zones of uniform energy dissipation and solids concentration, based on computational fluid dynamics (CFD) characterization, were used to simulate both precipitators.

PAPER 15.7 — 11:20

GIBBSITE CRYSTAL GROWTH FROM CAUSTIC ALUMINATE SOLUTIONS IN LAMINAR, TURBULENT AND CASCADING FLOWS, LABORATORY PRECIPITATORS.

T. LI, D. BEDELL, I. LIVK and D. ILIEVSKI, CSIRO Minerals, Bentley, Western Australia

Molecular crystal growth during gibbsite precipitation from caustic aluminate solution was studied in this work. Three different types of laboratory precipitators were used, namely, Taylor-Couette precipitator (TCP), stirred tank precipitator (STP), and bottle roller precipitator (BRP). The laboratory precipitators were operated under completely different hydrodynamic conditions. The TCP and STP were operated under laminar and turbulent flow regimes, respectively, while the BRP was operated in a complex flow regime, where fluid flows was generated by the end-over-end rotation of the bottles. The precipitation experiments were conducted at the same temperature, initial liquor composition, and seed type. Molecular crystal growth rate was extracted from the precipitation data using a differential parameter estimation technique. Gibbsite crystal growth estimates from the current work were tested against crystal growth theories and showed consistent results with previous gibbsite crystal growth studies, published in the literature.

SESSION 16: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

TECHNOLOGY APPLICATION: ARSENIC

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: Junior Ballroom C

Chairmen: N. WELHAM, A. J. Parker Centre for Hydrometallurgy, Murdoch University, Murdoch, WA, Australia
B. HARRIS, Montreal, Quebec, Canada

PAPER 16.1 — 8:30

THE REMOVAL OF ARSENIC FROM PROCESS SOLUTIONS: THEORY AND INDUSTRIAL PRACTICE.

B. HARRIS, Montréal, Québec, Canada

Much has been written over the past twenty years on the removal and stabilization of arsenic from metallurgical process solutions. This paper reviews again the latest developments in this field, and concludes as before that the high-iron arsenical ferrihydrites, together with the high-temperature arsenic minerals, scorodite, and Type II, remain as the best and most viable vehicles for industrial control and disposal. Data are also presented on a survey of industrial practice, which shows that arsenical ferrihydrite is by far the most widely-practiced and accepted method used worldwide. Finally, the disaster in Bangladesh is briefly discussed with reference to lessons that the metallurgical might learn from it.

PAPER 16.2 — 8:55

BIOLOGICAL WATER TREATMENT FOR DISSOLVED METALS AND OTHER INORGANICS.

B. WAHLQUIST, T. PICKETT and D.J. ADAMS, Applied Biosciences Corporation, Salt Lake City, Utah, U.S.A.

Biological water treatment of selenium, arsenic, cyanide, and nitrate has been successfully implemented at full-scale by Applied Biosciences Corporation at three plants in the United States. Many other metals have been removed from various water streams at bench and pilot scale. The company's proprietary technologies use site-optimized microbial cultures and nutrient blends in a fixed-bed bioreactor system to remove target parameters to below detection. Treatment costs are as low as US\$0.12 per 1000 gallons treated. Applied Biosciences has successfully tested waters from mining, oil refining, power generation, and other industries.

PAPER 16.3 — 9:20

SORPTION OF ARSENATE FROM AQUEOUS SOLUTION WITH MANGANIC FERRIC OXYHYDROXIDE.

G.R. CHAUDHURY, R.P. DAS, Regional Research Laboratory, Bhubaneswar, Orissa, India,

D.M. MUIR, CSIRO, Waterford, Western Australia, and

P. SINGH, Division of Science and Engineering, Murdoch University, Murdoch, Western Australia

Arsenic-contaminated drinking water drawn from groundwater is a major health problem in West Bengal, adjoining Bangladesh, and other parts of the world such as Taiwan, Thailand, Chile, Argentina, China, and Mexico. Due to its extreme toxicity, there is a need to remove the arsenic from contaminated drinking water. There have been various methods developed to treat hydrometallurgical process solutions and effluents and some of these can be applied to arsenic-contaminated drinking water. Adsorption techniques are probably most appropriate and these can be comparatively low cost and effective. Various adsorbents such as alumina, ferrihydrite, and manganese ores have been used. There is a great deal of literature concerning the removal of arsenic from aqueous solution using ferrihydrite as an adsorbent, but there has apparently been little investigation of modifying the structure of ferrihydrite to improve its adsorptive efficiency. In the present study the incorporation of manganese to replace iron in ferrihydrite was attempted by several techniques and the prepared materials used in arsenic adsorption experiments. The compounds were X-ray amorphous, but TGA/DTA and FTIR analysis showed some structural characteristics. Sorption studies reported in this paper indicate the excellent arsenic removal properties of the manganese/iron compounds. Adsorption rates are reported and the results fitted to adsorption and mass transfer models.

PAPER 16.4 — 9:45

PREPARATION, CHARACTERIZATION, AND SOLUBILITIES OF ADSORBED, CO-PRECIPIATED AND CRYSTALLINE IRON (III)-ARSENATE SOLIDS.

Y. JIA, G.P. DEMOPOULOS, Department of Metals and Materials, McGill University, Montréal, Québec, Canada,

N. CHEN and J. CUTLER, University of Saskatchewan, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada

Arsenic constitutes a major contaminant for the hydrometallurgical industry. Its removal and immobilization from process effluents typically involve lime neutralization and co-precipitation with ferric iron [Fe(III)/As(V)>3]. Alternatively, precipitation of scorodite [FeAsO₄·2H₂O(cr)] may be applied to arsenic fixation. The mechanism of arsenic fixation in the former process has been suggested to be surface adsorption. Unequivocal characterization of these products is difficult because of their amorphous nature, hence, a variety of methods need to be applied including particularly powerful method XAFS. In this study authors have investigated the preparation of arsenate-adsorbed ferrihydrite to compare its structure (by XAFS) to that of Fe(III)-As(V) co-precipitates and scorodite (both amorphous and crystalline). Furthermore, the solubilities of these Fe(III)-As(V) solids are measured as a function of pH. Their structures are elucidated and correlated to their solubilities and thereby the application of these findings to the practice of arsenic removal and disposal is assessed.

COFFEE BREAK — 10:10 – 10:30

PAPER 16.5 — 10:30

ADSORPTIVE REMOVAL OF ARSENIC AND FLUORIDE BY USING ORANGE JUICE RESIDUE.

K. INOUE, K.N. GHIMIRE, R. PRASAD DHAKAL, Department of Applied Chemistry, Saga University, Saga, Japan, and

K. MAKINO, Yamasoh Micron Inc., Kogawa, Wakayama, Japan

Industrial application of low-cost adsorbents is of immense importance for the treatment of environmental pollutants generated not only from various industrial sources but also from some geological sources such as ground and hot spring water. Two kinds of chemically modified orange juice residues were applied for the adsorptive removal of arsenic: phosphorylated orange juice residue (POJR) and saponificated orange juice residue (SOJR). The effect of metal ions immobilized on POJR gel were examined for the removal of fluoride and compared with the activated alumina, a commercially available adsorbent for fluoride. Adsorption tests of arsenic on iron(III)-immobilized-SOJR with active carboxylic functional groups showed that it has nearly the same adsorption power on the POJR with active phosphoric group. The exchangeable cations of the SOJR were as high as 2.64 mol/kg. Adsorptive removal of fluoride on cerium(IV) and lanthanum(III)-immobilized POJR have shown better removal behaviour as compared to activated alumina. Their loading capacities on such gels were almost the same, 1.7 and 1.8 mol/kg, respectively. Based on the fundamental adsorption tests, field test for the removal of arsenic was carried out for waste mine water from Harobetsu mine in Hokkaido, Japan, using SOJR. It was found that SOJR successfully achieved complete removal over wide pH range while some amount of arsenic was remained in the effluent treated by means of co-precipitation method together with iron(III) hydroxide by adding large amount of calcium or magnesium. In addition, some amount of co-precipitated arsenic was leaked from the precipitated iron sludge while no leakage of arsenic was observed from the SOJR adsorbent.

PAPER 16.6 — 10:55

REMOVAL OF ARSENIC BY RED MUD FROM CONTAMINATED WASTE WATER.

L.C. WHITE, E. PALING, P. SINGH and W. ZHANG, Division of Science and Engineering, Murdoch University, Murdoch, Western Australia, Australia

The use of red mud, which is a waste product of Bayer process for bauxite refining has been investigated for its effectiveness and efficiency of arsenic removal from aqueous solutions under various conditions. It is found that the red mud samples obtained from ALCOA, Western Australia, can remove As(III) effectively in the pH range 7.6 to 9 and As(V) in the pH range 5.5 to 6. The pre-washing of the mud with seawater considerably improves its arsenic adsorption capabilities. Maximum arsenic removal efficiency was achieved at the $[As_{initial} (mg/L)]:[mud (g/L)] = 1:8$. With sufficient dosage of red mud, the residual arsenic in solution is decreased below the regulated acceptable arsenic limit (0.1 mg/L) from aqueous industrial wastes. The arsenic adsorption follows first-order rate kinetics. The experimental data fits the Langmuir isotherm model. The results suggest that red mud is potentially a useful adsorbent for removal of arsenic from contaminated water or industrial waste solutions.

SESSION 17: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

LEACHING I: ALTERNATIVES AND THIOSULFATE 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 C

Chairmen: P. THOMPSON, Dawson Metallurgical Laboratories, Inc., Salt Lake City, UT, USA

M. NICOL, A. J. Parker Centre for Hydrometallurgy, Murdoch University, Murdoch, WA, Australia

PAPER 17.1 — 8:30

THE LEACHING AND RECOVERY OF GOLD WITH ALKALINE SULPHIDE HYDROMETALLURGY.

C.G. ANDERSON, CAMP, Montana Tech, Butte, Montana, U.S.A.

Globally, various alternatives for leaching and recovery of gold without the use of cyanide are again being considered. One economically viable and environmentally sound candidate is the alkaline sulphide hydrometallurgical system. This paper will outline the fundamentals of this technology. As well, pertinent applications and the associated, comparative economics will be illustrated.

PAPER 17.2 — 8:55

CHLORIDE METALLURGY AS AN ALTERNATIVE TO CYANIDE FOR THE EXTRACTION OF GOLD — GOING FULL CIRCLE?

C.J. FERRON, C.A. FLEMING, Lakefield Research Limited, Lakefield, Ontario, Canada,

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

P.T. O'KANE, O'Kane Consultants Inc., Vancouver, British Columbia, Canada

At the present time, cyanide is the most widely used reagent to extract gold from its ores and concentrates. However, its use in mining has become the focus of intense attack by various groups throughout the world; as a consequence, a renewed effort has been launched to find suitable alternative lixiviants to recover gold. Chlorination was the most popular process to extract gold, before it was rendered obsolete with the advent of the cyanidation process at the turn of the last century, not least because it required the use of chlorine to oxidize/complex the gold. Furthermore, the process was not suitable to treat sulphide ores, unless they were first roasted. The PLATSOL[®] process, originally designed to recover the platinum-group metals (PGMs) from their ores and concentrates, also provides an alternative to cyanide leaching for gold ores. The process generates oxidizing conditions in the autoclave that are capable of forming — the Au^{III} ion, and gold chlorocomplexes result from the addition of small quantities (5 to 10 g/L) of sodium chloride to the autoclave. The principles of the PLATSOL[®] process will be briefly described, and several applications of the process to gold concentrates will be presented. Various options available to recover gold from PLATSOL[®] leach solution will also be discussed.

PAPER 17.3 — 9:20

USING THIOCYANATE AS LIXIVANT FOR GOLD RECOVERY IN ACIDIC ENVIRONMENT.

R.-Y. WAN, Highlands Ranch, Colorado, U.S.A.,

J.A. BRIERLEY, Brierley Consultancy LLC, Highlands Ranch, Colorado, U.S.A.,

S. ACAR and K.M. LEVIER, Newmont Mining Corporation, Englewood, Colorado, U.S.A.

Thiocyanate was evaluated for gold recovery from low-grade refractory gold ores following bio-oxidation for an acidic heap leaching approach. One of the important features in using thiocyanate is that the leaching can be performed in acidic media, thus avoiding problems related to neutralization and material handling as leaching with alkaline cyanide. Also, the acidic leaching enables the use of ferric ion or bioleach solution as oxidants. In this study, Newmont-Nevada low-grade refractory sulphidic ore was bio-oxidized in columns at a particle size of minus 10.2 cm. Thiocyanate leach on the bio-oxidized ore sample was performed on both ground samples in pulps and coarse material in columns using ferric ion as an oxidant. The variables of thiocyanate and ferric ion concentrations were compared for effect on leaching. Thiocyanate leach results are encouraging and indicate potential for development of a practical process. Gold extractions by thiocyanate are comparable to cyanide leach. Thiocyanate consumption was higher than cyanide, but was in an acceptable level.

PAPER 17.4 — 9:45

A COMPARISON OF CYANIDE AND THIOSULPHATE LEACHING FOR THE RECOVERY OF GOLD FROM A COPPER-CONTAINING ORE.

X. DAI, C.K. CHU, M.I. JEFFREY and P.L. BREUER, Department of Chemical Engineering, Monash University, Clayton, Victoria, Australia

One of the biggest challenges for the gold industry in the 21st century is the presence of copper in gold-containing orebodies. This is because copper consumes large quantities of cyanide. In addition, copper cyanide species are more stable than free cyanide, and hence are problematic in events of tailings spillage. This paper compares cyanide and thiosulphate leaching for the recovery of gold from a copper-containing ore. For cyanide leaching, the extraction of gold using copper cyanide complexes instead of free cyanide was tested in the presence and absence of added ammonia. For thiosulphate leaching, the effect of the minerals present in the ore on the solution potential and thiosulphate consumption are illustrated.

COFFEE BREAK — 10:10 – 10:30

PAPER 17.5 — 10:30

A REVIEW OF THE CHEMISTRY, ELECTROCHEMISTRY, AND KINETICS OF THE GOLD THIOSULPHATE LEACHING PROCESS.

P.L. BREUER and M.I. JEFFREY, Department of Chemical Engineering, Monash University, Clayton, Victoria, Australia

Environmental and public concerns and the banned use of cyanide for the recovery of gold in some parts of the world have heightened the search for an alternative lixiviant to cyanide. Thiosulphate appears to be the most promising alternative to cyanide due to thiosulphate being non-toxic, relatively cheap compared to cyanide, and generally gold recoveries are similar to those of cyanide. The most widely researched thiosulphate process is one where copper ions and ammonia are added to the solution. This paper reviews the leaching of gold in thiosulphate solutions and the contributions of the research at Monash University to the understanding of the gold oxidation reaction in thiosulphate solutions, the solution chemistry when copper ions, ammonia, and oxygen are present, the influence of the changing solution chemistry on the gold leach kinetics, and the application of thiosulphate in the leaching of gold from ores. It is clearly shown that the gold oxidation rate is hindered in thiosulphate solutions. In the presence of copper ions the gold oxidation rate though is significantly enhanced and this is why copper(II) is more effective than other oxidants in the thiosulphate leach system. The copper-ammonia-thiosulphate leach solution chemistry is shown to be very complex, especially in the presence of oxygen as the rate of thiosulphate oxidation increases and the majority of the copper ions are not maintained in the copper(II) oxidation state. The thiosulphate oxidation rate must also be maintained low as an intermediate thiosulphate oxidation product hinders gold leaching. In optimizing the recovery of gold from ores with copper-ammonia-thiosulphate leach solutions it is important to evaluate and minimize any negative effect an ore may have on the leach solution chemistry, and hence, gold leaching.

PAPER 17.6 — 10:55

THERMODYNAMICS AND KINETICS OF THE DISSOLUTION OF GOLD IN AMMONIACAL THIOSULPHATE SOLUTIONS.

G. SENANAYAKE, X. ZHANG and M. NICOL, A J Parker Centre for Hydrometallurgy, Murdoch University, Murdoch, Western Australia

Despite the renewed interest in gold leaching with ammoniacal copper thiosulphate solutions, previous kinetic studies have suffered mainly due to a lack of detailed understanding of the nature of metal ion speciation and leaching chemistry. Although published Eh-pH diagrams indicate that the gold(I) diammine complex is more stable than the dithiosulfato complex at pH values greater than 9, recent results obtained in this laboratory have suggested that the reported stability of the diammine complex is overestimated by several orders of magnitude. Eh-pH diagrams based on the recently determined stability constants, showing the stability regions of relevant species are presented. The kinetics of dissolution of colloidal gold in ammoniacal copper thiosulphate show a reaction order of 0.4 to 0.6 with respect to copper(II), ammonia, and thiosulphate. The data can be rationalized on the basis of a shrinking sphere kinetic model. It is shown that the comparison of results from the present study with reported data for the dissolution of gold metal can be used to suggest possible chemical reactions on the gold surface and an alternative reaction mechanism.

PAPER 17.7 — 11:20

CAN A THIOSULPHATE LEACHING PROCESS BE DEVELOPED WHICH DOES NOT REQUIRE COPPER AND AMMONIA?

I. CHANDRA and M.I. JEFFREY, Department of Chemical Engineering, Monash University, Clayton, Victoria, Australia

It is generally recognized that the gold thiosulphate leaching system requires the presence of copper and ammonia in order for acceptable leaching kinetics to be observed. However, the presence of copper and ammonia complicate the chemistry of the system as thiosulphate is rapidly oxidized by oxygen under these conditions. In addition, the environmental impact of ammonia would need to be considered before the adoption of this system. This paper describes fundamental studies into the thiosulphate oxygen system. The two reagents for this system are thiosulphate and oxygen, and leaching is carried out at $\text{pH} < 7$. It will be shown using electrochemical techniques that both the reduction of oxygen and the oxidation of gold to gold thiosulphate are hindered. Thus, if leaching is to work under these conditions, then both half reactions need to be improved. The use of additives such as thiourea and lead have been shown to dramatically improve the oxidation of gold and the reduction of oxygen respectively. The leaching of gold in the presence of such additives is discussed.

SESSION 18: INTERNATIONAL SYMPOSIUM ON HYDROMETALLURGY IN HONOUR OF PROFESSOR IAN RITCHIE

LEACHING II: FUNDAMENTALS 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 D

Chairmen: C. YOUNG, Metallurgical and Materials Engineering, Montana Tech, Butte, MT, USA

P. TAYLOR, Metallurgical & Mining Engineering, Colorado School of Mines Golden, CO, USA

PAPER 18.1 — 8:30

SELECTIVE BACTERIAL LEACHING OF COBALT FROM A CHALCOPYRITE COPPER CONCENTRATE.

R.P. HACKL, Department of Metals and Materials Engineering, The University of British Columbia, Vancouver, British Columbia, Canada, and

R.J. VOS, British Columbia Research Inc., Vancouver, British Columbia, Canada

Bacterial leaching of the Doe Run Company's cobalt-containing copper concentrate at low pH (pH 1.0 to 1.2) and high redox potential (>750 mV vs SHE) enabled the cobalt to be preferentially dissolved over copper due to the rapid passivation of the chalcopyrite component. Selective leaching of the cobalt was achieved with a mesophilic culture comprising mainly *Leptospirillum ferrooxidans*. This finding led to the conception of a novel hydrometallurgical process for passivating chalcopyrite and recovering cobalt. The bacterial leaching process was tested extensively at the bench and pilot plant scales during 1997-1998. A pilot plant containing four leaching stages processed 30 to 40 kg/day of chalcopyrite concentrate continuously for 87 days. The cobalt extraction ranged from 75% to 86% during 6- and 8-day retention times respectively, whereas, the copper extraction was limited to about 9%. An engineering study confirmed the economic viability of the process based on the prevailing metal prices at the time.

PAPER 18.2 — 8:55

TRANSITION METAL AND PLATINUM GROUP METAL SEPARATIONS WITH SILICA POLYAMINE COMPOSITES AND NITROGEN SPECIES CATALYZED LEACHING.

C.G. ANDERSON, CAMP, Montana Tech, Butte, Montana, U.S.A.

Nitrogen species catalyzed pressure leaching has successfully been applied to cobaltite, chalcopyrite, and platinum-group metal (PGM) concentrates. New hydrometallurgical protocols for the separation of cobalt from copper and arsenic in cobaltite concentrate leach solutions using a tandem fixed bed arrangement of two metal selective silica polyamine composites (CuWRAM and WP-2) at pH = 3 have been developed. Good rejection of arsenic and efficient separation and concentration of copper and cobalt were realized. A different resin, WP-1, was used to separate nickel from palladium at pH = 0. Here, the separation of the transition metal from the precious metal was quantitative and excellent recovery of palladium was realized using acid-ammonium chloride strips at 50°C. The characteristics and synthesis of these novel technologies will be reviewed and the advantages of will be discussed.

PAPER 18.3 — 9:20

THE MECHANISM OF THE DISSOLUTION OF CHALCOPYRITE — AN ELECTROCHEMICAL STUDY.

I.M. LAZARO-BAEZ, Instituto de Metalurgia, San Luis Potosi, Mexico, and

M.J. NICOL, A.J. Parker Centre for Hydrometallurgy, Murdoch, Western Australia, Australia

A detailed study has been undertaken into the electrochemistry of the leaching of chalcopyrite in acidic solutions containing ferric ions. Mixed potential measurements have shown that the maximum potential achievable on a chalcopyrite disk in a ferric sulphate medium lies within the so-called passive or pre-wave region in the anodic behaviour of chalcopyrite. The formation of a copper sulphide-like species on the chalcopyrite surface in this potential region has generally been suggested as being responsible for the reduced reactivity of the mineral to leaching. A careful rotating ring-disk electrode (RRDE) study has enabled data to be obtained for the stoichiometry of the initial dissolution reaction to be obtained. Thus, in addition to the detection of soluble iron and copper as products in this potential region, a soluble sulphur species has also been detected. A comparison of the experimental with the expected collection efficiencies of the products on the ring has revealed that this soluble sulphur species is likely to be thiosulphate. The ring-disk electrochemical results also suggest that the formation of a copper sulphide phase on the surface is unlikely. The characteristic transient anodic behaviour of chalcopyrite in this potential region has been interpreted in terms of a rate limiting solid-state diffusion process. Thus, extrapolated rates based on reported measured solid-state diffusion coefficients for the mineral at elevated temperatures have been shown to be consistent with the potentiostatic current-time transients. The results of this investigation have been combined with a parallel study of the non-oxidative behaviour of chalcopyrite in order to derive a model for the dissolution process which is consistent with other published studies of the electrochemistry and dissolution of the mineral.

PAPER 18.4 —9:45

THE SONOCHEMICAL LEACHING OF CHALCOPYRITE.

N. ABED, Research and Development, Umicore Canada Inc., Fort Saskatchewan, Alberta, Canada, and
D.B. DREISINGER, Metals and Materials Engineering, The University of British Columbia, Vancouver, British Columbia, Canada

A fundamental study of the sonochemical leaching of chalcopyrite in ferric ion media has been performed to understand and quantify the effects of sonication and other parameters on leaching reactions. The study covers sulphate and chloride media. The main leaching reaction was found to be dependent on temperature and initial particle size, but less dependent on ferric ion concentration. Leaching was performed under a variety of sonication, thermodynamic, and physical parameters. The use of ultrasound activation showed a clear improvement in leaching kinetics and amount of copper extracted. Sonication has a catalytic-like effect on the leaching reaction. Compared to experiments without sonication, reaction rates were 2 to 3 times faster at the same temperature and can be faster by a factor of 20 for the same initial particle size. Regardless of initial particle size, the amount of copper extracted is comparable under sonication, and can be twice that under chemical leaching, implying the avoidance of fine particle grinding. Sonochemical leaching was found to be only temperature-dependent, where the best copper extraction was at 75°C. Parabolic leaching kinetics were established and confirmed from the estimation of different thermodynamic parameters and dependence on other physical parameters.

COFFEE BREAK — 10:10 – 10:30

PAPER 18.5 —10:30

LEACHING OF CHALCOPYRITE IN AMMONIACAL SOLUTIONS SPARGED WITH SO₂/O₂ GAS MIXTURE.

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

Ammonia-ammonium sulphate solutions were sparged in a glass reactor with a SO₂/O₂ gas mixture (2% SO₂ and 98% O₂) to leach copper from pure chalcopyrite and chalcopyrite concentrate. The SO₂/O₂ mixture produces higher and faster extractions than O₂ by itself. The effect of temperature, particle size and free ammonia concentration was investigated. The fastest and highest recoveries were obtained at 80°C from a chalcopyrite concentrate with a d₈₀ equal to 13 mm, with about 83 gpl free ammonia, an average pH equal to 8.75 and a stirring speed of 500 rpm. The extraction process was controlled by diffusion through a product layer, according to the shrinking core model, with an activation energy of 41 kJ/mole.

PAPER 18.6 —10:55

RAMAN INVESTIGATION OF SULPHIDE LEACHING.

G.K. PARKER, R. WOODS and G.A. HOPE, Griffith University, Brisbane, Queensland, Australia

In situ Raman spectroscopic investigations of copper sulphides in leach solutions have been undertaken. Coupling potentiodynamic techniques to Raman spectroscopy produces a powerful tool for studying mineral surface response to changing conditions, while ESEM and high-vacuum techniques provide complementary information on surface structure and composition ex situ. Ore samples and synthetic films oxidatively leached in acid developed regions of a covellite-like phase with bonded sulphur pairs. The potential of the appearance of S-S bonds indicates non-stoichiometric metastable phases exhibit this pairing. Leaching of chalcopyrite led to non-homogeneous product distribution. Raman spectroscopy was able to identify the products formed on the mineral surface in situ while leaching was occurring. Mapping and imaging demonstrated a surface distribution of the products which can be related to composition and structure changes of the mineral surface. The implications of these findings with respect to the feasibility of hydrometallurgical processing of copper sulphides are discussed.