

SPOTLIGHT

on solvent extraction

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The Ammtec-Henkel Solvent Extraction Symposium was held at the Burswood Convention Centre in Perth on 24th and 25th July, 1990. The Symposium attracted 76 delegates and speakers from Australian mining, engineering-design, and chemical companies, and 6 people from overseas.

Altogether 18 papers were presented over the two days. The first day was concerned mainly with the solvent-extraction (SX), theory and chemistry of leaching (as part of the process), SX of specific metals, and pilot-plant testing. The second day was devoted to specific operations in Australia, although one speaker dealt with SX in China. Five speakers from organizations supplying mixers and diluents each gave a short discourse on their specialities prior to the final discussion session.

The Symposium was opened officially by Dr Murdoch Mackenzie, Manager, Mining Chemicals Division of Henkel Australia. He spoke on the increasing importance of SX to the Australian mining industry, especially where valuable metals are present in solution at low concentrations.

SX Chemistry and Leaching

Dr Gary Kordosky, Technical Director, Minerals Industries Division, Henkel Corporation of USA, gave the first paper, entitled 'An Overview of Solvent Extraction Chemistry'.

The paper dealt with the objectives of SX, described the extractable species, listed successful reagent requirements, and then discussed in some detail the chemistry of the four classes of SX reagents: chelation extractants, ion-pair extractants, solvation or neutral extractants, and organic-acid extractants. Then the paper discussed the solution properties that can be controlled to effect metal separations: pH, oxidation potential, and concentration and temperature of common anions, giving examples of each. The paper closed with several examples of the use of solution properties to effect certain metal separations.

Dr Gary Kordosky gave a second paper, this one entitled 'Leaching for Solvent Extraction'. This paper classified leachants into five categories and gave examples of each: inorganic acids, mixtures of inorganic acids, basic reagents, oxidizing agents, and bacteria. It then discussed the ways in which leachants and ores are contacted.

The paper closed with a discussion on the problems of SX associated with leach liquors. These are clarity, dissolved organic matter, dissolved silica, temperature, emf, and incorrect chemistry.

Australian Practice

The next paper, 'Introduction to SX Technology and Practice in Australia', was given by Dr Murdoch

Mackenzie.

He said that significant SX technology had originated from Australian engineers and scientists. In 1989, SX plants produced about 7 per cent of Australia's copper, compared with the 10.5 per cent supplied by SX plants worldwide. The Australian uranium industry also uses SX after a sulphuric acid leach.

SX was formerly used for the recovery of gallium from Bayer liquor at Pinjarra (until September 1990), and has been used for about ten years for the separation of tantalum and niobium at Greenbushes. If the cost of acid could be decreased in Australia, it might be possible to produce more copper and nickel by SX. Queensland Nickel is the only plant in the world using ammoniacal SX technology to recover nickel from laterites.

Crud is a problem in most uranium SX plants, and can be separated by either agitation and acid treatment or by centrifuge treatment and filtration. A precoat filter may be more effective and reliable than a centrifuge if two types of crud (i.e. soluble and polymeric silica) are present.

Dr Jim Limerick of the Department of Resources Development in Western Australia, in a paper entitled 'Potential for SX in Western Australia', described the potential of the Resolute Resources laterite nickel deposit at Bulong, near Kalgoorlie. It had been assumed that sulphuric acid could be produced economically from sulphur dioxide (now emitted to the atmosphere near Kalgoorlie), and then used to leach laterite. Nickel sulphide deposits with potential for SX were mentioned, although alternative methods of recovery are now used.

Uranium deposits at Kintyre and Yeelirrie could also use a sulphuric acid leach. A carbonate leach in a pilot-plant stage is used on ore from the latter deposit, which may obviate the use of SX. Major potential lies in the recovery of rare earths from monazite. Such deposits occur in mineral sands and at Mount Weld. Future SX plants will depend upon a decision as to how much down-stream processing is to be undertaken in Western Australia. 'Do not stop at the first saleable product. We should endeavour to add value to Australia's exports', Dr Limerick said.

SX and Electrowinning

Dr Gary Kordosky (co-author S. Olafson), gave the next paper: 'Modern Copper Solvent Extraction-Electrowinning (SX-EW)'. The presentation started with a historical perspective briefly detailing the first ten years in the development of SX-EW technology. It then broke the process into the three unit operations: leaching, SX, and electrowinning, discussing each in some detail while emphasizing their interdependence.

A description was then given of the various copper-leaching techniques (dump, heap, vat, thin-layer, agita-

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tion, and *in situ*), and of ore-pretreatment techniques and bacterial leaching.

The SX discussion centred on the two types of copper extractants available commercially: ketoximes and aldoximes. The strengths and weaknesses of each type of extractant were discussed, along with suggestions as to which type is best suited to certain applications.

Crud generation, which can be a significant operating problem in some circuits, was discussed. Data showing the relationship of crud generation to certain reagent modifiers, which must be used with aldoxime-based reagents, was presented along with data on the relationship of crud generation and reagent losses. The authors also suggested that blends of ketoxime and non-modified aldoxime reagents could be tailored to meet the needs of virtually any leach liquor without from any of the bad side effects that might accompany modifiers.

The discussion dealt with the quality of covered cathodes typical tankhouse design and electrowinning operating parameters, types of lead alloys for anodes, anode design, and the use of starter sheets for cathode plating versus the deposition of full-size cathodes on stainless-steel blanks.

The presentation then moved to a discussion of general design parameters for modern mixer-settlers, emphasizing that most of the recently completed plants have square or nearly-square settlers built on grade, with multiple mixing chambers sunk slightly below grade.

Copper SX-EW production in the USA and the world was mentioned, and the industry view of copper hydrometallurgy in the early 1960s was contrasted with its view today.

SX of Nickel, Copper, and Cobalt
'Nickel Solvent Extraction' was the title of the next

paper, also given by Dr Kordosky. The discussion started with a listing of the objectives of SX: purification, concentration, and alteration of the metal matrix. The speaker then discussed four different nickel SX circuits, each of which illustrated one or more of the SX objectives listed above. The first nickel EW plant, at SEC in Texas, selectively extracted copper from a refinery bleed stream using pH control (pH 1,5 to 2,0) prior to the use of ammonia to adjust the solution to between about 9,0 and 9,5 and then extracting nickel.

The Nippon metal-recovery plant used SX to selectively extract zinc and then cobalt prior to adjustment of the pH for the nickel extraction. The nickel-extraction circuit was similar to that of SEC.

The nickel SX plant of Queensland Nickel is unique in that the SX had to fit in with the chemistry of the then existing Queensland Nickel Refinery, i.e. nickel had to be extracted from a dilute ammonia solution and stripped into a much more concentrated ammonia solution.

The SX plant at Falconbridge extracts copper and cobalt from a concentrated nickel-containing acidic chloride solution using a tertiary amine. This serves as an example of the use of SX to remove impurities from the desired metal species prior to final recovery of the metal.

Dr Kordosky's presentation on 'The Copper-Ammonia SX System' first drew some parallels with the copper-dilute sulphuric acid system. It then discussed the availability of two extractants, the ketoxime-based LIX 84 and the betadiketone-based LIX 54, and compared their properties. LIX 84 is best suited to those leach liquors having a high concentration of free ammonia from which a very high copper recovery is needed. LIX 54 is best suited to leach liquors having a lower concentration of free ammonia and/or from which a high copper recovery



Speakers at the Ammttec-Henkel Extraction Symposium (left to right):

Back row. Assoc. Prof. D. Muir, Dr I. Corrans, Dr G. Kordosky

Middle row. Z. Meka and Greenelsh

Front row. M. Price, C. George, G. Miller, Dr P. Middlebrook, A. May, Dr M. Mackenzie, and Prof. T. Zhu

is not a necessity. It was pointed out that LIX 54 can be readily stripped with only about 10 to 20 g/l of free sulphuric acid.

Testing

The presentation on 'Laboratory and Pilot Plant SX Testing', also by Dr Kordosky, stressed the importance of working with actual, fresh leach liquors. Whereas synthetic leach liquors, made up to metal concentrations equal to those of actual leach liquor, can give meaningful metallurgical data, such as the extent of metal extraction, the selectivity of extraction of one metal over another, and metal-extraction kinetics, these liquors do not usually give representative physical data on entrainment, phase separation, and crud generation. On-site testing with actual plant liquors is the best way of showing how a plant can be expected to run physically.

The paper then discussed the Henkel ISOCALC program, which is designed to generate copper-extraction and stripping isotherms in the acid sulphate system, to use these isotherms for the generation of McCabe-Thiele diagrams under a variety of conditions, and then to calculate a circuit mass balance. Finally, the Henkel METCALC computer program, which generates capital costs and simple design parameters, was discussed briefly.

Precious Metals, Rare Earths, and Uranium

Turning to precious metals, Associate Professor David Muir of Murdoch University outlined current developments in his paper, 'Solvent Extraction of Precious Metals'. He described how Inco (UK), Matthey Rustenburg (UK), and Lonrho (RSA) employ various solvents to extract and separate gold, platinum, and palladium from concentrated chloride leach liquors after processing high-grade feed material such as anode slimes.

Muir then discussed solvent extractants for $\text{Au}(\text{CN})_2^-$, which are being researched as an alternative to carbon for clarified liquors. However, more research will have to be undertaken before a solvent-in-pulp approach can compete with CIP.

Professor Jack Harrowfield of the University of Western Australia gave the next paper: 'Solvent Extraction of the Rare Earths'.

In the separation of rare-earth (lanthanide) species, the main problems are their disparate concentrations and their chemical similarity. The main rare-earth minerals are monazite, bastnaesite, and xenotime, all of which consist of complex mixtures. Yttrium is the principal component of xenotime, and lanthanum and cerium predominate in both monazite and bastnaesite. The most valuable components, such as europium and terbium, are usually present in very low concentrations, while radioactive elements such as thorium can be present in significant quantities in monazite.

SX is still an efficient method for the separation and purification of these difficult materials, even though selectivity across the whole group only reaches about 600, even for the most effective reagents. Current research is directed towards advanced chemistry in the development of higher selectivity.

With the benefit of plant experience, Dr Murdoch Mackenzie and Steve Olafson gave the next paper: 'Uranium SX and pH Control'.

The most widely used selective extractants for uranium are the tertiary amines, C8-C10 symmetrical amines. A target for the loading of uranium is usually about 1,2 g/l of U_3O_8 per 1 per cent amine, and concentrations usually range from 2 to 10 per cent amine. Crud is always a problem in uranium plants. Scrubbing is usually necessary (except in some plants preceded by ion exchange) to remove anionic species, entrained acid, and extracted bisulphate ions. Gaseous or concentrated ammonia is used for stripping, which takes place at a pH of 3,4 to 3,8 in strip No. 1, and a pH of 4,8 to 5,0 in strip No. 5.

Crud consists of an emulsion of organic drops in an aqueous phase stabilized by a fine layer of solid particles (i.e. clay or silica) at the interface, which is usually extracted by a centrifuge and settler. The name *crud* apparently came from a uranium producer and is an acronym for *Chalk River unidentified deposit*.

Laboratory Testing

On the subject of laboratory testing, Dr Ian Corrans of Ammtec gave a paper entitled, 'Hydrometallurgical Testing'.

He discussed important aspects of leaching and SX in the testing of flowsheet (or process) development. The stages described include leaching or dissolution, solution purification, and recovery from solution.

Ammtec recently carried out work on the leaching of nickel from a laterite using sulphuric acid. Cobalt was oxidized to the cobaltic state with peroxide to minimize its extraction. Lime was added to precipitate the metal hydroxides that were leached with ammonium carbonate. Nickel ammine ($\text{Ni}(\text{NH}_3)_6^{2+}$) was extracted with 50 per cent LIX 84 in Shellsol 2046. The loaded organic matter was then stripped with sulphuric acid so that nickel could be recovered by electrowinning. SX results from a continuous mini-plant were also given.

Operating Plants

Alan May of Gwalia Minerals, in a paper entitled 'Greenbushes SX Operations', said that the production of tantalum oxide at the Greenbushes SX plant amounts to about 50 000 lb per annum, although the plant could produce 100 000 lb annually.

The process uses a hydrofluoric acid leach, removes residues by filtration, and uses MIBK in counter flow to solvent-extract the leach liquor, followed by washing with 10 N sulphuric acid to remove impurities. Then sulphuric acid is added to strip niobium from the loaded organic matter, and a back-wash with MIBK strips tantalum from the aqueous stream. Tantalum is then stripped with water. Both tantalum and niobium are precipitated as hydroxides by gaseous nitric acid and finally produced as calcined Ta_2O_5 and Nb_2O_5 .

The reagent costs amount to 50,2 per cent of the total costs, labour to 24 per cent, and stores to 11,3 per cent, while assays, maintenance, fuel, and utilities comprise the remaining costs.

MIBK soluble losses are a problem, but crud and emulsions do not occur. Safe working procedures have been developed for the handling of hot liquors containing hydrofluoric acid.

In his paper 'Olympic Dam Operations SX', Chris George described the SX operations in their very inte-

grated plant. Copper production amounts to about 45 000 t/a and the copper SX plant produces about 4500 t/a, or 10 per cent of the total copper production.

Uranium is produced by separate leaching of the flotation concentrates and tailings with sulphuric acid, and amounts to approximately 1200 t/a. Conical mixer-settlers and fibreglass tanks are used in the SX plant. A high concentration of chloride ions in the leach liquor prevents the use of stainless-steel tanks. As few hills are available at Roxby Downs for gravity flow, an elevated settling tank is used. A scrubbing stage was included because earlier pilot-plant tests had indicated the necessity for the removal of impurities. Polyethylene glycol is used to limit the dissolved silica to a maximum of 1200 p.p.m.

In the copper circuit, potable water (70 p.p.m. of chloride) is used in the EW section to scrub chloride from the loaded solvent. A copper skin is added to the stainless-steel starting sheets in the tankhouse to prevent corrosion by chlorides.

Returning to nickel, Mal Price of Queensland Nickel gave his paper entitled 'Queensland Nickel ASX Operations'. The ASX process separates nickel from cobalt in an entirely ammoniacal system. This new process was commissioned in July 1989, and was based on pilot-plant work from 1985 to 1988. Before this development, cobalt had been removed by sulphiding pregnant leach liquor, which produced a mixed nickel-cobalt with a nickel-to-cobalt ratio of 2.5 to 1, and nickel oxide further downstream. The new plant oxidizes Co^{+2} to Co^{+3} with air and peroxide, enabling nickel to be selectively extracted by SX over cobalt. The nickel is then stripped with strong $(\text{NH}_4)_2\text{CO}_3$ solution. This allows the plant to produce a purer nickel oxide product and a purer cobalt sulphide product while retaining most of the earlier flowsheet.

Dr Peter Middlebrook of CRA gave his paper 'Pasmaico SX Operations', which described the dross leaching plant at Pasmaico Sulphide (Newcastle). The plant produces 5000 t/a of copper sulphate from copper-lead fine dross (45 per cent copper, 35 per cent lead) using an ammonia-ammonium carbonate leach followed by SX with LIX 54 and a strip with sulphuric acid-cupric sulphate to crystallize out copper sulphate as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The second Pasmaico plant described was the BHAS copper-lead matte plant at Port Pirie, which produces 3500 t/a of copper cathodes from a matte byproduct containing 35 per cent copper, 38 per cent lead, and sulphur. A chloride-sulphate oxygenated leaching process was developed at BHAS, with the ICI/Acorga P5100 reagent used to transfer copper to a sulphuric acid solution for electrowinning. The two plants have been operating successfully since 1983 and 1984 respectively.

Professor Tun Zhu from Beijing gave the next paper: 'Solvent Extraction in China'. He noted that SX has been used to separate and recover uranium and other radioactive elements, rare earths, cobalt-nickel, zirconium-hafnium, niobium-tantalum, germanium, gallium, indium, titanium, lithium, and vanadium on a commercial scale in China. The extraction of tungsten and molybdenum has also been researched extensively, and has been used in commercial production.

All the extractants used in the industry are produced in China. Professor Zhu then described some current research showing that the separation of cobalt from nickel

at low concentrations of chloride ions (less than 200 g/l) can be achieved by the use of quaternary ammonium chloride, which has a higher distribution coefficient than that of tertiary amine.

China is one of the world's leaders in the SX of rare earths, and new processes using 2-ethylhexyl phosphonic acid and 2-ethylhexyl ester, with simultaneous separation of three elements, have been developed in recent years.

Bob Greenelsh of MIM Holdings Ltd gave the next address, followed by a video: 'The Isa EW System'. This system is based on a simple approach using permanent stainless-steel cathode plates.

Its success depends on careful production of the hanging blade, edge strip, and waxing of the bottom. The advantages of this system include its flexibility and simplified work schedules. Furthermore, the cathodes are processed more frequently, and they hang straighter and closer together. Savings in electrical energy are attainable with closer spacing of electrodes. Also, the productivity is higher and the manpower requirements lower.

Graeme Miller of CMPS gave a brief talk on the commissioning of the SX-EW plant located at Mount Isa. The plant treats leach liquors from a low-grade copper-ore dump leach.

The Jameson column-flotation cell (a quarter of the height of a conventional column) is used by MIM at the SX plant, where it removes entrained organic matter from the electrolyte.

The mixers were constructed in round rather than square tanks, which are made of fibreglass. The deposition of copper in the EW section was achieved within 12 months of the go-ahead from MIM. The EW plant now produces cathode-grade copper of 99.99 per cent purity.

'Mixing and Solvent Extraction' was the title of a paper by Graham Fraser of Lightnin Mixers. An important consideration in all SX plants is the design of mixers since this affects both the mass-transfer rates between the phases and the nature of the physical dispersion. Fraser described specific mixer applications, and stressed the importance of shear rates, which vary throughout the mixing tank. Scale-up from small-scale tests must generally allow for the impeller-zone shear rates (producing dispersion) to increase on scale-up, while the average tank shear rates (maintaining the dispersion) will decrease.

Zimi Meka of Minproc Engineers spoke about the Gunpowder SX-EW plant, owned by Adelaide Brighton Cement Ltd. This project involves an *in situ* underground leach that should produce a liquor containing about 4 g of copper per litre. The mixers are in open 316L stainless-steel square tanks, similar to those at the Arizona plants. An Alfa Laval centrifuge is used for the treatment of crud. The SX plant uses two stages for extraction and two stages for stripping. The EW cells are painted with epoxy, and have 34 anodes and 33 cathodes in 52 cells. This Isa Process EW system should soon produce 7500 t/a of LME-grade copper.

Peter Shelley of Shell Chemicals gave a talk based on his Tokyo conference paper: 'Performance of Two New Nil Aromatic Diluents in The Recovery of Copper, Uranium and Rare Earths'.

The results cited were based on laboratory tests using pregnant plant liquors, which indicated that low-aromatic Shellsol 2046 and nil-aromatic Shellsol 2037 are equi-

valent diluents for copper. For uranium, Shellsol 2046 was the best, whilst Shellsol 2037 was probably the best for rare earths. Crud problems in uranium plants were more likely to occur with high-aromatic diluents.

David Goodman of Krebs, USA, gave a lively talk about problems encountered in SX plants. Difficulties can arise from a variety of causes. Typically in uranium plants, insufficient clarification after leaching and the presence of very fine or dissolved silica give rise to crud. In copper plants, problems are caused by dissolved species such as chloride. Generally, incorrect mixer-tip speeds lead to poor operation, and a decrease in tip speed produces a lower shear rate in the impeller zone. This results in the formation of less crud and overall better performance.

Bill Elliot of Exxon Chemicals reported that suppliers of diluents would prefer kerosene to be known as a specialized product. Exxon can also supply low-aromatic diluents and modifiers for SX plants.

Closure

Dr Ian Corrans, after a short discussion session, closed the Symposium by posing a question: 'Technology often presents a frightening dilemma: does one specialize in a narrow field, or endeavour to know a little about everything?' He hoped that the Symposium had taught the delegates at least a little about SX and that it would be of assistance in their business endeavours.

Copies of the notes can be purchased from Dr Ian Corrans, Ammtec, tel: (09)3442416, fax: (09)3454688.

Minerals and the environment

A conference on 'Minerals, Metals, and the Environment' is being organized by The Institution of Mining and Metallurgy in association with other national and international bodies. The Conference, which will be held in Manchester from 4th to 6th February, 1992, will bring together experts in the field—operators, researchers, legislators, and providers of technology and equipment—to exchange information and, most important, to produce definitive data.

In addition to invited papers from experts worldwide, special discussion periods will allow those who attend the Conference the opportunity to seek solutions to their environmental questions. The Organizing Committee, which consists of representatives from several commodity, technical, and geographical areas, has maintained as its primary term of reference the need for accurate, up-to-date, and comprehensive data to be made available. It is the aim of the Committee that no person attending the Conference should leave without either finding the information that he or she seeks or without knowing where it can be found.

The Conference will cover all aspects of the industry—from initial exploration, through mining, quarrying, processing, refining, to marketing, waste disposal, and secondary treatment—activities will be examined with respect to safety, occupational hygiene, and environmental factors.

The subjects to be covered include the following:

- Safety during operations
- Use of contractors
- Mining methods for deep mining, coal mining, open-pits, quarries, solution mining, and offshore mining
- Processing plants, including concentrators, smelters, and refineries
- Hazards at work, including dust, radiation, diesel fumes, temperature, humidity, noise vibration, chemicals, and toxic materials
- Environmental impacts, including drainage, airborne/water/soil emissions, subsidence, waste management, land use/availability, transport, and rehabilitation
- Recycling
- Decommissioning
- Restoration/rehabilitation.

In addition to the formal presentations, panels are being organized to debate and discuss items of particular importance, including

- Meeting the legislation—theory and practice
- Are mineral products socially acceptable?

Further information is available from
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