Base Metals Market Research

INTRODUCTION

Australia is a major producer of base metals (principally copper, lead, zinc, nickel and cobalt) with total export earnings from nickel, copper and zinc of A$14.3 billion in 2007-2008 (ABARE estimate).

Five base metals producers – BHP Billiton, Minara Resources, Rio Tinto, Straits Resources and Nyrstar – are amongst the Industry Participants in the Parker Centre. Two engineering firms and three industry suppliers involved in the base metals processing sector are also Industry Participants: these companies are Hatch Associates, WorleyParsons, Ciba Speciality Chemicals, Nalco Australia and Outotec.

Australia is endowed with a substantial share of the world's economic demonstrated mineral resources (EDR) of base metals. Australia has the world's largest EDR of nickel (38%), lead (30%) and zinc (24%), and the second largest EDR of cobalt (21%) and copper (11%) [Geoscience Australia 2007].

Minerals present in Australian deposits include sulfides, although there are also significant quantities of silicates, carbonates and hydroxy-oxides in weathered surface deposits. In particular, Australia's nickel laterite deposits represent a major resource.

As high grade reserves are becoming depleted, new technologies for processing progressively more marginal ores are urgently needed. The challenges faced by the base metals industry includes lower grade deposits, increased ore complexity, less accessible deposits and the growing importance of the abundant low-grade resources of chalcopyrite (copper iron sulfide) ores (which are quite refractory or resistant to leaching).

Parker Centre research students with the "Electrostatic Solvent Extraction" project: PhD student Mr Marc Steffens (right) and Honours students Mr Simon Assmann (left) and Mr Alex Logan (middle).

BASE METALS MARKET LEADER:

DR DAVID ROBINSON

(FROM SEPTEMBER 2007) (CSIRO MINERALS)

Increasingly, hydrometallurgical processes are being developed to deal with current challenges. Hydrometallurgical processes lend themselves to:

- processing ores in large or small deposits and in remote areas
- processing ores that contain minerals that make pyrometallurgical process routes unacceptable, for instance arsenopyrite
- companies developing "mine to metal" operations in remote sites
- improving processing performance and reducing the environmental impact of wastes and tailings.

The Centre's base metals research is undertaken by a group of 22 full-time equivalent researchers from all four of the Research Participants in the Centre. Chemists, metallurgists, microbiologists, mineralogists, chemical engineers and modellers contribute to the research effort. These researchers have access to a broad range of laboratory and pilot scale equipment and sophisticated instrumentation.

The research projects undertaken in the Centre's Base Metals Market include CRC-funded projects, two collaborative industry-sponsored projects and one-to-one projects with minerals processing companies.

Collaborative links exist with researchers around the world, including researchers at the Hahn-Meitner Institut (Germany), the Korea Institute of Geoscience and Mineral Resources (KIGAM) in South Korea, the University of Cape Town (South Africa), Bangor University (UK), Mokpo National University (South Korea), the University of British Columbia (Canada), the University of Toronto (Canada) and the Universidade Federal de Minas Gerais in Brazil.

BASE METALS RESEARCH CAPABILITIES

- quantitative mineralogical analysis for ores and leach residues
- ore comminution and beneficiation as related to processing
- pressure leaching (nickel laterite minerals)
- pressure oxidation (sulfide minerals)
- reductive leaching (oxide minerals)
- electrochemical investigations of leaching processes (sulfide minerals)
- studies of solution properties and solution chemical species (metal sulfate solutions)
- surface chemistry (chalcopyrite)
- process chemistry
- microbiology and bioleaching (sulfide minerals)
- metal ion separation & concentration using solvent extraction and ion exchange
- gaseous reduction (metal sulfate solutions)
- crystallisation (nickel powder)
- electrowinning of base metals
- computer modelling of solvent extraction equipment, reactors and processes.

BASE METALS RESEARCH AREAS

The Centre's research for the base metals market focuses on hydrometallurgical processes for treating nickel laterites and base metal sulfide ores and concentrates. The CRC-funded projects span all areas of hydrometallurgy, namely leaching, separation and metal recovery (by reduction).

Further details of the specific research in each of the CRC-funded projects are provided in the following list. The Centre also undertakes industry-funded projects but confidentiality considerations preclude discussion of the majority of these projects.

LEACHING

- Electrochemical investigations of the leaching of sulfide minerals is contributing to the Parker Centre's Process Fundamentals activity theme, and includes:
  - studying electrochemical behaviour during leaching of selected sulfide minerals
  - developing methods and techniques for low temperature leaching and then applying them to high temperature, high pressure leaching.
- Research on reductive leaching of mixed oxides relevant to ilmenite (iron titanium oxide) and laterites is contributing to the Parker Centre's Process Fundamentals activity theme, and is focusing on:
  - determining the effects of ligands (sulfate, chloride, sulfite and novel ligands)
  - developing thermodynamic and kinetic (rate) data and models for mineral dissolution.
- Pressure hydrometallurgy research in the area of leaching is contributing to the Parker Centre's Process Fundamentals activity theme, and includes:
  - understanding the leach reaction chemistry occurring in autoclaves
  - reducing nickel/cobalt losses in pressure acid leaching of laterite ores
  - the impact of process water quality on pressure oxidation of copper and nickel sulfides
  - developing a new capability in *in situ* leaching that uses pressurised vessels.
- The research on processes for low-grade nickel laterites and sulfide ores includes:
  - understanding the effect of ore mineralogy on leach chemistry
  - examining atmospheric acid leach technologies for processing low-grade laterite ores
  - investigating ways of modifying the physical properties of ores to increase pulp density and enhance nickel production from autoclaves
  - examining the benefits of co-processing laterites and sulfides in heaps and autoclaves.
- Biooxidation in process water research is contributing to the Parker Centre's Process Fundamentals activity theme, and focuses on:
  - quantifying and modelling the effects of high salinity, high total dissolved (ionic) solids process water on biooxidation
  - establishing the limitations to adaptation to water quality by the microbes catalysing sulfide mineral oxidation.
- Research in the area of biohydrometallurgy is contributing to two Parker Centre activity themes (Breakthrough Technologies and Process Fundamentals), and includes:
  - bioleaching of low-grade sulfide ores (nickel, copper)
  - mineralogical characterisation of ores and residues (tailings)
  - prospecting for new native bioleaching bacteria: enriching, isolating, identifying and testing leaching ability.
- Bio-inspired hydrometallurgy research is contributing to the Parker Centre's Breakthrough Technologies activity theme, and involves:
  - a scoping study aimed at mimicing or taking inspiration from selected biological processes (eg biological mineral synthesis) to develop a new hydrometallurgical approach to metal extraction.

Base Metals Market Research

SEPARATION

- Solvent extraction chemistry research is contributing to the Parker Centre's Process Fundamentals activity theme, and involves:
  - studying metal-extractant reactions and interactions in synergistic solvent extraction (SSX)
  - developing methods to monitor extractant performance in SSX systems.
- Solvent extraction (SX) technology research is contributing to the Parker Centre's Process Fundamentals activity theme, and includes:
  - developing and testing novel SX and synergistic SX systems for metal(s) separation to meet industry needs
  - improving SX equipment such as mixer-settlers and pulsed columns.
- Research related to electrostatic solvent extraction is contributing to the Parker Centre's Process Fundamentals activity theme, and focuses on:
  - an alternative to conventional SX that uses electrostatic charge for agitation
  - investigating the fundamentals of electrostatic agitation to disperse small droplets of the aqueous phase into the organic phase
  - examining mass transfer in electrostatically agitated SX
  - designing, constructing and assessing an electrostatic SX contactor.

METAL RECOVERY (BY REDUCTION OF METAL IONS)

- Gaseous reduction processes research is contributing to the Parker Centre's Process Fundamentals activity theme, and is focusing on:
  - pressure reduction of copper ions in copper sulfate solutions
  - evaluating the technical feasibility of using natural gas instead of hydrogen as the reductant in pressure reduction of copper.

INDUSTRY BENEFITS

The potential benefits to the minerals industry of the Centre's base metals research include:

BENEFITS ARISING FROM BREAKTHROUGH TECHNOLOGIES RESEARCH

- an improved understanding of heap leach chemistry and microbiology, and insights on a chalcopyrite heap leach "operating window", which would complement the development of a heap leach model that could assist the copper industry to extend their heap leach capability
- a new technology (inspired by a biological process) that has broad applications in hydrometallurgy.

Ms Sin Wei Lim, a participant in the Parker Centre's Summer 2007-2008 Student-Industry Research Program, taking a sample from an autoclave during one of her experiments.

BENEFITS ARISING FROM PROCESS FUNDAMENTALS RESEARCH

- new operating strategies and conditions to optimise pressure leaching of sulfide minerals, developed through a better understanding of how selected sulfide minerals dissolve under typical pressure leach conditions
- a mineralogical tool that uses electrochemical characterisation to identify minerals and can also provide quantitative information
- novel ambient/moderate temperature selective leaching and separation methods for metal/metal oxide extraction from ilmenite and nickel laterites
- the potential to improve biooxidation process performance in industry through assessment of the response of chemolithotrophic microorganisms (used for bioleaching) to the presence in the biooxidation process water of specific ions of interest to clients
- the ability to provide reliable cost-benefit analyses of the effects of process water of varying quality, and different treatment options, on biooxidation in operating industrial bioleaching plants
- demonstrated operational strategies for improving the rate and recovery in the heap bioleaching of copper from secondary sulfide ores such as chalcocite
- native Australian bioleaching bacteria with enhanced copper leaching ability over previously known strains available for evaluation and test work
- demonstrated technique for tracking different types of microbes in bioreactors to help manage the right mix of microbes in the microbial community needed for effective bioleaching.

The "Biooxidation Process Water" project's apparatus for measuring the Eh (the solution potential) in multiple flasks of chemolithotrophic cell cultures. The common reference electrode is on the far right. The flasks from right to left show the progression of a batch culture as it converts approximately 100% iron(II) to around 100% iron(III) over 40 hours. Chemolithotrophic cells (used for bioleaching) catalyse biooxidation of sulfide minerals by oxidising iron(II) to iron(III) and creating a microcosm on the target sulfide mineral surface.

- greater nickel recovery during high pressure acid leaching of nickel laterites through understanding how nickel losses occur during leaching
- identification of process conditions for copper and nickel sulfide pressure oxidation informed by fundamental understanding of the impacts of process water quality and additives on autoclave reaction chemistry and thus metal extraction
- process options for low-grade, mineralogically-complex nickel laterites and sulfides that currently cannot be processed economically
- new analytical methods to understand the chemistry of novel synergistic solvent extraction (SSX) systems developed by the Centre, to demonstrate that a SSX system is chemically robust and to monitor extractant performance in a processing plant
- novel solvent extraction and synergistic solvent extraction technologies for improved metal separation and recovery that have been tested for selected target applications in industry
- recommended modifications to the design of solvent extraction equipment (mixer-settlers and pulsed columns) which will increase the separation and purification efficiency of the equipment
- an alternative solvent extraction contactor that utilises electrostatic dispersion, which leads to high mass transfer of the desired metal ions – without moving parts – and has other advantages over the mixer-settler contactors currently used in industry
- a preliminary technical and economic evaluation of a pressure reduction process using natural gas as the reductant for copper production as an alternative to electrowinning: if feasible, this process could have major economic benefits for the Australian copper (and possibly also nickel) industry
- increased skills and knowledge for industry personnel via technology transfer, including AMIRA project review meetings with sponsors, workshops and training courses.

Base Metals Market Research

Base Metals Market Highlights 2007-2008

TECHNOLOGY TRANSFER & IMPACT

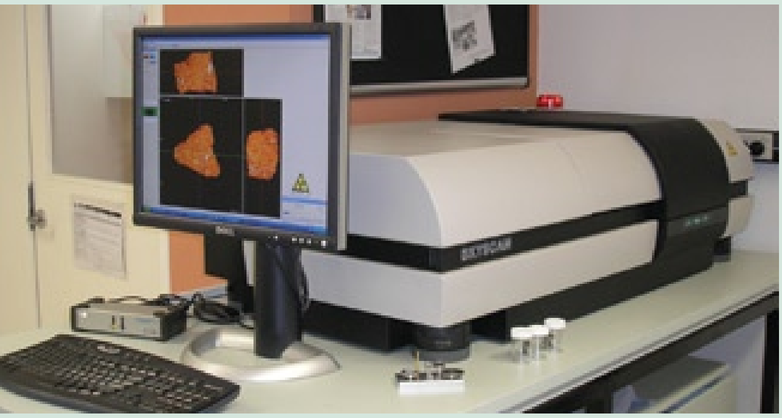
- There is increased recognition in the minerals industry of the usefulness of synergistic solvent extraction (SSX) as the technology of choice for a number of metal systems including nickel and cobalt extraction and purification. New commercial applications of the Parker Centre's novel SSX systems for recovering nickel and cobalt from laterite leach solutions and for the recovery of cobalt and zinc from the Baja Mining operation are nearing fruition and further development and testing of SSX technology has attracted attention from major mining companies around the world.
- There has been increased use by industry of the quantitative methods (quantitative X-ray diffraction, QEMSCAN and X-ray microtomography) developed and refined by the Centre to quantify the mineralogy of ores, concentrates and leach residues. This is coupled with the growing recognition of the value, as shown by the Centre, in using quantitative mineralogical analysis of feed materials to predict the leaching performance of the feed materials and identify optimal leaching conditions.
- Two extensive reviews of existing and developing technologies for the atmospheric (acid) leaching (AL) of nickel laterite ores were published. The first paper reviewed sulfuric acid technologies, and included comparison of AL processes with high pressure acid leaching (HPAL) technology and the emerging hybrid HPAL/AL and heap leaching technologies. The second reviewed chloride and organic acid (bio-acid) leaching. The reviews highlighted several areas worthy of further study on behalf of the nickel industry and have resulted in increased industry engagement.

ADVANCING THE SCIENCE

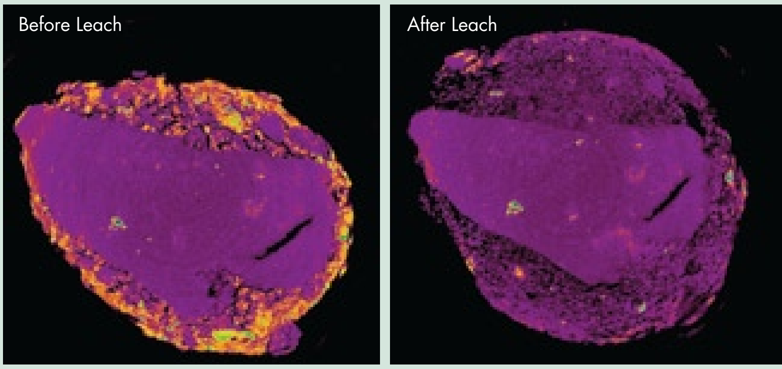
- A significant breakthrough was made in the understanding of the roles of the varying reagents in synergistic solvent extraction (SSX) systems, and in particular the roles and relative performance of varying ratios of the two stereoisomer forms of the oxime extractant and hence further optimise reagent usage in SSX system as intended to be implemented in industry.
- A microbial culture was successfully demonstrated to operate in hypersaline conditions (at a sodium chloride concentration of 28,000 parts per million) and catalyse biooxidation of a nickel sulfide, with laboratory-scale proof of nickel recovery and culture habituation obtained. Such a salt-tolerant culture would be potentially valuable for use in industrial bioleaching operations with high-salinity process water.
- Gaining the next level of understanding needed to develop strategies to manage heat generation by large industrial sulfide ore bioleaching heaps to optimise metals extraction was assisted by the design, construction and commissioning of a new programmable column. The dynamically controllable instrumented column is being used to study the auto-heating characteristics of different sulfide ores and relate them to ore mineralogy, and to trial heat-control management strategies.
- Fundamental studies of simple salt solutions and oil-water mixtures (ubiquitous in nature) commenced as part of investigations into specific biological systems that show promise as sources of ideas to generate novel bio-inspired hydrometallurgical technology.

DEVELOPING RESEARCH CAPABILITY

- The Centre's solvent extraction (SX) pilot facilities, including the re-commissioned pulsed column, two SX pilot plants (using mixer-settlers) and semicontinuous test facilities, have been integrated into one piloting process bay at CSIRO Minerals to better serve the minerals industry in the area of solvent extraction for metal separation and recovery.
- New test scale facilities were established to enable the Centre to branch out into researching non-biological heap leaching of nickel laterites.



The X-ray microtomography (MicroCT) system being used by the Parker Centre across a wide range of research areas. The MicroCT takes three-dimensional (3D) images through samples: these images are used to build up 3D models to understand the structure of the systems being studied.



X-ray microtomography is one of the methods the Centre is utilising in research that focuses on understanding the relationship between the quantitative mineralogy of feed materials (ores and concentrates) and their leaching behaviour in hydrometallurgical processing. MicroCT analysis is a non-destructive analytical technique, which allows samples to be imaged before and after a process, eg leaching.

Electrochemical Investigations of the Leaching of Sulfide Minerals

OBJECTIVES

Sulfide minerals are a major resource for base and precious metals. Traditional pyrometallurgical processing of many of these ores is no longer environmentally acceptable nor economically viable with the growing importance of low-grade deposits and/or "dirty" concentrates.

Hydrometallurgical process alternatives are increasingly being considered but are often not viable if leaching is undertaken at normal temperatures. Advances in fine milling, pressure and bacterial leaching have extended the boundaries of hydrometallurgical processing of sulfide minerals, but further extension is needed.

The project aims to address this emerging extractive metallurgical problem by:

- conducting research into the electrochemical and leaching behaviour of sulfide minerals (nickel and copper sulfide minerals in particular) under oxidative and non-oxidative conditions, and under both ambient and elevated temperatures and pressures
- using the knowledge gained from the fundamental work to develop new processing options and to optimise existing pressure leach and pressure oxidation processes
- further application of the previously developed novel method for studying fine mineral particles as an investigative and potentially useful mineralogical tool.

OUTPUTS

- A paper on the electrochemistry of covellite (copper sulfide) in chloride solutions was published in the *Journal of Applied Electrochemistry*.
- Two papers were delivered at the Hydrometallurgy 2008 International Symposium in Phoenix (Arizona, USA), one of which presented more data on the catalytic EC′ mechanism for the cathodic reduction of copper(II) and iron(III) on a covellite surface.
- Significant progress was made in a fundamental electrochemical study of the dissolution of nickel sulfide minerals.
- The anodic behaviour of several zinc sulfide minerals was investigated using a previously developed technique for the study of the electrochemistry of fine mineral particles.
- An investigation into the neutral or slightly alkaline leaching of nickel sulfides under conditions that may be appropriate for heap leaching of nickel sulfide ores was completed.

Reductive Leaching of Metal Oxides

OBJECTIVES

Dissolution or precipitation of various iron oxides/salts (eg goethite, hematite and jarosite) and other base metal oxides play an important role in the leaching and separation of valuable metals/metal oxides from laterite ores and ilmenite (an iron titanium oxide mineral).

There is an increasing interest in developing ambient/moderate temperature hydrometallurgical processing routes to avoid currently practiced roasting and pressure leaching steps in treating laterites and ilmenite. These hydrometallurgical processes would involve the reductive leaching of the relevant metal oxides.

However, the development of new processing methods for the reductive leaching and separation of metal oxides will require improved fundamental understanding of the thermodynamics and kinetics (rates) of the dissolution of the metal oxides.

Therefore, the objectives of this project include:

- generating reliable thermodynamic and kinetic (rate) data and models for metal oxide dissolution
- investigating the effect of free acid and various anions on the leaching of synthetic oxides and ores
- determining metal ion speciation (chemical species) and their influence on leaching and separation using ion-exchange resins and solvent extraction.

OUTPUTS

- After characterisation of different types of laterite ores, oxide tailings and synthetic oxides (FeOOH, NiFeOOH, CoFeOOH, NiCoFeOOH and Fe_3O_4), comparisons were made between the rates of dissolution of metal ions per unit surface area in a range of lixiviants (dissolving agents) at different temperatures and acidities.
- The first order dependence of the leaching rates of the synthetic oxides on acid concentration could be modelled on the basis of surface reaction-controlled mechanisms.
- The atmospheric leaching of nickel and cobalt from some of the ores and tailings reasonably agreed with the dissolution behaviour of metals from the synthetic oxides, but the presence of manganese, aluminium or magnesium led to complexities in the case of ores and tailings, which depended on the mineralogy.
- In all cases, reducing agents such as sulfur dioxide or iron(II) were essential to improve the leaching of metals from high-valent oxide materials, as predicted from the potential-pH diagrams.

Pressure Hydrometallurgy

OBJECTIVES

Nickel production is a major industry in Western Australia (laterites and sulfides). One challenge for the industry is the losses of both nickel and cobalt that occur during pressure acid leaching of laterite ores. The full extent and mechanism(s) of these losses need to be understood to increase extraction efficiency.

Another challenge is that process water chemistry, particularly in WA, is seldom optional. Previous research has determined the effect of water quality on nickel extraction by pressure leaching of laterites, and how additives can be used to improve nickel recoveries. The effects of process water quality on the pressure oxidation of nickel and copper sulfides also requires investigation, as does the potential of improving metal extraction by employing additives.

This project aims to assist industry to improve process efficiency and metal extraction from oxide and sulfide ores through:

- gaining an understanding of nickel and cobalt losses during pressure acid leaching of laterites in terms of leach feed mineralogy and leach residue composition, morphology (shape) and mineralogy
- developing methods for the pressure oxidation of nickel sulfide ores and copper sulfide ores, and describing the effects of water quality and additives on metal extraction
- developing equipment to enable *in situ* (in place) leaching studies to be undertaken.

OUTPUTS

- Two papers that reviewed technologies utilised in the atmospheric leaching of nickel laterites were published in the journal *Hydrometallurgy*: one on sulfuric acid technologies and the other on chloride and bio-technologies.
- The experimental work examining the effect of chloride on the pressure oxidation of a chalcopyrite ($CuFeS_2$) concentrate under conditions defined by the Phelps Dodge Placer Dome process was completed. X-ray diffraction (XRD)/scanning electron microscopy (SEM) analyses are now required before this research can be written up for publication.
- A study on the deportment (location) of nickel in high pressure acid leaching (HPAL) residues was completed. The improved resolution of the Hyperprobe compared with the Microprobe (0.1 μm versus 0.5 μm) was unable to discriminate the elemental compositions of hematite (iron(III) oxide) and amorphous silica due to their small particle sizes and intimate mixing in the residues. Studies have commenced to synthesise residue phases (both individually and mixtures) from synthetic liquor, both with and without an amorphous silica source, under HPAL conditions. The materials produced will be characterised and their nickel content(s) determined.
- A Student-Industry Research Program project examined the *in situ* solubility of metals in nickel laterite heap leach liquor samples. This research concluded that the processing of the heap leach liquor should employ neutralisation using a suitable ore sample under HPAL conditions and that calcium precipitation in the pre heater could pose a problem.
- A suitable design for the construction of *in situ* (in place) leaching columns was identified. The use of materials such as titanium, polytetrafluoroethylene (PTFE) or Viton and a high pressure liquid pump would enable the column to withstand internal pressures of up to 1000 psig.

Processes for Low-Grade Nickel Ores

OBJECTIVES

The demand for nickel is rising steadily but the global reserves of nickel sulfide ores are declining. Surface deposits of nickel laterite ores are most likely to fill the shortfall with ~60% of the world's measured land-based nickel resources present in this oxidised form.

Currently, Australian nickel production is dominated by the processing of sulfide ore bodies, but the majority of Australia's nickel resources are low-grade, marginally-economic lateritic ores. Western Australia is particularly well endowed with nickel laterites, which are characterised by complex mineralogy and require selective mining, pre-treatment and hydrometallurgical processing technologies. Processing plants have been established at Murrin Murrin and Cawse near Kalgoorlie and a new plant is under construction at Ravensthorpe.

This project seeks to provide a better understanding of low-grade, complex nickel laterite and sulfide ores and examine options for physically or chemically processing the ores more efficiently and economically. The work aims to:

- refine methods of quantitatively identifying Australian ore mineralogy and examine options to improve ore quality (beneficiate) prior to processing
- identify ways to maximise nickel recovery through a fundamental understanding of the impact of mineralogy on the hydrometallurgical processing of laterite and sulfide ores. The applied studies focus on heap leaching, atmospheric leaching and processing of ores with sulfuric acid in autoclaves at high temperatures.

OUTPUTS

- QEMSCAN automated mineral analysis (a novel, rapid operating mode) and differential thermal analysis-thermogravimetry analysis (DTA-TGA) were developed as techniques to complement quantitative X-ray diffraction (QXRD) analysis for analysing laterite ores and leach residues. Both QEMSCAN and DTA-TGA were found to add value in combination with more traditional analyses.
- A systematic evaluation indicated that selective extraction is a promising tool that provides information about the relative reactivities of elements or minerals in laterite samples to various reagents, and can be used to complement quantitative mineralogical characterisation.
- Wide variations in the rheological properties of different ore slurries were observed. The effects of mineral blends and different size fractions of quartz particles, and of viscosity modifiers and chemical additives, are being examined. Some combinations have been found to reduce slurry viscosity significantly.
- Extensive literature reviews on sulfuric acid technologies and on chloride and organic acid (bio-acid) leaching were published. Heap leaching, the emerging hybrid high pressure acid leaching/atmospheric leaching (HiPAL/AL) technology and some unconventional processes were examined.

Biohydrometallurgy of Sulfides

OBJECTIVES

Heap bioleaching – the use of bacteria to extract metals from generally low-grade ore heaps – is now commercially used for gold ores and for leaching copper from copper oxides and secondary copper sulfide ores such as chalcocite.

Its application to other sulfides, particularly chalcopyrite (copper iron sulfide), pentlandite (iron nickel sulfide) or sphalerite (zinc sulfide), has been less successful. Industry interest in developing a viable heap bioleaching process for other sulfides is strong, as it is a low-cost process for recovering metals from low-grade and difficult-to-process ores and mine wastes, that minimises environmental impacts and enables operations to produce the final product on site.

The objective of this project is to broaden the application of heap bioleaching for whole ore processing through fundamental understanding of reaction chemistry and microbiology, leading to operational strategies to optimise processing, demonstration of the benefits of selected strategies and testing at heap scale with an industry partner.

OUTPUTS

- A key to the knowledge generated in this project has been the development and application of various methods:
  - Three molecular methods for monitoring microbial species in leach solutions and leached residues of low grade ores were evaluated; a combination was applied to the analysis of bioleaching columns.
  - An electrochemical method for continuous monitoring of ferrous and ferric ions in experimental solutions was developed and applied to studies on biooxidation in the presence of soluble solution contaminants.
  - Combinations of quantitative X-ray diffraction (QXRD), QEMSCAN and X-ray microtomography have proved particularly informative in elucidating the leach chemistry of different ores.
- The research this year has included a strong focus on heap bioleaching:
  - Native bacteria were isolated from a current copper sulfide heap in northern Western Australia. They were identified using molecular techniques and their physiological capabilities with respect to bioleaching are being characterised. The bacterial population in the copper heap operation was monitored.
  - A dynamically controllable instrumented column was designed and commissioned to study the auto-heating characteristics of different sulfide ores and relate them to ore mineralogy. Ultimately the goal is to manage heat generation in bioleaching heaps to optimise metals extraction.
- The biohydrometallurgy capabilities of the Parker Centre were publicised and promoted:
  - Project team members were actively involved in the Centre's education activities with supervision and co-supervision of three PhD, one Honours and three 4th year students, and also four vacation students participating in the Centre's Student-Industry Research Program.
  - Research results were disseminated through conference presentations (five) and publication in peer-reviewed journals (five papers published or accepted) and technical magazines (three articles).

Biooxidation Process Water

OBJECTIVES

Chemolithotrophic cells (used for bioleaching) catalyse the biooxidation process by oxidising iron(II) to iron(III) and creating a microcosm on the target sulfide mineral surface. Optimising the biooxidation process requires maximising the cell growth rate and the rate at which those cells oxidise iron(II).

A method developed in previous work had been used to quantify cell growth rate as a function of common contaminants in the process water used in biooxidation systems (eg chloride, sodium and sulfate ions). This enables evaluation of the effect of the quality of the process water (determined by the water composition) on biooxidation.

This project aims to extend the previous research on chemolithotrophic cell cultures by:

- measuring the inhibition of cell growth and iron oxidation due to other process water contaminants (eg gangue components, products of mineral oxidation and organics leaking from the cells) and changes in their concentration during biooxidation
- describing and measuring interactions between cells and mineral surfaces, and determining the effect of water quality on the crucial attachment of cells to the target mineral surface
- developing methods to collect and examine the structure(s) and rate of production of the solid iron oxide phases whose formation is also catalysed by biooxidation cell cultures.

OUTPUTS

- The techniques developed during the project to examine the growth of chemolithotrophic cells were used to investigate:
  - the chemical energy involved in the synthesis of cell biomass
  - the limits of biomass production and the theoretical maximum yield of cells from an iron system
  - the separation of 'catalyst activity' into cell reproduction activity and iron oxidation activity
  - the chemical energy available in the systems where reduced sulfur forms the main energy substrate.
- There were a number of significant developments from the work on solid sulfur begun during the final year of the project:
  - The work resulted in a hypersaline-tolerant culture with a catalytic effect demonstrated in leaching of nickel from its sulfide more.
  - This led to the development of cultures able to oxidise reduced sulfur compounds at hypersaline concentrations and an understanding of the magnitude of the tolerance.
- An understanding of the effect that sulfur allotropes exert on the oxidation of bulk sulfur was developed: this work is being prepared for publication.
- Solution models capable of determining the addition of sulfate as a function of pH were developed.
- A sulfur culture was successfully demonstrated to operate at a sodium chloride concentration of 28,000 ppm (parts per million), and bench-scale proof of nickel recovery and culture habituation was obtained.

Bio-inspired Hydrometallurgy

OBJECTIVES

Biologically-inspired (bio-inspired) approaches to research and development focus on the use of biological processes, organisms and systems as potential sources of innovative solutions for technological or engineering problems. This approach has a strong track record in the materials industry, with the development of advanced materials inspired by natural examples, such as the strength of spider silk, the elasticity of cartilage and the dry adhesion of gecko foot hairs.

Certain biological organisms have evolved to extract mineral constituents with high selectivity and efficiency from an aqueous environment, and to manipulate the extracted elements to produce very specific and well-defined structures. The vast majority of these processes occur at ambient temperature and pressure and moderate pH. Such processes are environmentally benign and sustainable.

Biomineral synthesis, in contrast to conventional mineral processing, generates mineral materials with exquisite control over shape, size and crystal structure. And many biological systems that operate with supersaturated solutions have no problems with scale formation, which is a universal problem throughout hydrometallurgy.

This project proposes to use fundamental understanding of biological processes as a starting point to generate novel bio-inspired hydrometallurgical technology. Specific objectives include:

- selecting two or three biological processes that show promise as a source of ideas to apply to hydrometallurgy
- developing a detailed understanding of these bioprocesses that can be used to design an original non-biological system for minerals processing
- ensuring that the new bio-inspired system has an acceptable efficiency for industry application as reaction rates of bioprocesses are typically orders of magnitude slower than required for industrial processes.

OUTPUTS

- A review of existing bio-inspired industrial applications was compiled.
- An extensive broad scoping literature review was completed, identifying a number of specific biological processes that offered potential in developing a new or an improved hydrometallurgical approach to metal extraction.
- Fundamental studies of simple salt solutions and oil-water mixtures (ubiquitous in nature) commenced.
- A technique for investigating the interaction of bacteria with mineral surfaces was established and advanced.

Solvent Extraction Chemistry

OBJECTIVES

Previous work on improving efficiency and selectivity in solvent extraction has focused on reagent analysis and identifying degradation products and their impact on efficiency, and on developing and testing synergistic solvent extraction (SSX) systems. SSX uses a combination of extractant and synergist which work together to improve metal selectivity.

Research to date has indicated that different metals react differently with extractants and synergists in a SSX system, and that control of the ratio of the synergist to extractant may be necessary in an operation to maintain optimum element separations.

Therefore this project aims to:

- realise the potential of SSX through fundamental understanding of what complexes are formed between extractants/synergists and different metals and under what conditions
- develop methods to measure the concentrations of multiple reagents (extractants/synergists) in SSX solutions so SX circuits can be optimised and monitored for best operation
- assess the chemical stability of prospective SSX systems under potential operating conditions
- understand reagent degradation mechanisms and therefore modify operating conditions where possible to minimise such degradation
- demonstrate the developed capabilities to industry and use to solve industry problems.

OUTPUTS

- Four journal papers were published and five papers were accepted for presentation at the International Solvent Extraction Conference (ISEC 2008) in Tucson, Arizona, USA in September 2008.
- Work identifying factors that affect inter-conversion between the *syn* and *anti* isomers (stereoisomers) of oxime extractant was performed.
- Industry-funded research into reagent stability in two synergistic SX systems was undertaken.
- Industry-funded research into a novel application of the synergistic SX system was conducted.

Solvent Extraction Technology

OBJECTIVES

A limited number of extractants are available commercially for the separation of metals in solvent extraction, and the development and production of new extractants is extremely expensive. This has generated strong interest in synergistic solvent extraction (SSX) systems which use a combination of two existing extractants to improve metal separation or effect new metal separations. In SSX systems, one of these two organic reagents is utilised as the synergist to increase the metal selectivity of the other (the extractant).

The minerals industry largely uses mixer-settler technology for solvent extraction circuits. Improvements in the design and operation of mixer-settlers would benefit industry, as would evaluation and optimisation of newer technologies such as pulsed columns.

This project's objectives are to address industry's general and/or specific SX needs, particularly but not exclusively for nickel and cobalt recovery from nickel laterite leach solutions, by:

- developing new synergistic and conventional SX systems, with emphasis on novel SSX systems, to separate, concentrate and/or purify metals of interest to industry
- undertaking scaled laboratory to pilot scale test work on selected SX systems, and then working with industry on their application in industry
- improving the efficiency of current and new SX equipment (mixer-settlers and pulsed columns).

OUTPUTS

- A new direct solvent extraction (DSX) process using a novel synergistic SX system was developed.
- New SX technology was developed to separate cobalt from nickel in leach solutions based on extraction kinetic (rate) differences.
- Novel SX technology to separate metals in high chloride solutions were tested with encouraging results.
- An Australian provisional patent was re-lodged for the recovery of manganese from waste streams and solutions from the leaching of low-grade manganese ores.

Electrostatic Solvent Extraction

OBJECTIVES

The use of solvent extraction (SX) in the minerals industry has numerous advantages: it can be used for a wide range of metal ions and over a broad range of pH values; it enables complete separation of chemically similar metals (eg nickel and cobalt) and it allows simultaneous separation/concentration of metals from both dilute and concentrated solutions, making it particularly useful in the processing of low-grade ores.

However, a major drawback is that SX is generally undertaken in mixer-settlers which use mechanical agitation for mixing. Mixer-settler contactors have some inherent shortcomings that can impact on the SX process and also on downstream operations such as electrowinning. For example, the intensity of agitation can cause problems: insufficient mixing reduces the efficiency while excessive mixing can result in high shear and poor separation of the organic and aqueous phases. Operating costs are high because mechanical agitation requires a considerable power input and maintenance of the moving parts can be costly.

Therefore, there is a need to develop alternative contactors for industrial use. This project is investigating electrostatically agitated SX which uses an electrostatic field to disperse the aqueous phase into the organic phase. A number of studies, including previous work undertaken by the project team on the electrostatic pseudo liquid membrane technique, have shown that electrostatic SX has the potential to combine the advantages of conventional SX and electrostatic agitation.

Since fundamental understanding of electrostatic SX is limited and no application in hydrometallurgy has been commercialised, the objectives of this project include:

- investigating the fundamentals of electrostatically-induced dispersion and dispersed phase motion in electrostatic SX
- studying mass transfer in electrostatic SX
- developing and assessing an electrostatic SX contactor.

OUTPUTS

- Investigation of the fundamentals of electrostically induced dispersion continued:
  - data on the effect of the conductivity of the organic phase was generated
  - data on the effect of different frequencies of the applied field was generated.
- Analyses of the data on the effect of the various experimental variables on droplet dispersion were undertaken.
- The mechanism of droplet dispersion under the influence of an electrostatic field was investigated.
- A method was developed to study mass transfer in electrostatic solvent extraction: this work included the design, construction and testing of specialised equipment.

Base Metals Market Research Portfolio

Project	Research Team	Research Collaboration	Project Duration	Activity Theme Contribution
CRC-funded Projects				
Electrochemical Investigations of the Leaching of Sulfide Minerals	Mike Nicol (Project Leader), Hajime Miki, Suchun Zhang, Man-Seung Lee (Visiting Research Fellow), Dmitry Pugaev (PhD student) (Murdoch University)	BHP Billiton, Mokpo National University (South Korea)	2006-2009	Process Fundamentals
Reductive Leaching of Metal Oxides	Gamini Senanayake (Project Leader), Michelle Hollingworth, Mike Nicol, Stephen Taylor, Jonathon Childs (Honours student), Alexander Senaputra (MSc student) (Murdoch University)		2006-2009	Process Fundamentals
Pressure Hydrometallurgy	Robbie McDonald (Project Leader), Peter Balding, David Muir (retired February 2008; subsequently a CSIRO Honorary Research Fellow), Barry Whittington, Sin Wei Lim (Student-Industry Research Program student)		2005-2008	Process Fundamentals
Processes for Low-Grade Nickel Ores	David Muir (Project Leader – retired February 2008; subsequently a CSIRO Honorary Research Fellow), Peter Balding, Goutam Das, Helen Fletcher, Said Hirad, Nick Kelly, Jian Li, Robbie McDonald, Barry Whittington, Nicole Botsis (PhD student), Nikita Kovalenko (Student-Industry Research Program student), Priscilla Macieira (Student-Industry Research Program student) (CSIRO Minerals)	CSIRO Minerals' Materials Characterisation Group, Curtin University's Department of Applied Geology, Curtin University's Department of Imaging and Applied Physics	2006-2008	Process Fundamentals
Biohydrometallurgy of Sulfides	Helen Watling (Project Leader), David Collinson, Alex Elliot, Helen Fletcher, David Maree, Lesley Mutch, Felicity Perrot, Suzanne Rea, Denis Shiers, Elizabeth Watkin, Barry Whittington, Melissa Corbett (PhD student), Anna Grosheva (Student-Industry Research Program student), Daniel Hoath (Honours student), Tsun Yao Mak (Student-Industry Research Program student), Richard O'Rourke (Honours student), Tracey Richards (Student-Industry Research Program student), Carla Zammit (PhD student)	CSIRO Minerals, Curtin University, CSIRO Land & Water, Hahn-Meitner Institut (Germany)	2005-2008	Breakthrough Technologies Process Fundamentals
Biooxidation Process Water	David Ralph (Project Leader), Kyle Blight, Ragat Hans, Matthew Menzel, Rachel Candy (Honours student), Jeremy Hartley (Honours student), Denis Shiers (PhD student) (Murdoch University)	Hydromet Innovations, Korea Institute of Geoscience and Mineral Resources (KIGAM)	2005-2008	Process Fundamentals
Bio-inspired Hydrometallurgy	Mark Ogden (Project Leader), Tom Becker, Nicole Gorham, Don Ibana, Franca Jones, Adrian Murdock, Bill Richmond (Curtin University)		2006-2009	Breakthrough Technologies
Solvent Extraction Chemistry	Keith Barnard (Project Leader), Tiffany Hill, Nicole Turner, Denis Shishin (Student-Industry Research Program student) (CSIRO Minerals)		2005-2008	Process Fundamentals
Solvent Extraction Technology	Chu Yong Cheng (Project Leader), Yoko Pranolo, Weiwei Wang, Wensheng Zhang, Zhaowu Zhu, Li Zeng (PhD student) (CSIRO Minerals)	Korea Institute of Geoscience and Mineral Resources (KIGAM)	2005-2008	Process Fundamentals
Electrostatic Solvent Extraction	Don Ibana (Project Leader), Simon Assmann (Honours student), Joel Collard (PhD student), Evan McKernan (Honours student), Marc Steffens (PhD student) (Curtin University - WASM)		2006-2009	Process Fundamentals
Gaseous Reduction Processes for Metal Ions	Aleks Nikoloski (Project Leader), Mike Nicol, Soo-Kyung Kim (Visiting Scientist) (Murdoch University)	Korea Institute of Geoscience and Mineral Resources (KIGAM)	2006-2009	Process Fundamentals
Collaborative Projects				
AMIRA P705A Project: Improved Anode and Cathode Processes in the Electrowinning of Base Metals	Mike Nicol (Project Leader), Anthony Blackett, Justin McGinnity, Manickam Minakshi, Venny Tjandrawan (PhD student) (Murdoch University)	CSIRO Minerals' CFD Group	2006-2009	
Multiple Sponsor Project: Improving Solvent Extraction Technology	Dave Robinson (Project Leader), Chu Yong Cheng (Project Supervisor for CSIRO Minerals' SX Technology Group), Phil Schwarz (Project Supervisor for CSIRO Minerals' CFD Group)	CSIRO Minerals, CSIRO Minerals' CFD Group	2007-2010	

Industry Collaboration

In 2007-2008, the Parker Centre's Base Metals Market engaged with the following companies through collaboration and one-to-one projects:

Amdel, AMIRA International, Anglo Platinum, Anglo Research, Ausenco, Bateman Engineering, Bateman Litwin, BHP Billiton, Chemistry Centre (WA), Cominco Engineering Services (CESL), Direct Nickel, Freeport McMoran Copper & Gold, Gladstone Pacific Nickel, Hatch Associates, HiTec Energy, Hudson Marketing, Hydromet Innovations, Jervois Mining, Kahama Mining Corporation, LionOre Technology, Minara Resources, Mineral Engineering Technical Services (METS), Nyrstar, Oxiana, OZ Minerals, Pearl Mining, Phelps Dodge Mining Company, Queensland Nickel (QNI), Rio Tinto, RSR Technologies, SGS Lakefield Oretest, Sherlock Bay Nickel Corporation, Sons of Gwalia, Straits Resources, Teck Cominco, Vale, Vale Inco and Zinifex

Postgraduate Projects

Project	Postgraduate Researcher	Supervisor(s) (Organisation)
Thermodynamic and Related Studies of Copper(II) Sulfate Solutions	Chandrika Akilan (PhD student)	Glenn Hefter (Murdoch University)
The Prediction, Modelling and Fundamental Understanding of Nickel Laterites and its Impact on the Leaching Process	Nicole Botsis (PhD student)	Bill van Bronswijk (Curtin University), Helen Watling (CSIRO Minerals), Puru Shrestha (BHP Billiton)
Extraction and Separation of Cobalt and Nickel from PAL Solutions Using Electrostatic Pseudo Liquid Membrane	Joel Collard (PhD student)	Don Ibana (Curtin University - WA School of Mines)
The Study of *Leptospirillium* Gene Pathways Within Bioleaching Systems	Melissa Corbett (PhD student)	Elizabeth Watkin (Curtin University), Helen Watling (CSIRO Minerals)
The Co-precipitation of Iron and Silica from Industrial Zinc Solutions	Laurence Dyer (PhD student)	Bill Richmond (Curtin University), Phillip Fawell (CSIRO), Mr David Palmer (Nyrstar)
Modelling and Flowsheet Design for Solvent Extraction Circuits	Heather Evans (PhD student)	Parisa Arabzadeh Bahri (Murdoch University), John Rumball (CSIRO Minerals)
Better Batteries via Controlling the Properties of Electrolytic Manganese Dioxide	Jonathon Morton (PhD student)	Andrew Rohl (Curtin University), Mark Ogden (Curtin University), Chris Ward (HiTec Energy), Mike Nicol (Murdoch University)
The Mechanisms of the Dissolution and Passivation of Base Metal Sulfide Minerals	Dmitry Pugaev (PhD student)	Mike Nicol (Murdoch University)
Catalysis of Base Metal Sulfide Dissolution	Denis Shiers (PhD student)	David Ralph (Murdoch University), Helen Watling (CSIRO Minerals)
Extraction and Separation of Metals using Electrostatic Solvent Extraction (ESX) Columns	Marc Steffens (PhD student)	Don Ibana (Curtin University - WA School of Mines
The Effect of Manganese on the Corrosion Behaviour of Lead Anodes in Copper and Zinc Electrowinning	Venny Tjandrawan (PhD student)	Mike Nicol (Murdoch University)
The Kinetics and Mechanism of the Dissolution of Chalcopyrite in Chloride Solutions	Lilian Velásquez (PhD student)	Mike Nicol (Murdoch University)
Economic Operability Assessment of Leaching Process at Kwinana Nickel Refinery	Travis Woodward (PhD student)	Parisa Arabzadeh Bahri (Murdoch University)
Biomining Action of Microorganisms Under High Levels of Total Dissolved Solids	Carla Zammit (PhD student)	Elizabeth Watkin (Curtin University), Lesley Mutch (Curtin University), Helen Watling (CSIRO Minerals)
The Development of SX Processes to Recover Vanadium and Molybdenum from Spent Hydrodesulfurisation Catalysts	Li Zeng (PhD student)	Qixiu Zhang (Central South University, China) Chu Yong Cheng (CSIRO Minerals)
The Leaching of Nickel Sulfides	Alexander Senaputra (MSc student)	Gamini Senanayake (Murdoch University), Mike Nicol (Murdoch University)
Mass Transfer in Electrostatic Solvent Extraction	Simon Assmann (Honours student)	Don Ibana (Curtin University - WA School of Mines)
Lithotrophic Cultures in Minimal Media	Rachel Candy (Honours student)	David Ralph (Murdoch University)
Reductive Leaching of Laterite Ores	Jonathon Childs (Honours student)	Gamini Senanayake (Murdoch University)
Biooxidation of a Stannite Mineral	Jeremy Hartley (Honours student)	David Ralph (Murdoch University)
Identification of Potentially Novel Iron Oxidising Chemolithoautotrophs Associated with Inland Acid Sulfate Soils	Daniel Hoath (Honours student)	Elizabeth Watkin (Curtin University), Lesley Mutch (Curtin University), Ron Watkins (Curtin University)
Extraction of Zinc by Electrostatic Pseudo Liquid Membrane (ESPLIM) Using D2EHPA	Evan McKernan (Honours student)	Don Ibana (Curtin University - WA School of Mines)
Determination of Microbial Populations in Experimental Bioleaching Systems Using Quantitative PCR	Richard O'Rourke (Honours student)	Elizabeth Watkin (Curtin University), Lesley Mutch (Curtin University), Helen Watling (CSIRO Minerals)
Leaching of Copper Matte and Concentrate	Russell Shedden (Honours student)	Don Ibana (Curtin University - WA School of Mines
Nickel Extraction Using Sieve Plate Pulse Column	Thomas Waters (Honours student)	Don Ibana (Curtin University - WA School of Mines