Thinking process gets results

BY **NANCY MILLS**

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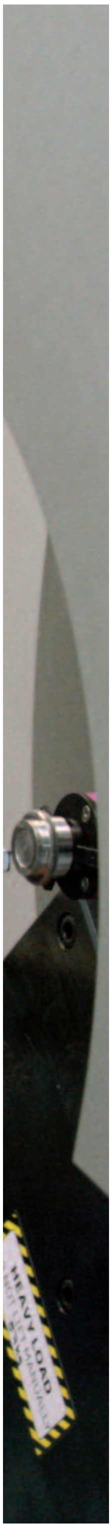
Not just a pretty space, the Australian Synchrotron is being used to achieve industrially valuable outcomes.

Nicola Scarlett (left) and Kia Wallwork (right) mount the capillary heater on the powder diffraction beamline at the Australian Synchrotron.



Australian researchers are increasingly turning to their national synchrotron as a source of fast, accurate and often unique information about a wide range of materials and systems. It's a good source of publishable results: the lifeblood of many a successful research career.

The synchrotron is also helping to strengthen the connections between research and practical real-world applications that benefit Australian industries. Take the minerals industry, for example.

Work in process

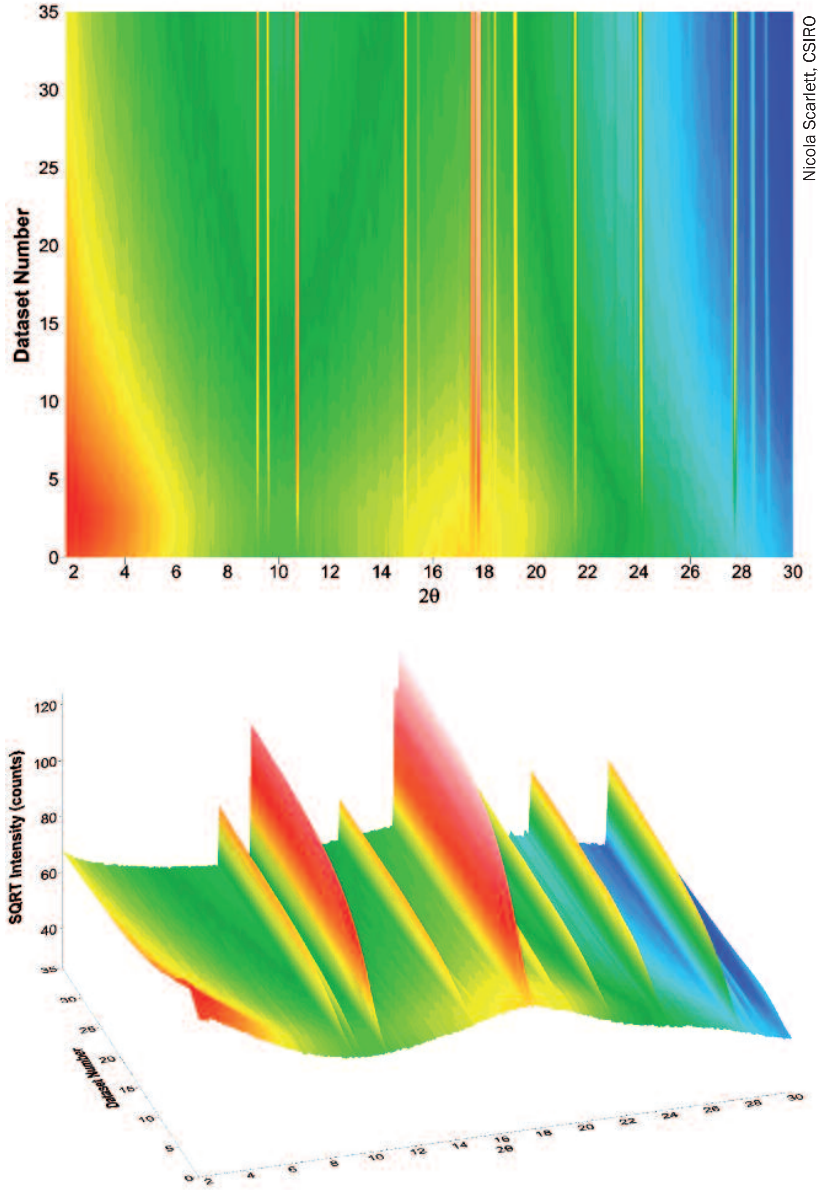
Once considered an unattainable goal, real-time in-situ analysis of mineral processing reactions is helping to position Australia's massive mining industries for the years ahead: cutting greenhouse emissions, raising productivity and extracting valuable metals from previously discarded low-grade ore.

Over the decades, improvements to processing methods have largely been based on empirical observations, laboratory analyses of 'before and after' samples, and measurements of process characteristics such as temperature, pH and concentration.More recently, advances in analytical techniques have enabled researchers to begin looking at what actually happens during the processing stage.

'The in-situ approach lends itself to a range of industrial and environmental problems,' says X-ray diffraction expert Nicola Scarlett from CSIRO Process Science and Engineering's diffraction team. 'In-situ analyses aim to collect data while processes are occurring and thus avoid the risks associated with drawing conclusions from post-mortem samples, which may contain artefacts from the sampling itself.'

Nicola and her colleagues are using powder diffraction (PD) at the Australian Synchrotron to study a range of processes relevant to the Australian resources sector, including high-pressure acid leaching of nickel laterites, leaching and scale formation in bauxite processing, molten salt electrowinning of titanium and sintering of iron ore. Nicola says the PD beamline 'provides high-resolution, high-intensity diffraction data in timeframes that enable real-time in-situ study of process reactions'.

The group has also used the Australian Synchrotron's small and wide angle X-ray scattering (SAXS/WAXS) and PD beamlines in parallel to investigate the nucleation



Accumulated synchrotron powder X-ray diffraction patterns showing the formation of jarosite from solution over time. The data are represented as a three-dimensional plot with diffraction angle (2θ) along the *x*-axis, dataset number (which relates to elapsed time) along the *y*-axis and intensity along the *z*-axis. The top figure views the data down the *z*-axis. The bottom figure views the patterns from an angle that clearly shows the growth of the jarosite peaks.

and crystallisation of jarosite-related minerals. Jarosite, $KFe_3(SO_4)_2(OH)_6$, is found in 'a myriad of natural and industrial environments'; it forms kinetic barriers in bioleaching systems and in flotation circuits involving bacterial conditioning, and can lead to groundwater contamination due to acid and heavy metal release from acid mine drainage environments. The presence of jarosite has also been reported on Mars and provides the best evidence that liquid water has existed at some time in that planet's history.

'The SAXS/WAXS beamline allows us to study the earliest stages of nucleation and growth while the PD beamline provides information about the kinetics and structure of the crystalline product,' Nicola says. 'Preliminary SAXS/WAXS results suggest nucleation followed by growth rather than continuous nucleation, and the high resolution of the PD beamline has revealed the formation of jarosite with monoclinic symmetry rather than the rhombohedral symmetry more commonly encountered. We're now investigating the magnetic properties of the material.

'For us, the Australian Synchrotron provides a world-class facility without the need to take large pieces of tailor-made equipment overseas. The PD beamline has gradually been equipped with many of the specialised sample environments that these types of studies require, so that groups like ours sometimes have the luxury of arriving only with samples.

'Our team has diffraction experts working in close conjunction with context-based specialists so that the information we gain from our analyses becomes immediately available to the industries and processes to which it relates.'

More minerals to make the grade

In response to continuing growth in world demand for minerals such as copper, the minerals industry is increasingly seeking to process low-grade ores, overburden and waste from current mining operations.

Bacterially assisted leaching (bioleaching) of low-grade sulfide ores is an attractive option because it is potentially less expensive, less intensive and more environmentally friendly than traditional methods such as high-temperature processing. Bioleaching has successfully been used to extract copper on a commercial scale from secondary sulfide minerals such as chalcocite. Bioleaching of the refractory primary copper sulfide chalcopyrite, $CuFeS_2$, has yet to be implemented on a commercial scale.

Researchers have established that the main factor hindering commercial bioleaching of chalcopyrite is its slow dissolution rate. The flow of bacteria, nutrients, oxidants and reaction products to and from the chalcopyrite surface is impeded by the formation of Cu–S intermediate species, sulfur, iron-hydroxy precipitates and others on the mineral surface. However, despite a number of scanning electron microscopy – energy-dispersive spectrometry, X-ray diffraction, X-ray photoelectron spectroscopy and electrochemical studies, the bioleaching mechanism of chalcopyrite remains poorly understood.

Synchrotron powder diffraction can provide unique insights into the relationships between the structure and the properties of many different microcrystalline materials.

Miao Chen from CSIRO Minerals recently joined forces with Qinfen Gu at the Australian Synchrotron to develop a new electrochemical cell for in-situ synchrotron X-ray powder diffraction studies of chalcopyrite and other sulfide mineral electrodes. Miao used the cell to study the mechanism and kinetics of the mineralogical and chemical changes taking place at the chalcopyrite-bioleaching solution interface.

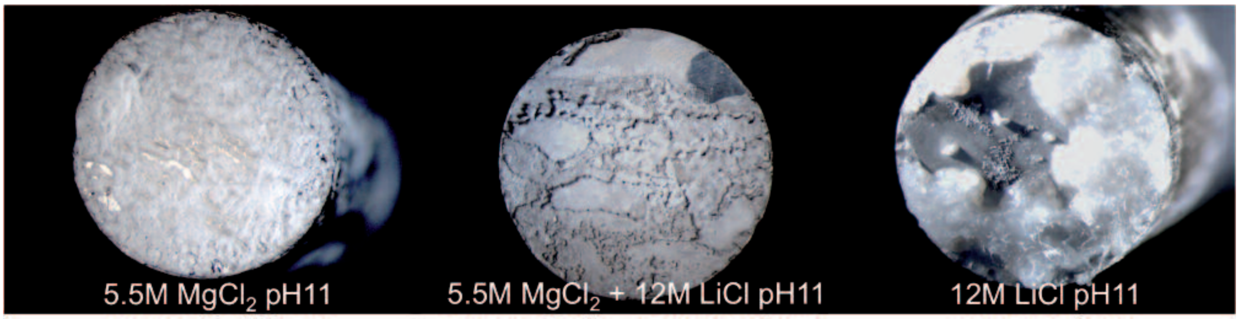
'Bioleaching is a complex chemical, electrochemical, biochemical interaction between the bacteria and the ore,' Miao says. 'The synchrotron offers higher X-ray flux and better resolution than laboratory sources, which is very important when tracking small changes taking place in a short timeframe in a complex system.

'Our synchrotron data were sufficiently sensitive for us to observe the phase mineralogy transformations during bio- and chemical leaching of chalcopyrite. This work will help us to characterise the dissolution of chalcopyrite and other sulfide minerals, taking us several steps closer to understanding the bioleaching mechanism.'

'The ultimate goal is to see bioleaching of chalcopyrite become a commercially viable process, enabling the mineral industry to efficiently extract the copper that is currently locked away in vast reserves of chalcopyrite.'

Material differences

'Most people are more interested in the appearance of a new car or the capabilities of a new medical device than in the materials these are made of,' says George Collins, national president of Materials Australia. 'But form and function depend on having the right materials, and for that you need a very good understanding of material properties.'



Patrick Howlett, ACES

Optical micrographs of Mg electrode (1 cm diameter) after discharge in various 'high salt' electrolytes.

'Synchrotron powder diffraction can provide unique insights into the relationships between the structure and the properties of many different microcrystalline materials,' says Kia Wallwork from the Australian Synchrotron. 'The PD beamline is typically promoted as a valuable tool for the mining industry, which it certainly is, but in fact we host more materials research projects than mining ones.'

Salt and battery charge

It sounds as though it was dreamt up by a wannabe sci-fi novelist, but a battery that stores some of its charge in the air is already partway to becoming a reality.

Patrick Howlett and his team at the ARC Centre of Excellence for Electromaterials Science (ACES) at Deakin University are working on a magnesium–air battery with a cathode that reduces oxygen from the atmosphere during discharge, 'essentially storing its charge in the air outside the battery'.

Magnesium is a reactive, low-density, electropositive metal that can be used for high-voltage devices carrying a large amount of charge per weight. Other factors in magnesium's favour include its abundance – around 18 000 trillion tonnes in the ocean – relatively low cost and potential for recycling.

'The combination of an air cathode and a magnesium anode is very attractive, particularly for applications that require high-capacity, lightweight cells,' Patrick says. 'Magnesium–air batteries have enormous potential as high-energy density storage systems for applications ranging from small-scale medical devices such as cochlear ear implants to large-scale electric vehicles.

'Magnesium–air batteries are also potentially biocompatible, which means they could find use as implantable power sources for medical devices such as 'lab on a chip' or for controlled release of drugs or growth factors in nerve repair.'

Patrick's aim is to develop ionic liquid electrolyte systems that support high-rate discharge while also solving the problem of magnesium electrode corrosion during storage. He is using powder diffraction at the Australian Synchrotron to investigate the thin salt film (just hundreds of microns thick) that forms on the magnesiuum surface in contact with the electrolyte during storage and discharge. This salt film is the main factor behind differences observed in discharge rate and cell voltage during operation and self-discharge (corrosion) during storage.

The ACES team has adapted a cell developed by collaborators at the UK's Diamond Light Source. Their modified cell allows in-situ study of battery processes, enabling them to determine the nature, composition and crystallinity of the salt film and to correlate these characteristics with how the device functions as electrolyte and cell discharge parameters change. Removing the film from the cell for analysis is not an option, as this would 'completely compromise' the sample.

'Our most important finding so far is that the best electrolytes – the ones that allow for long discharge times, high rates and low self-discharge – form entirely amorphous salt films on the magnesium surface,' Patrick says. 'Conversely, highly crystalline salt films appear to be associated with problematic battery operation.

'If we can solve the problems associated with controlling anode corrosion, these devices have the potential to replace lithium-ion batteries in many applications. We're excited by the prospect of moving this work closer to commercial reality.'

Synchrotron cells expertise

The synchrotron also provides opportunities for joint development of research tools by researchers and commercial businesses.

Melbourne company MiniFAB is working with the Australian Synchrotron's Mark Tobin and Ljiljana Puskar to develop and commercialise specialised new equipment for use in medical and biological research. Mark and Ljiljana are developing new sample chambers and accessories that extend the capabilities of synchrotron infrared microspectroscopy. Working with Rick Barber and Erol Harvey from MiniFAB, the synchrotron scientists are applying their international synchrotron experience to the task of developing sample chambers that keep cells alive while minimising water thickness in the chamber so that the water doesn't interfere with the analysis of key chemical components in the cells.

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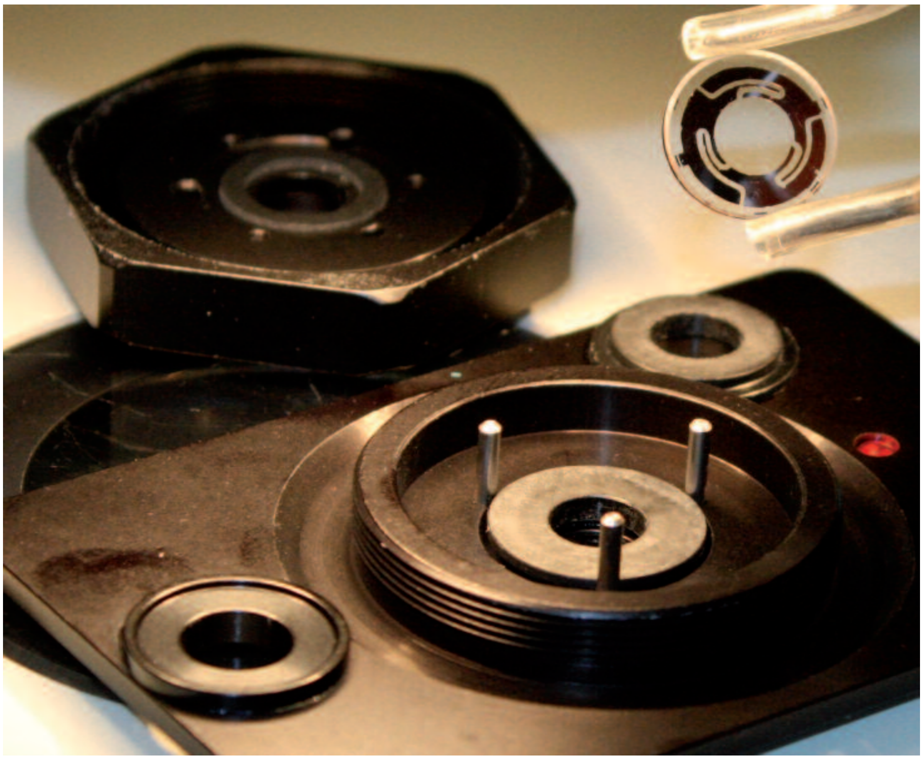

A lithographically patterned calcium fluoride window (13 mm diameter) being lowered into a micro compression cell. The window is part of a specialised sample chamber that enables living cells to be studied by infrared microspectroscopy.

Synchrotron infrared microspectroscopy provides information about chemical composition and bonding in individual cells with much greater sensitivity than is possible with laboratory infrared sources. This capability is invaluable in many areas of medical and biological science, including examination of early-stage neural sheath damage caused by multiple sclerosis, studying degeneration of cartilage in joint disease, and understanding the action of antileukaemia drugs.

Determining the wavelengths of infrared light absorbed by a cell or other sample at particular points of interest selected by looking at the sample under an optical microscope helps identify the chemical composition of the sample. Infrared microspectroscopy can also highlight minor changes in the immediate environment around a particular chemical group. Because synchrotron infrared microspectroscopy is so sensitive to small chemical changes, it has the potential to identify the early signs of some diseases and health conditions such as multiple sclerosis well before any changes can be seen by any other technique, even high-magnification optical microscopy.

However, when research in this field is extended to the study of live cells, the technique is limited to some extent by the fact that water also absorbs infrared light, which can make it difficult to see spectral features that appear nearby, such as the amide I and lipid carbonyl peaks typical of proteins and fats respectively. Having the water in the sample chamber less than 10 μm thick largely overcomes the problem, but is easier said than done. Human cells, for example, are typically 10 μm across.

To help them construct an improved sample chamber, Mark and Ljiljana selected 0.5 or 1.0 mm thick sample-chamber windows to maximise the chamber's infrared transmission properties. Using these windows, MiniFAB fabricated surface-bonded gaskets of the required thickness, and then worked with the synchrotron scientists to further improve chamber performance so that samples could be studied for up to an hour at a time.

Mark and Ljiljana recently took their new sample chambers to the Soleil synchrotron in France, where they were used to study cellular changes during the signalling response to growth factor molecules. This work was funded by FAST, the French Australian Science and Technology program.

MiniFAB has already produced the same design of gasket for a second customer and anticipates a growing interest in such devices. Their micro-fabrication capabilities enable them to customise the gasket design to suit specific application requirements.

Looking ahead

'For Australia's manufacturing and mineral processing sectors to grow and maintain their competitive edges in the face of global supply chains and complex international business linkages, they will require new high-tech products and processes,' says George Collins. 'A good understanding of how the constituent materials behave at the nano level is absolutely fundamental. Australians are fortunate to have good access to leading-edge characterisation tools, such as those available at the Australian Synchrotron.'

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