ChemCentre
EXPERT SOLUTIONS

TOOLS FOR MINE SITE CLOSURE PLANNING: LEACHING POTENTIAL ASSESSMENTS AND WASTE MANAGEMENT

October 2013

Acid Base Accounting (ABA)

Australian Standard Leaching Protocol (ASLP)

Kinetic Tests

Research and Development

THE GOVERNMENT OF WESTERN AUSTRALIA

DETAILS

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Expert Solutions

It's one of the first questions a new client asks us : 'Why 'Expert Solutions?' What does it mean?'

To ChemCentre, Expert Solutions represents our entire approach to science and our relationship with clients. It means we take pride in understanding our results and in being able to share this knowledge with our clients. It allows us to help you with your unique challenges.

We are different to other analytical providers. Part of this is due to our history as the Western Australian analytical authority, but mostly it is down to our belief that you as the client should receive more than numbers in a report. You should be able to speak to the person who generated those numbers, and access years of scientific knowledge to assist you in answering your own, unique questions.

Our experts are qualified, knowledgeable scientists. They translate their commitment to excellence into quality assured results and are always prepared to assist clients in understanding how these results relate to their challenges and requirements.

Our solutions are tailored to suit individual clients, allowing you to edit and change off-the-shelf packages, or commission your own analytical suite. This ensures you receive both value and meaningful results. A comprehensive and current understanding of the latest developments in chemistry can be combined with requests for research, creating a more flexible approach to your projects and investigations.

Expert Solutions is our approach to assist you in supporting, protecting and building your reputation and your business.

It is our point of difference, and our promise.

About ChemCentre

ChemCentre is a leading provider of expert solutions to industry and regulators in the mining sector. Through excellence in chemistry, we are committed to ensuring our clients achieve high levels of safety, quality and value.

Housed in multi-million dollar facilities in Bentley, Western Australia, ChemCentre has core responsibilities in areas including forensic science, emergency response, chemical crises and public and environmental health.

Our scope of work means we are experienced in tailoring our scientific services to meet client needs, with highly skilled staff working in routine analysis, tailored method development and testing and scientific project management services.

The origins of ChemCentre date back to the 1890s and through our heritage as the leading analytical chemistry facility in Western Australia we have established ourselves as the laboratory of choice for a number of high profile state, national and international clients in the mining and oil and gas industries as well as various environmental consulting firms. Government clients include the Department of Environmental Regulation (DER), Department of Water (DoW), the Department of Health WA and Water Corporation. ChemCentre is also a member of the Cooperative Research Centre for Contamination Assessment and Remediation of Environments (CRC CARE) and the Western Australian Marine Science Institute (WAMSI).

As a Western Australian Government statutory authority we combine the values of high ethical standards with the commercial client focus that is necessary to prosper in a price competitive market. Our unique history has provided the foundations of an organisation with an uncompromising attitude to quality – from our multi-million dollar laboratory with the latest state-of-the-art equipment to our recruitment strategy, identifying the highest calibre scientists capable of providing expert advice on the best sampling and analysis methods. Through our experience in providing qualitative and quantitative data that stands up to legal scrutiny we have the experience and management processes that will protect our clients from issues of regulatory compliance and reduce risks of prosecution and compensation.

ChemCentre's uncompromising attitude towards quality science, customer-focussed advice and accredited certainty makes us the prudent choice as your accredited laboratory and analysis advisory partner.

Why Choose ChemCentre?

Reliability

120 years of uncompromising service

Credibility

Provider of choice for Government agencies in Western Australia and around the world

Expertise

Wide staff knowledge base with over 30% of staff holding PhDs

Defensibility

Expert interpretation and legally defensible results

World class facilities

$40m laboratories and equipment in a central location

Quality Assurance and Accreditation

ChemCentre has a mature Quality Management System that reflects a history of accreditation dating back to 1950. ChemCentre was one of the first laboratories in Australia to achieve NATA accreditation and holds the record for the oldest standing continuous NATA accreditation.

As an analytical facility, ChemCentre maintains an extensive scope of accreditation within the fields of Chemical Testing and Forensic Science. As specified in NATA Policy Circular 15, there is crossover between aspects of ISO 9001 and ISO/IEC 17025. ISO 9001 applies to the requirements of quality management systems. Meeting ISO/IEC 17025 means the laboratory demonstrates both technical competence requirements and has management systems in place to ensure consistent delivery of valid test results and measurements. Consequently, ChemCentre is recognised through its NATA accreditation as complying fully with all relevant clauses of ISO/IEC 17025 and meeting the principles of ISO 9001.

Our systems are actively reviewed, managed and are subject to regular external scrutiny by both accreditation bodies and the justice system. Regular independent audits are conducted by NATA authorities to ensure ChemCentre meets requirements set out by NATA for accreditation. In addition to this ChemCentre have several staff members who are NATA technical assessors and who regularly audit external chemical laboratories and industrial sites.

ChemCentre maintains a strict internal auditing and quality management system, which includes aspects such as corporate and laboratory quality manuals, proficiency testing and performance evaluation. In addition to this commitment to accredited methodology, ChemCentre fosters a strong quality culture among staff, with integrity, discipline, efficiency and effective service delivery embedded in our organisational values.

New methods are constantly being considered for NATA accreditation or peer review. Clients choosing to use ChemCentre for their analytical requirements are therefore independently assured of the quality of service and reliability of information they will receive.

For further information regarding the scope of our accreditation please refer to the NATA website http://www.nata.asn.au or contact the ChemCentre Quality Manager Allison Hewitt on 08 9422 9833 or ahewitt@chemcentre.wa.gov.au.

Our Services: Mining Chemistry Solutions

ChemCentre provides leading-edge, reliable and fit-for-purpose analyses in accordance with international standards, Western Australian and Federal guidelines.

Through careful research, development and collaboration with mining industry professionals and regulatory agencies, ChemCentre is offering the following tools as analytical services – with successful mine site closure as the desired end-goal for our clients:

- Acid Base Accounting (ABA)

ABA tests are the basic, initial static tests used to determine the potential for acid generation from mine waste rock. Measurements include pH and Acid Neautralisation Capacity (ANC). Analytes include sulphur, sulphate and carbon.

- Australian Standard Leaching Protocol (ASLP)

ASLP tests are used to assess the leaching potential of wastes, sediments and contaminated soils, including processed mine waste (e.g. tailings) and hence help to inform mine site closure planning and waste storage and management.

- Kinetic Tests

Kinetic tests complement static tests by demonstrating over time the long-term leaching potential of mining waste rock material.

For more information about the above analytical tools, including lists of analytes, please refer to the "Tools for Mine Site Closure Planning" section of this brochure. To view a summary of other services ChemCentre offers, please refer to **Appendix A: Additional Services**.

In keeping with our promise of expert solutions, ChemCentre will provide chemistry-related interpretation of your results and offer sound recommendations and advice for follow-up action. ChemCentre is committed to your financial and environmental security and seeks to provide comprehensive analytical solutions that will help you achieve your objectives. Throughout the life of the mine, we are here to listen and respond to the chemical risk management needs of your operation.

Research and Development: Responding to the needs of the mining industry

ChemCentre is dedicated to listening and responding to the needs of our clients and we are forward-thinking in our approach in developing tomorrow's tools today. We partner with industry and regulatory agencies to develop innovative and practical solutions that will ensure the long-term prosperity and security of the mining industry in Western Australia (WA).

For a number of years, ChemCentre has discussed and reviewed regulatory and environmental issues with the mining industry, WA licensing, regulatory and environmental approval agencies to address key challenges with regards to environmental approvals and mine site closure planning.

The challenges identified by the mining industry and regulators included:

- Knowledge gaps pertinent to the impact of mining on ground and surface water quality;
- Reliability of current Acid Base Accounting methods (static tests) in predicting long-term leaching potential of rocks;
- A lack of a WA regulatory framework to enable by-product re-use and classification.

In response to these needs, ChemCentre took on a suite of projects to tackle each challenge. These include evaluating the suitability of existing and alternative methods for the application of Acid Metaliferous Drainage (AMD) assessment of mining materials, waste management and by-product assessment and advice for re-use.

With a focus on reducing risk and improving certainty, ChemCentre initiated the development of a Western Australian capability in new mining chemistry analytical tools through industry funded projects, some of which are outlined below:

- Development of WA framework for by-product re-use and classification;
- Validation and standardisation of sequential leaching tests to better predict the impact of mining on ground and surface water quality;
- Comparative assessment of static method suites used for the prediction of acid and metaliferous drainage (AMD) in low-sulphur containing mining materials;
- Development of new tools to better predict long-term impacts on mine pit lake water quality.

By-Product Leaching Potential

Methodologies adopted by the European Union and the USEPA are used to analyse mineral processing by-products that may be viable for re-use for commercial and industrial purposes. Subject to regulatory agency approval, this potentially turns what are now considered liabilities (waste) into revenue-generating assets.

ChemCentre is in the process of adopting new leachate assessment tools recently introduced in the EU and USA. These standard methods are more suited for use in assessing the suitability of by-products derived from waste and recycled materials.

The methods described below have been through a process of validation by the USEPA and are subsequently adopted as a standard for the analysis of waste materials.

- Method 1313: Liquid-Solid Partitioning as a Function of Extract pH using a Parallel Batch Extraction Procedure.
- Method 1314: Liquid-solid partitioning as a function of liquid-solid ratio for constituents in solid materials using an up-flow percolation column procedure.
- Method 1315: Mass transfer rates of constituents in monolithic or compacted granular materials using a semi-dynamic tank leaching procedure.
- Method 1316: Liquid-Solid Partitioning as a Function of Liquid-to Solid Ratio in Solid Materials Using a Parallel Batch Extraction Procedure.

Methods 1313, 1314 and 1316 are intended to be used as part of an environmental leaching assessment for the evaluation of disposal, beneficial use, treatment effectiveness and site remediation. These methods are not applicable for characterizing the release of volatile organic analytes (e.g., benzene, toluene and xylenes).

These tests are currently being introduced into WA in collaboration with industry and will be available as services in 2014.

Tools for Mine Site Closure Planning

Acid Base Accounting (ABA)

ChemCentre offers a suite of static tests that can be performed to determine the potential for acid generation from mine waste, based on a number of parameters (see table below).

We are investigating and improving the effectiveness and reliability of ABA tests, as static tests alone are often not sufficient to provide the certainty required for mine site closure planning and waste management.

We therefore recommend ABA tests as a preliminary measure of acid generating potential. Our scientists will work with you to discuss your results and provide advice for further analyses by other tools such as sequential leaching and/or long-term kinetic tests.

Acid Base Accounting (ABA)				
Measured parameters	Notation	Lowest reporting limit (LRL)	Units	Purpose/Method/ Comments
Slurry $pH_{1:2}$	$pH_{1:2}$	0.1		Determine existing acidity using pH electrode
Slurry (1:2) Electrical Conductivity	$EC_{1:2}$	0.2	ms/m	Conductivity electrode
Total sulphur	S_{Total}	0.01	%	By combustion
Sulphate sulphur	$S_{Sulphate}$	0.005	%	By acid digestion with ICPAES finish
Total carbon	C_{Total}	0.05	%	By combustion
Total inorganic carbon	C_{In}	0.05	%	By combustion
Acid Neutralisation Capacity (ANC)	ANC_{BT}	0.5	kg H_2SO_4/tonne	Modified Sobek method with reanalysis by filtration and peroxide attack if sample has a positive ANC but acidic NAG pH (< 4.5)
Net Acid Generation (NAG)	NAG	0.5	kg H_2SO_4/tonne	By multiple addition method
Sequential Net Acid Generation	NAG_{SEQ}	0.5	kg H_2SO_4/tonne	Sequential oxidation of sample gives a better estimate of NAG
Mineralogy	Outsourced			X-ray diffraction
Calculated parameters				
Gross Acid Production Potential (GAPP)	GAPP	3	kg H_2SO_4/tonne	Calculated from total sulphur
Corrected Gross Acid Production Potential	GAPP*	3	kg H_2SO_4/tonne	Calculated from total oxidisable sulphur
Total oxidisable sulphur	TOS	0.01	%	Sulphide sulphur

ABA is based on calculation of acid production from sulphur content, preferably the non-sulphate sulphur (= sulphide sulphur), and the Acid Neutralisation Capacity (ANC) of the rock. A confirmation of the calculation is achieved by the Net Acid Generation (NAG) test, which is additional to ABA.

For more information about ABA, ANC and NAG, please refer to **Appendix B: More information on Acid Base Accounting**.

Australian Standard Leaching Protocol (ASLP)

The Australian Standard Leaching Protocol (ASLP), is derived from the USEPA Method 1311(Toxicity characteristic leachate procedure or TCLP). The main difference is that the ASLP method calls for the particle size of the test material to be less than 2.4 mm and it allows the use of a DI water extraction, whereas the TLCP method allows the particle size of the test material to be up to 9.5 mm.

The ASLP method is applicable to the 1:20 extraction of wastes which are primarily solids (not liquids) by tumbling extraction for the analysis of metals and non-volatile compounds.

Reports include analysis of leachate, the pH of the fluid used and the final pH of the leachate.

Australian Standard Leaching Protocol (ASLP)				
Analyte	Symbol	Lowest Reporting Limit (LRL)*	Units	Purpose/Method/Comments
Metals				
Aluminium	Al	0.001	mg/L	ICPMS(3125)
Arsenic	As	0.001	mg/L	ICPMS(3125)
Boron	B	0.0005	mg/L	ICPMS(3125)
Barium	Ba	0.0001	mg/L	ICPMS(3125)
Beryllium	Be	0.0001	mg/L	ICPMS(3125)
Cadmium	Cd	0.0001	mg/L	ICPMS(3125)
Chromium	Cr	0.0005	mg/L	ICPMS(3125)
Cobalt	Co	0.0001	mg/L	ICPMS(3125)
Copper	Cu	0.0001	mg/L	ICPMS(3125)
Lead	Pb	0.0001	mg/L	ICPMS(3125)
Manganese	Mn	0.0001	mg/L	ICPMS(3125)
Mercury	Hg	0.0001	mg/L	ICPMS(3125)
Molybdenum	Mo	0.001	mg/L	ICPMS(3125)
Nickel	Ni	0.001	mg/L	ICPMS(3125)
Silver	Ag	0.0001	mg/L	ICPMS(3125)
Selenium	Se	0.001	mg/L	ICPMS(3125)
Sufur	S	0.1	mg/L	ICPAES(3120)
Tin	Sn	0.0001	mg/L	ICPMS(3125)
Vanadium	V	0.0001	mg/L	ICPMS(3125)
Zinc	Zn	0.001	mg/L	ICPMS(3125)
Non-Metals				
Chloride	Cl	1	mg/L	Colourimetric (DA 4500Cl-E)
Cyanide	CN total	0.01	mg/L	Digestion colourimetric (DA 4500CN-C)
Fluoride	F	0.05	mg/L	ISE (DA 4500F-C)
Other measured parameters				
pH (fluid)	pH	0.1	pH units	Meter (4500 H+)
Final pH of leachate	pH	0.1	pH units	Meter (4500 H+)

*For regulatory requirements, a useful resource to refer to is Contaminated Sites Management Series: Assessment levels for soils, sediment and water (February 2010).

Kinetic Methods

Longer-term kinetic tests complement static tests to reveal how quickly a sample will react in the field.

Basic kinetic test methods include leaching columns and humidity cells. Leaching columns have water added to a column of the crushed sample. The leachate is collected and analysed for a variety of parameters. In between wetting, the columns are warmed by heat lamps to mimic wetting and drying cycles in the field. The minimum recommended duration of leach column testing is **six months**. Humidity cells are similar but do not have a drying cycle. A vented lid is placed over the cell to maintain a humid atmosphere.

ChemCentre offers the following kinetic tests:

Kinetic Methods					
	Notation	Lowest reporting limit (LRL)	Units	Method/ Comments	Recommended duration
Leaching columns	-	-	Various	Wetting and drying under heat lamps to simulate field conditions. Similar to AMIRA Free Draining Leach Column test.	12 months (6 months minimum)
Humidity cells	HCT	-	Various	Sample wetted weekly and allowed to dry naturally. Follows ASTM D5744 Option B.	12 months (6 months minimum)
Acid Buffering Characteristic Curve	ABCC	0.5	kg H_2SO_4/tonne	Slow titration	8 hours
Kinetic Net Acid Generation NAG	$NAG_{Kinetic}$	0.1 pH, 1°C	°C and pH units	Addition of hydrogen peroxide; measurement of temperature and pH.	8 hours

Appendix A: Additional Services

ChemCentre is a 'one-stop shop' for chemical analysis and offers routine analyses for a wide range of analytes. We have leading-edge expertise in six key service areas and where required in accordance to Western Australian and Federal guidelines:

1. **Forensic Science**. Scientific services to police, coroners & agencies involved in justice administration.
2. **Environmental**. Monitoring, evaluation and advisory services on the state of the environment (including soil, air and water).
3. **Emergency & Crisis**. Emergency response to hazardous materials crises including fires, toxic spills, Chemical Biological and Radiological (CBR) incidents, and white powder and other contamination events.
4. **Bioanalysis**. Testing and analysis in numerous fields including drug discovery and bioprospecting.
5. **Occupational Health**. Industrial and workplace monitoring and testing to ensure health and safety compliance.
6. **Research and Development**. Scientific research either on a collaborative or contract basis.

Appendix B: More information on Acid Base Accounting

Acid Generation

The ABA tests are widely used to determine the potential for acid generation from mine waste. Variations exist on many of the individual tests in order to refine their predictive power. An early variation was to determine oxidisable sulphur rather than total sulphur. It is recognised that sulphates generate minimal acidity (exceptions being jarositic type sulphates) and their inclusion leads to over estimation of potential acidity. Sulphate sulphur is determined in a hydrochloric acid extract of the sample by inductively coupled atomic emission spectrometry (ICPAES). Most sulphates are soluble in acid. Sulphides are either insoluble in acid (e.g. pyrite) or if soluble, release the sulphide as hydrogen sulphide which is lost from the system leaving only sulphates in solution. The calculated acidity based on total sulphur is known as the Gross Acid Production Potential (GAPP). It is known as the modified GAPP if based on sulphide sulphur (sometimes noted as GAPP*). The GAPP value does not give an indication of lag time before acid is produced in the field.

Acid Neutralisation

The acid neutralisation capacity (ANC) test is subject to several errors. Acid is added to the sample which is then heated to dissolve carbonates. The unreached acid is then back titrated with sodium hydroxide to determine how much acid was consumed, from which the ANC is calculated. The acid volume and strength added is determined by the sample's "Fizz Rating "which is based on the reaction of several drops of acid on the dry sample. Underestimating the acid required will mean repeating the test with stronger acid. Over estimating the Fizz Rating will result in stronger acid than necessary being added to the sample. This may result in significant over estimation (up to a factor of five for a low ANC samples) due to dissolution of otherwise non reactive components of the sample.

Another error occurs when siderite ($FeCO_3$) is present in the sample. The carbonate will neutralize acid but the released ferrous iron will generate acidity on oxidation. This generated acidity exactly matches the acid neutralisation capacity from the carbonate. If not accounted for, this will result in over estimation of ANC. One variation of the ANC test adds two drops of hydrogen peroxide (modified Sobek method) to oxidise the ferrous iron prior to the completion of the back titration. Excessive hydrogen peroxide will lead to oxidation of sulphide sulphur which will generate acid reducing the measured ANC. If insufficient hydrogen peroxide is added, not all the iron will be oxidised. The method is claimed to handle up to 15% siderite content without oxidation of sulphides.

If the siderite content is considered to be high the sample is filtered before back titration to prevent oxidation of sulphides. The filtrate has hydrogen peroxide added and is heated to complete the oxidation prior to the back titration. This is a time consuming step that should only be needed if there is a high siderite concentration.

The inorganic carbon content is useful when evaluating the ANC. It is assumed to be carbonate carbon and the corresponding ANC can be calculated. This may confirm the observed ANC of the sample. The full ANC of the sample may not be realised in nature. The calculated stoichiometry of acid neutralisation is valid in strong acid environments.

In weakly acidic environments neutralisation efficiency is halved as the reaction stops at the bicarbonate stage rather than going to completion with evolution of carbon dioxide. For this reason the ANC should be equal to or greater than the maximum calculated acid production before the sample can be considered non acid forming (NAF). With large particles of ANC material this ratio will need to be increased further.

In the field the full ANC is often not realised. This can be due to coating of the neutralising particles with insoluble neutralisation products ("armouring"). Another cause is slow reaction rate of neutralisation of some minerals. Rapid acid generation can overwhelm the neutralisation process. Particle size has a very large influence on ANC. Finely divided particles have a much greater surface area allowing more rapid neutralisation. Additionally armouring is less of a problem. A method used to assess the effective ANC is known as Acid Buffering Characteristic Curve (ABCC). Acid is added in small increments to the sample over a period of hours until the pH reaches 2.5. The cumulative acid volume added allows calculation of the available ANC.

Net Acid Generation (NAG)

The NAG test involves addition of hydrogen peroxide to oxidize sulphides to sulphuric acid. Any neutralizing material present in the sample will react with the acid. In an ideal world the net acidity observed would agree with that calculated from the ABA accounting. There is usually a difference which will give an insight into the sample. Calculation of acidity based on sulphide content is subject to a number of errors. Firstly not all sulphides are acid generating and some actually consume acid. The factor for calculating acid production is based on one of several reactions involving pyrite oxidation which can result in seven different reactions. Each reaction has a different factor. Depending on the environment (oxidising, reducing, presence of manganese, existing pH) this factor can vary from zero to 125. Convention is to accept a value of 30.6 to convert percent sulphide to kg H_2SO_4/tonne.

Presence of metals such as copper can catalyse the breakdown of the hydrogen peroxide before it has oxidised all the sulphide. Heat also breaks down the peroxide. Multiple additions of peroxide are used to overcome this problem. Sequential NAG involves filtering off the sample supernatant and attacking the residue with fresh peroxide. This sequence is repeated until there is no longer acidity produced in the filtrate. This is a tedious method limited to research rather than routine evaluation.

Organic sulphur is included in the NAG even though it has minimal acid producing potential. In addition to this, the oxidation of organic material may also give rise to acidity. An extended boiling time of 4 hours can remove this acidity but this is laborious step that may also reduce the real acidity value.

Summary of ABA

From the above it can be seen that ABA involves many assumptions which can lead to an incorrect assessment. It is important to look at all the tests, including NAG, to make a valid assessment.

Glossary and Abbreviations

ABA – Acid Base Accounting

ABCC – Acid Buffering Characteristic Curve

AMD – Acid Metaliferous Drainage

ANC – Acid Neutralisation Capacity

ASLP – Australian Standard Leaching Protocol

CRC CARE – Cooperative Research Centre for Contamination Assessment and Remediation of Environments

DER – Department of Environmental Regulation

DMP – Department of Mines and Petroleum (WA)

DoW – Department of Water

EU – European Union

GAPP – Gross Acid Production Potential

ICPAES – Inductively coupled atomic emission spectroscopy

IEC – International Electrotechnical Commission

ISO – International Organisation for Standardisation

NAG – Net Acid Generation

NATA – National Accreditation Testing Authority

TLCP – Toxicity Characteristic Leachate Procedure

USEPA – United States Environmental Protection Agency

WA – Western Australia

WAMSI – Western Australian Marine Science Institute

XRD – X-ray Diffraction

Units

ms/m – Millisiemens/meter (Electrical conductivity)

kg H_2SO_4/tonne – Kilogram of sulphuric acid per tonne of material