SUMMARY REPORT: ACID MINE DRAINAGE TEST RESULTS FOR VALENCIA LEACHED RESIDUE

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Completed by: SGS Lakefield Research Africa (Pty) Limited

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1. BACKGROUND

A sample of leached residue from the Valencia project metallurgical testing was submitted to the SGS Lakefield Research Africa (Pty) Ltd Environmental Laboratory for the following testing:

- Acid base accounting (ABA) by the Modified (Lawrence) method
- Net acid generation (NAG) testing
- Mineralogical examination
- Total analysis
- Acid rain (ARLP) leach testing as per the South African Department of Water Affairs and Forestry (DWAF) minimum requirements

The following report provides a summary and brief interpretation of the testing completed.

2. SAMPLE RECEIPT AND PREPARATION

A ~1-kg sample of the leached residue with 3% by mass CaO added was received.

A 200 g portion was split from the crushed sample and milled to 80% passing 75 µm for use in the ABA test, NAG test and total analysis. A further portion of the material was submitted for mineralogical examination.

3. TEST DETAILS

Acid Base Accounting

Static ABA testing, using the Modified EPA (Lawrence) test was completed on the milled portion of the residue. This test is considered to be the most reliable method for determining a practical NP value (MEND project 1.16.3, July 1996).

The Modified ABA test is a static prediction test method, designed to examine the balance between the acid producing and acid consuming components of a sample. The method does not take into account the relative rates of acid production and consumption.

The acid production (AP) is calculated by assuming that all the sulphide sulphur present converts to sulphuric acid (sulphate) at a production of four moles of hydrogen ion per mole of pyrite oxidised. The sulphide content of a sample is determined by LECO furnace (induction furnace-infrared analysis). An initial total sulphur assay is completed, the oxidisable sulphur component is roasted off and a second LECO assay is performed to determine the residual sulphur content (defined as the sulphate concentration). The difference between the total and residual sulphur assays is defined as the sulphide sulphur concentration. As elemental sulphur (S^o) will also be oxidised and removed through the roasting process, where S^o is present in significant quantities this will result in overestimation of the sulphide sulphur content. The LECO method is also used to produce a carbonate analysis.

The neutralising potential (NP) is determined by treating a portion of the sample with excess hydrochloric acid (HCl) at ambient temperature for 24 hours. The amount of standardised HCl to be added initially is determined using a fizz test. Sufficient acidity for reaction is maintained by adding acid as necessary. After the acid treatment, any unconsumed acid is titrated with standardised base to pH 8.3. The calcium carbonate ($CaCO_3$) equivalent of the acid consumed is then calculated.

In addition to the sulphur speciation, carbonate analysis and NP determination, a paste pH test is also completed on the sample by mixing a portion with water at a low liquid to solid ratio and measuring the pH of the resulting paste.

The data obtained during the tests is then used to calculate the acid/base balances (net NP, NP/AP ratio) and classify the sample as either having a large potential to generate acidity, a potential for no acid generation or, if the results fall within a certain range, uncertainty with respect to net acid generation potential.

Net Acid Generation Test

The static NAG test was completed on the milled portion of the residue.

In the NAG test the sample reacts with hydrogen peroxide overnight to encourage complete oxidation of all oxidisable sulphur species. The available neutralising minerals also react. The excess hydrogen peroxide is then boiled off and the sample allowed to cool to room temperature.

The pH of resulting solution is measured before titration with sodium hydroxide to pH 4.5 and pH 7. The net result is determined to be either one of acid generation or not. The test can give neither rates of reaction, nor any information on resultant leachate quality. The final (NAG) pH and NAG values (where applicable) are reported.

Mineralogical Examination

A portion of the residue was submitted for mineralogical examination, including an X-ray diffraction (XRD) scan, optical microscopy on a thin section and a report. The XRD is used to determine the bulk mineral assemblage of the sample. The thin section microscopy is essential for the examination of sulphide and carbonate species.

Mineralogical examination is becoming an important diagnostic tool in understanding potential acid rock drainage. The amount and type of sulphides present and the availability of neutralising minerals will affect the rates and extent of acid generation. Neutralisation is provided primarily by carbonate minerals, however, some silicates and clays can also provide neutralisation. Knowledge of the type and abundance of various mineral phases is therefore important for the understanding of the acid generation potential.

Total Analysis

Total analysis for Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni P, Pb, Sb, Se, Si, Sn, Sr, Ti, U, V, Zn and Zr was completed on the milled portion of the residue by a combination of multi-acid and aqua regia digests and peroxide fusion with either inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) finish. F and Cl were analysed by fusion - ion selective electrode finish and acid digest - titrimetric finish, respectively.

Acid Rain Leach Procedure

The ARLP test was carried out on the residue as received. The objective of the ARLP test is to determine the leaching characteristics of solid waste materials under mild acidic rain conditions. The test is used to obtain information on the apparent potential for metals release. The ARLP test is well suited to mining operations.

A carbonic acid solution (carbonated deionised water) is diluted and the pH of the solution adjusted to pH 3.6 to 3.8 with dilute nitric acid. Two litres of the resultant solution is then added to a pre-determined 100 g dry weight of the solid sample. The sample is then agitated end over end for a period of 20 hours and the resultant solution is filtered prior to analysis. The DWAF recognise this test method as suitable for the characterisation of wastes in a mono-disposal setting.

The leachate was analysed for a standard suite of parameters, based on the DWAF Acceptable Risk Limits (ARL), as specified in the “Minimum Requirements for the Classification, Handling and Disposal of Hazardous Waste” documentation (Volume 1, second edition, 1998). The ARL is based on the median lethal dose (LC_{50}), which is defined as the amount of substance which will kill 50% of a given population of aquatic organisms under standard conditions (ARL = 0.1 x LC_{50}).

Table 1: Suite of analysis for leachates with quantification limits

Parameter	Limit (mg/L)	Parameter	Limit (mg/L)	Parameter	Limit (mg/L)
Ag	0.003	Hg	0.003	Se	0.02
Al	0.08	K	0.11	Sn	0.34
As	0.0005	Li	0.02	Sr	0.02
B	0.07	Mg	0.02	Ti	0.02
Ba	0.02	Mn	0.01	V	0.07
Be	0.02	Mo	0.05	U	0.0005
Bi	0.20	Na	0.05	Zn	0.17
Ca	0.05	Ni	0.05	Zr	0.05
Cd	0.0005	P	0.53	Cl	5
Co	0.12	Pb	0.002	F	0.1
Cr	0.001	S	0.60	Cr VI	0.005
Cu	0.02	Sb	0.31		
Fe	0.02	Si	0.37		

4. RESULTS

Acid Base Accounting

Table 2 summarises the results of the ABA testing. The full report and classification are contained in the appendix.

Table 2: Summary of Modified ABA Test Results

Sample ID	Paste pH	Sulphide S (%)	AP	NP	Net NP (NP-AP)	NP/AP
Leached residue	11.9	0.01	0.31	20.1	19.7	64.2

The residue sample has a low AP and a medium NP, which is largely not due to the presence of carbonate. Based on a review of the sulphur species concentration, carbonate value, the AP, NP and Net NP values and the NP/AP ratio, the sample is classified as having medium neutralising potential.

Net Acid Generation

Table 3 summarises the results of the NAG testing. The full report is contained in the appendix.

Table 3: Summary of NAG Results

Sample	NAG pH	$NAG_{4.5}$ value (kg/tonne $H2SO_4$)	NAG_7 value (kg/tonne $H2SO_4$)
Leached residue	10.3	-	-

At the end of the test the final pH of the NAG solution was over 7, resulting in a zero NAG value. A sample with a final NAG pH of >4.5 is considered to be non-acid forming.

Mineralogical Examination

Table 4 summarises the results of the mineralogical examination. The full report is contained in the appendix.

Table 4: Summary of Minerals Identified

Mineral	Approximate Quantity (%)
Quartz	20-50
Microcline	20-50
Plagioclase	10-20
Biotite	10-20
Chlorite	<3
Pyrite	<3

The lack of carbonate minerals and the relatively low sulphide mineral (pyrite) content confirm the results from the ABA and NAG tests. The neutralising potential observed in the ABA test is partly as a result of the microcline, plagioclase, chlorite and biotite which range from intermediate to very slow weathering with respect to acid neutralising capacity. Another contributing factor to the neutralising potential is very likely the lime added to the sample.

Total Analysis

The total analysis indicated that Al, K, Mg, Na and Si are the major elements present (>2%). Present in significant amounts are C, Ca, F, Fe, Mg, Mn, SO_4 and Ti (0.05-2%). Ba is present at a low level (0.02-0.05%). Cr, Cu, Li, Ni, P, Pb, Sr, U, V, Zn and Zr are present in trace amounts (<0.02%). All other elements were found to be present at levels below the quantification limit.

Acid Rain Leach Procedure

The results of the ARLP water leach are summarised and compared with the DWAF ARL in Table 5. The full report and certificate of analysis are contained in the appendix. Values exceeding the ARL are highlighted in **yellow**. Drinking water and aquatic ecosystem toxicity limits would typically be lower than the ARL and limits for mining effluents would usually be higher, although this is very much dependent on the individual mine licences.

As there is no ARL for U, this has been compared with the World Health Organisation (WHO) guidelines for drinking water quality (2004).

Table 5: ARLP leach test results

Parameter (mg/L)	ARL	Leached Residue	Parameter (mg/L)	ARL	Leached Residue	Parameter (mg/L)	ARL	Leached Residue
Final pH	-	6.0	**Fe**	9	<0.02	**Se**	0.26	<0.02
Ag	2	<0.005	**Hg**	0.022	<0.003	**Si**	180	2.1
Al	10	<0.08	**K**	43.5	1.9	**Sn**	2	<0.34
As	0.43	0.0047	**Li**	1.7	<0.02	**Sr**	-	0.18
B	2.7	<0.07	**Mg**	-	1.2	**Ti**	0.73	<0.02
Ba	7.8	0.31	**Mn**	0.3	**0.37**	**U**	0.015**	0.011
Be	1.2	<0.02	**Mo**	3.7	<0.05	**V**	1.3	<0.07
Bi	-	<0.2	**Na**	-	1.9	**Zn**	0.7	<0.17
Ca	-	110	**Ni**	1.2	<0.05	**Zr**	2	0.06
Cd	0.031	<0.0005	**P**	10	<0.53	**F**	1	0.15
Co	6.9	<0.12	**Pb**	0.1	<0.002	**Cl**	-	<5
Cr	4.7*	<0.001	**S**	-	7.9	**Cr VI**	0.02	<0.005
Cu	0.1	<0.02	**Sb**	1	<0.31			

*As Cr III
** WHO drinking water quality guideline

The residue increased the final pH of the leachate relative to the blank. As, Ba, Ca, F, K, Mg, Mn, Na, S, Si, Sr, U and Zr were found to present in the leachate above the quantification limit. Of these, Mn was found at a level above the DWAF ARL. U is found at a concentration close to the WHO drinking water quality guideline. All other parameters were found to be present at levels below the respective quantification limits.

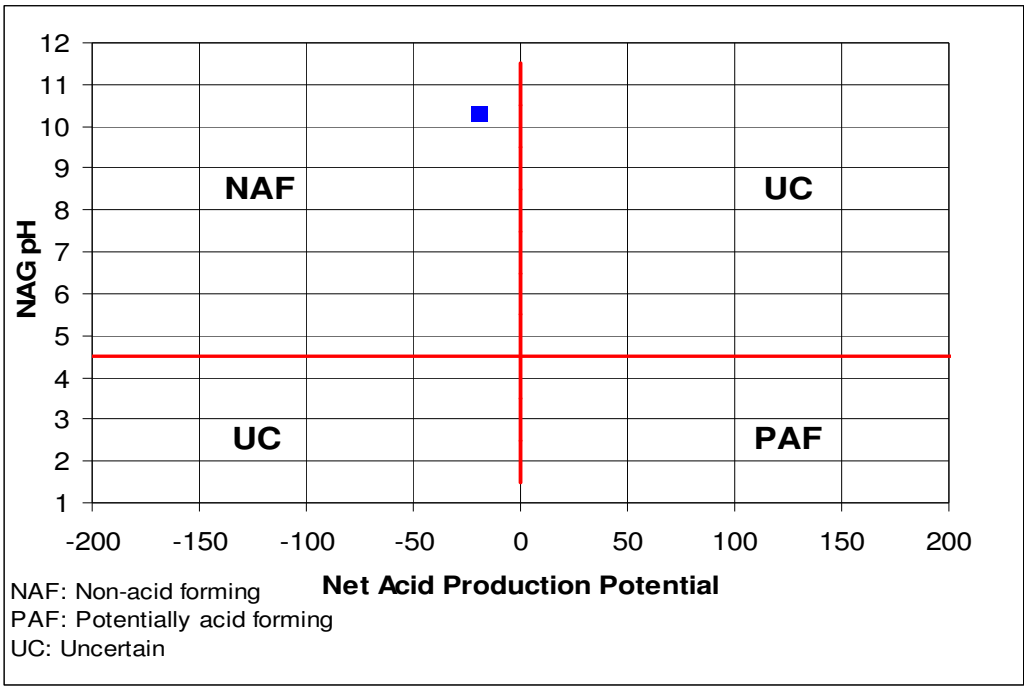
5. SUMMARY AND DISCUSSION

The leached residue sample showed low sulphide content with correspondingly low potential to generate acidic drainage. The neutralising potential is medium and is mostly not due to carbonate content. Thus the results of the ABA test, using the Modified method, indicate a medium neutralising potential.

The results obtained in the NAG test indicate that either insufficient sulphide sulphur is present to generate acidity or sufficient neutralising potential is available in the samples to neutralise any acidity produced. A sample is considered to be non-acid generating if the NAG pH is above 4.5.

If the NP, AP and NAG pH are considered and a plot made of net acid production potential (AP-NP) versus NAG pH (Figure 1 below), the sample falls within the non-acid forming area.

Figure 1: Classification plot



Generally, it is considered unlikely that a net acid leachate will be generated from the oxidation and leaching of materials having a sulphide content of less than 0.3%.

It is important to keep in mind that these test methods merely provide *an indication* of the potential for acid generation. Whether or not acidic drainage will result is largely a function of the mineralogy, the availability of each acid generating and neutralising mineral present, the physical characteristics of the material and the environmental setting. Additional testing will be required to establish the rate and extent of the formation of acid and depletion of neutralising minerals.

The mineralogical examination indicates that the sulphide content of the sample is low and is largely present as pyrite. A large part of the sample is composed of minerals which are considered to be neutralising, however the acid neutralisation is slow relative to that of carbonate mineral. Quartz, which is inert with respect to acid formation and neutralising capacity, makes up the balance of the sample. The lime addition to the sample is very likely a source of neutralising potential. The mineralogy of the sample corroborates the results obtained from the ABA and NAG tests.

The results from the ARLP leach testing (as per the DWAF method, performed in the laboratory) showed that only Mn leached at levels above the DWAF ARL and U leached at levels that may be of concern. Other parameters also leached and this will contribute to increased dissolved salts in any run-off that may occur from any storage facility. It is recommended that the leachate quality be compared to background levels and the limits specified in mine permits.

The above report is respectfully submitted by
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Sarah Newton
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APPENDIX

Laboratory Reports and Certificates of Analysis

(Enclosed as separate files in electronic version)