MINE WASTE MANAGEMENT
GREENROAD GROUP

301E Blenheim Road,
Christchurch 8041, New Zealand

T. +64 3 242 0221
E. admin@minewaste.com.au

# MEMORANDUM

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| ***Recipient:*** | Damian Spring – Santana Minerals |
| ***From:*** | Paul Weber – Mine Waste Management |
| ***Date:*** | 25 September 2023 |
| ***Cc:*** | Hamish McLauchlan – Santana Minerals; Ryan Burgess – Hydro Geochem Group; Rachel Rait – Mine Waste Management |
| ***Document Number:*** | J-NZ0233-002-M-Rev0 |
| ***Document Title:*** | Sampling and Analysis Plan for Geochemical Characterisation |

Mine Waste Management Ltd (MWM) has been engaged by Santana Minerals Limited (Santana) to undertake an assessment of environmental geochemistry effects for the proposed Bendigo-Ophir Gold Project (the Project). As part of the assessment, it is proposed that laboratory testing will be undertaken on materials that will be generated by the Project such as waste rock, ore, low grade ore (LGO), tailings, and legacy materials.

The purpose of the work is to understand the environmental geochemistry risks for waste rock and tailings including:

- Quantify the acidity generating characteristics and likely geochemical nature of the waste rock, LGO, ore, and tailings, and any geological and/or geochemical variations within these materials; and
- Determine the likely seepage/surface water quality that could be generated by these materials.

This memorandum describes the sample and analysis programme (SAP) that is required to provide data to understand the potential environmental geochemistry risks and to provide an explanation / justification of how samples were selected for the proposed analysis program.

## BACKGROUND

Bendigo-Ophir mineral resource covers 251 square kilometres in the Central Otago goldfields and has a resource estimate of 3 Moz gold @ 1.9g/t (0.25 g/t Au lower cut-off grade, no top-cut), which is based on drill results to December 2022. The Bendigo-Ophir resources occur in 4 deposits (Come in Time (CIT), Rise and Shine (RAS), Shreks (SHR), Shreks SE (SRE) that are inferred to extend in a northerly direction within the Rise and Shine Shear Zone (RSSZ), which hosts gold mineralisation over a recognised strike length of >20 km (Figure 1).

### Mine Plan

The mine plan for the Project, focusing on RAS is still advancing. For the purposes of this assessment, it is assumed to include the following components:

- An open pit, targeting the Rise and Shine deposit.

- A waste rock storage facility (WRS) / engineered landform (ELF) with an associated seepage/run-off water retention pond.
- Plant and processing area, where cyanide heap leaching may be used as part of the ore recovery process.
- A tailings storage facility (TSF) with an associated seepage collection system.
- A LGO stockpile area that is likely to be a long-term facility.
- An ore stockpile area.
- And other ancillary support services / structures (e.g., roads, water management infrastructure, etc)

Additional deposits (i.e., Come in Time, Shreks, Shreks SE) may be developed as part of future mine plans. A final decision has not been made on whether to proceed with these as part of the proposed mine plan. This SAP focuses on RAS.

**Geology**

The regional geology of Central Otago goldfields surrounding the Project consists of chlorite and biotite schists. RSSZ, a late metamorphic deformation zone (Cox et al., 2006), runs through the project area. The RSSZ occurs only in the footwall TZ4[1] schist in close association with the Thomsons Gorge Fault TGF), which cuts and truncates the Rise & Shine Shear Zone against the unmineralised TZ3[2] schist (Cox et al., 2006). There is no mineralisation associated with the TGF itself, and Au mineralisation had ceased by the time of formation of the TGF (c. 100 Ma) (Cox et al., 2006).

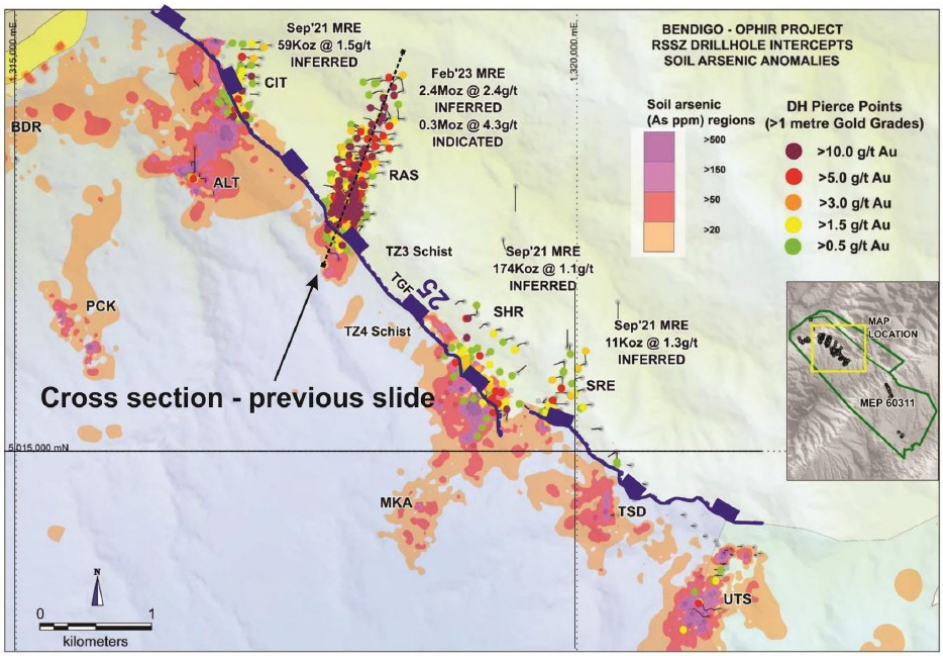


Figure 1. Plain view of the Bendigo-Ophir mineral deposits.

*Source: Allibone (2023)*

[1] *TZ4 = Textural Zone 4*
[2] *TZ3 = Textural Zone 3*

The hanging wall consists of the TZ3 chlorite zone greenschist facies schist, and the footwall is the TZ4 garnet-biotite-albite greenschist facies schist (Mortimer, 2000; Turnbull, 2000). Previous studies in the project area indicated most mineralisation was identified in the TZ4 zone, including pyrite, arsenopyrite, and gold (Cox et al., 2006). TZ3 schist has low or zero mineralisation. Field observations by Santana note that the fault zone is a visual boundary in core samples indicated by significant lithological changes in the RSSZ above TZ4.

Santana noted that TZ3 is higher in carbon compared to TZ4. Allibone (2023) notes the presence of ankerite and siderite alteration within the RSSZ as well as arsenopyrite, galena, and sphalerite where:

- Fe-bearing carbonates can compromise ANC tests and generate Fe-rich drainage from NAF materials; and
- The identified sulfide minerals could contribute to the risk of neutral metalliferous drainage (NMD) elevated in As, Fe, Pb, and Zn.

Such issues need to be considered as part of the SAP and additional testing is recommended to understand these hazards.

## SAMPLE AND ANALYSIS PLAN

### Sample Analysis

The following environmental geochemistry laboratory testing will be undertaken:

Table 1: Proposed analyses for the samples

| PHASE | TEST DESCRIPTION | NUMBER OF SAMPLES | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | ORE | LOW-GRADE ORE[1] | WASTE ROCK | TAILINGS | CRM | HISTORIC MATERIAL | TOTAL |
| PHASE 1 | Paste pH/EC (1:2) | 5 | 5 | 37[3] | 5 | 3 | 5 | 60 |
| | Rinse pH/EC (1:5)[4] | 5 | 5 | 37 | 5 | 3 | 5 | 60 |
| | ANC | 5 | 5 | 37[3] | 5 | 3 | 5 | 60 |
| | Total Sulfur / Total C | 5 | 5 | 37[3] | 5 | 3 | 5 | 60 |
| | NAG (pH and acidity) | 5 | 5 | 37[3] | 5 | - | 5 | 60 |
| | pXRF[2] | 5 | 5 | 37[3] | 5 | - | 5 | 60 |
| PHASE 2 | Shake Flask Extraction | 1 | 1 | 10 | 3 | - | 5 | 20 |
| | Column Leach (12 months) | - | 1 | 3 | 2 | - | - | 6 |
| | Detailed Mineralogy | 1 | 1 | 5 | 3 | - | 2 | 12 |

*1. Where LGO is defined as 0.25 – <0.5 g/t.*

*2. pXRF will be completed by Santana (on sample pulps).*

*3. Thirteen samples are from Drillhole MDD145, which has already been analysed by SGS Westport (total C pending).*

*4. Rinse pH to be undertaken on primary crush material rather than pulps.*

**Phase 1 Analysis Program**

The Phase 1 program is designed to provide supporting geochemical data to understand the geochemical nature of the materials (e.g., PAF[3] or NAF[4]).

**Acid base accounting** (ABA) and NAG testing: It is proposed that a comprehensive suite of tests be undertaken in Phase 1. This will include paste pH/EC, and rinse pH/EC, ANC, total S, NAG pH, and NAG acidity as detailed by AMIRA (2002).

It is understood that pXRF testing is being undertaken on sample pulps by Santana. pXRF should be undertaken on all samples tested as part of this scope of works, but it is not included in this SAP This data should be assessed to determine the geochemical abundance index (GAI) to understand potential elevated metals (e.g., Forstner et al., 1993). This is a general approach used to understand source hazard risk, where the hazards are assessed by column leach testing / shake flask testing to understand mobility.

All samples should be characterised by these methods, which is in alignment with other projects in the region. The samples that are proposed to be analysed are shown in Attachment A. The sample numbers are provided as a preliminary number until mine plans /geological models are finalised. Further testing might be proposed at a later date to ensure sufficient sample numbers and also spatial distribution.

The ore and tailing analysis plan should:

- Use the same sample interval for testing of the ore and the tailings.
- However, the tailings sample used should correspond to the portion of rock that has undergone a BLEG analysis (Bulk Leachate Extractable Gold), thus being the best representation of the tailings' composition.

The collection of historic materials is pending, and these samples need to be assessed at a later date.

**QA/QC**: The laboratory is expected to conduct its own quality assurance and quality control (QA/QC) procedures. In addition to this, we will include three Certified Reference Materials (CRM) in the analysis for ABA tests to ensure accuracy of the laboratory data. See Attachment C for further information.

Phase 1 results will be reviewed to select samples for Phase 2 testing, to support an informed analysis approach for the more complex and costly testing procedures.

**Phase 2 Analysis Program**

**Shake flask testing**: It is proposed to undertake shake flask testing (deionised water) to confirm what contaminants are mobile from materials. This will provide an analogue source term that can used in the water model, with application to ore, LGO, waste rock, tailings, and historic materials. The testing programme proposed is provided in Table 1.

[3] *PAF = Potentially acid forming*
[4] *NAF = Non-acid forming*

Oxic shake-flask testing is proposed. Anoxic testing is also proposed on tailings samples to understand any mobility of arsenic under reducing conditions. It may be better to do these tests at a bespoke laboratory.

**Column leach testing (Phase 2)**: it is proposed that 6 column leach tests (AMIRA, 2002) will be undertaken (12 months) to understand water quality trends. The waste rock samples will be obtained from the footwall, hanging wall, and RSSZ materials that are available.

**Detailed mineralogy** will be undertaken on a total of 12 samples as shown in Table 1. This will include analysis by XRD and mineral composition using SEM EDS. Such testing will confirm the proportions of minerals and also their composition (e.g., Fe content in ankerite).

**Sample Selection Rationale**

Santana has supplied a drillhole database containing samples available for geochemical characterisation. These samples, listed in a spreadsheet (MATGOL storage 15.6.23.xlsx), are part of a QA/QC program and are specifically derived from the mineralized zone, encompassing the RSSZ and TZ4 geological units. For sample selection purposes, it is assumed that previously tested samples from HoleID MDD145 are also accessible, as these represent the only samples from the hanging wall (TZ3). The following criteria was considered to determine the selection of samples:

- Spatial distribution of the samples.
- Arsenic and sulfur contents where available.
- Geological units.
- Au concentration and range classification for: ore, low-grade ore, and waste rock.

A representative cross section of the RAS project is depicted in Figure 2. Here, the hanging wall consists of the TZ3 geological unit situated above the mineralised area (TZ4 and the RSSZ). Depending on the mining method employed, particularly in the case of an open-pit mining approach, the TZ3 geological unit is expected to constitute a significant portion of the waste rock.

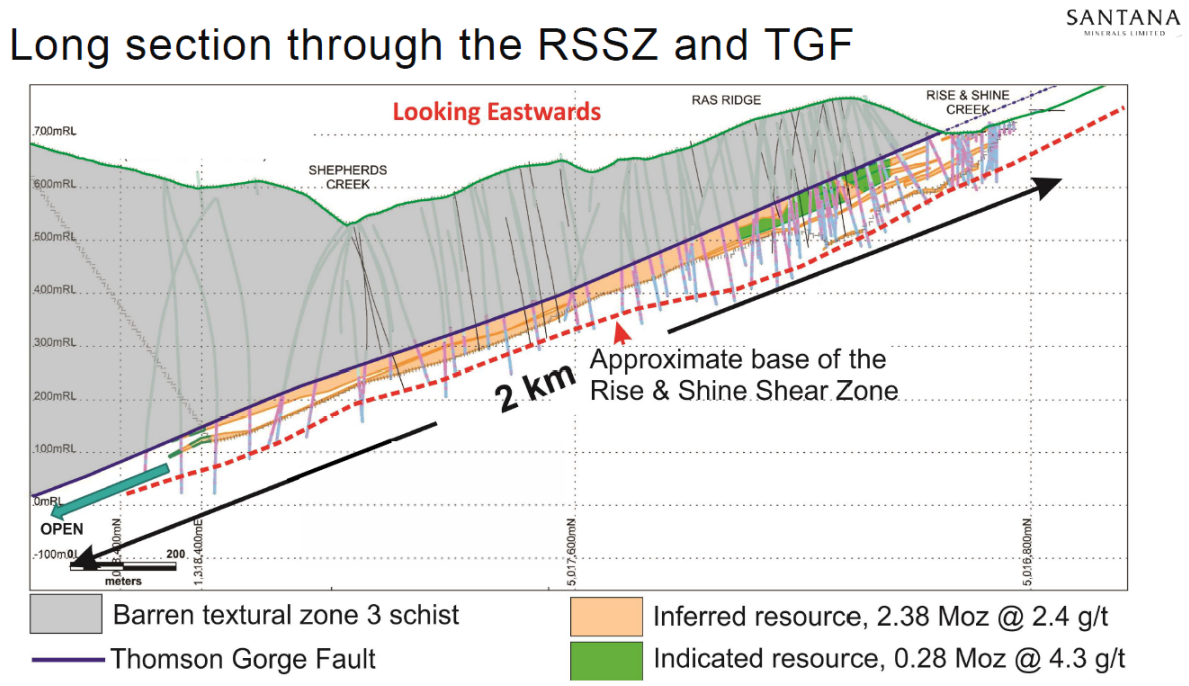


Figure 2. Cross section of the RAS mineral deposit.

*Source: Allibone (2023)*

Some of the samples that are available were additionally analysed using pXRF (136 samples) and Total Sulfur by LECO (33 samples), revealing a positive correlation between Arsenic (As) and Sulfur (S) in the RSSZ rocks (Figure 3). Based on the sample population available, samples for geochemical testing were selected based on:

- As and S contents within the rock. The distribution of As and S, as well as the corresponding classification, is presented in Attachment B.
- Spatial distribution of samples was also considered (Figure 5, Figure 5).

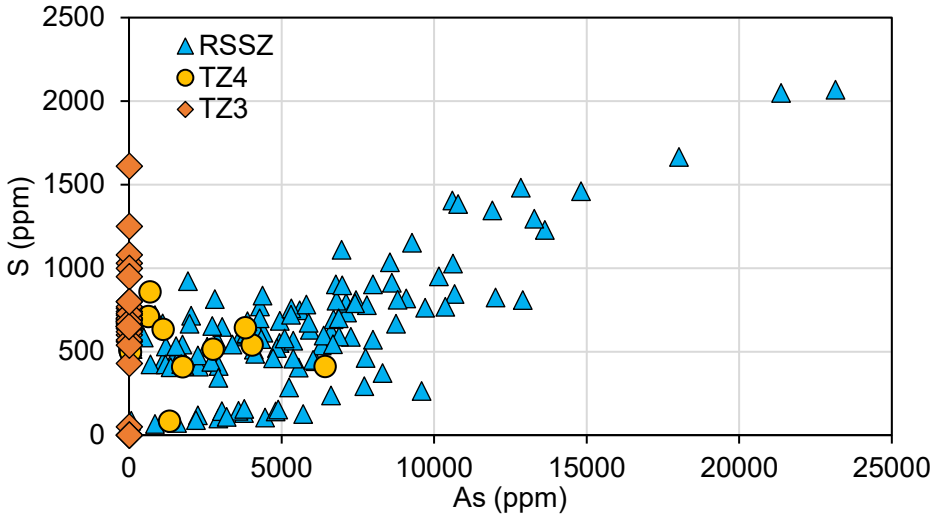


Figure 3. Arsenic and sulfur relationships.

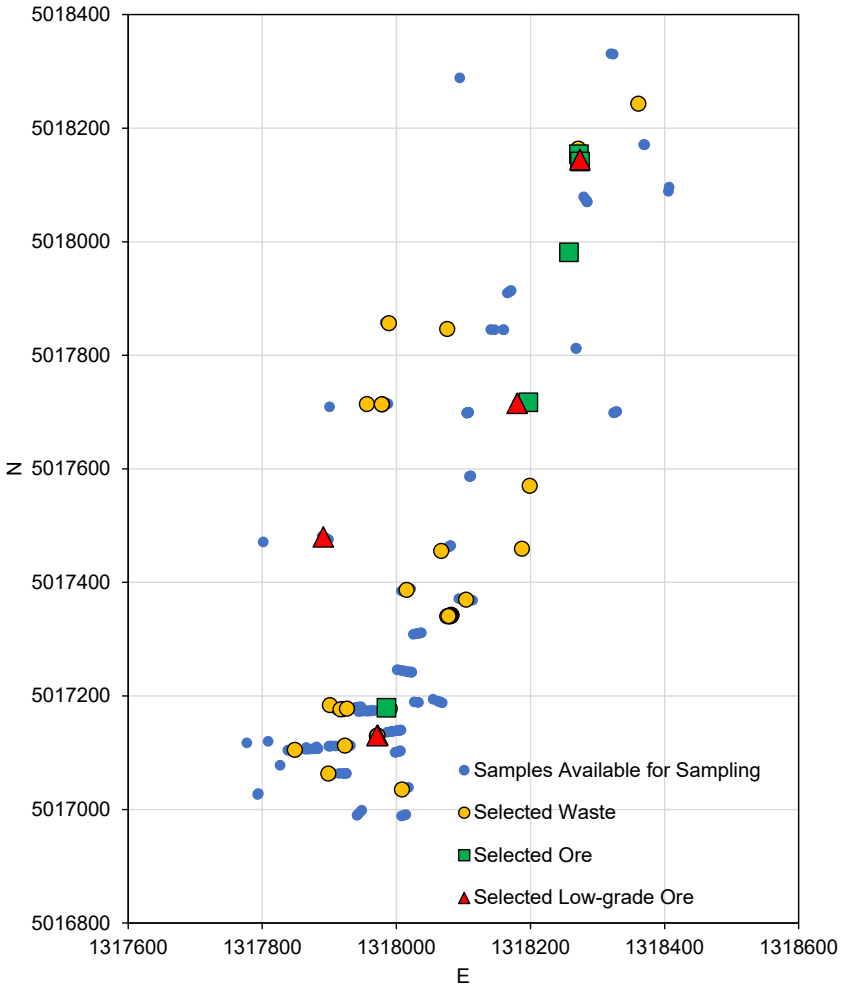


Figure 4. Plan view of the selected samples

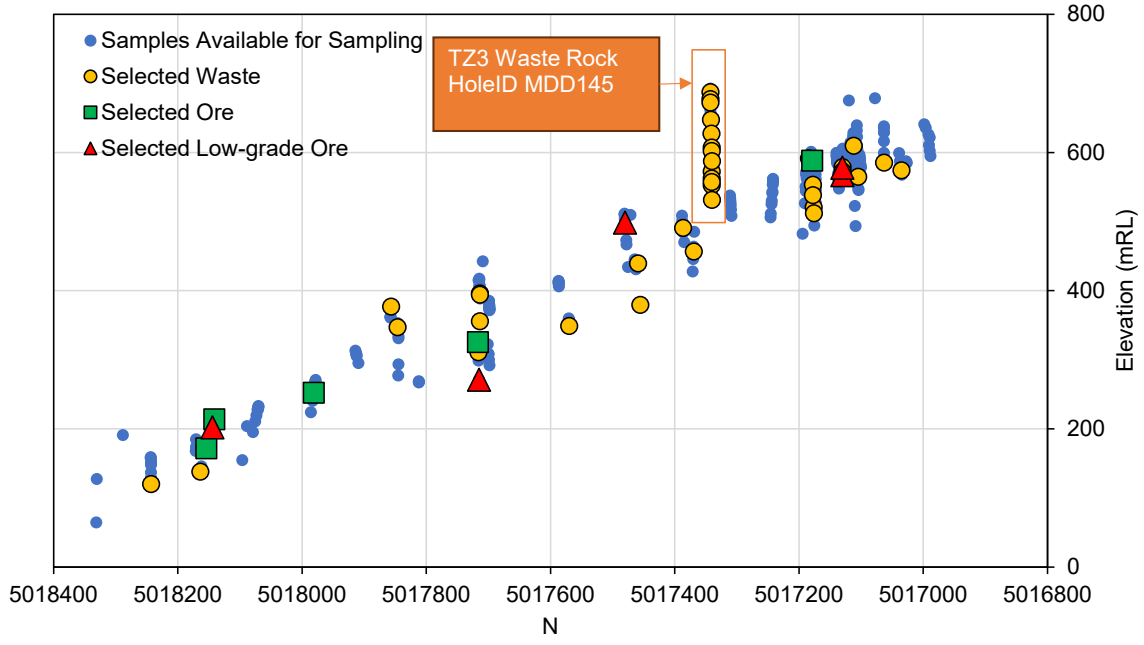


Figure 5. Lateral view of the selected samples

## SUMMARY

The samples proposed for testing are provided in Attachment A. Attachment B provides an explanation of arsenic and sulfur distribution and how this was used to developed categories (high to low concentrations) for sample selection.

## CLOSING REMARKS

Please do not hesitate to contact Paul Weber. at 027 294 5181 or paul.weber@minewaste.com.au should you wish to discuss this memorandum in greater detail.

Attachments: Attachment A – List of selected samples for testing
Attachment B – Arsenic and sulfur contents and categories
Attachment C – Certified Reference Materials for acid base accounting

## REFERENCES

Allibone, A., 2023. Mineralisation at the Rise and Shine Gold deposit, Bendigo District. Presentation for the Australasian Institute of Mining and Metallurgy (AusIMM) 2023 New Zealand Branch Conference, August 2023, Christchurch, New Zealand. 19 pp. https://santanaminerals.com/investors/reports.

AMIRA, 2002. ARD Test Handbook - Project P387A Prediction and Kinetic Control of Acid Mine Drainage. AMIRA International Limited. Melbourne, Australia.

Cox, L., MacKenzie, D. J., Craw, D., Norris, R. J., & Frew, R. (2006). Structure and geochemistry of the Rise & Shine Shear Zone mesothermal gold system, Otago Schist, New Zealand. New Zealand Journal of Geology and Geophysics, 49(4), 429-442.

Förstner, U., Ahlf, W., and Calmano, W., 1993. Sediment Quality Objectives and Criteria Development in Germany. Water Science & Technology, 28:307-316.

Mortimer, N., 2000. Metamorphic discontinuities in orogenic belts: example of the garnet-biotite-albite zone in the Otago Schist, New Zealand. International Journal of Earth Sciences 89: 295-306.

Turnbull, I.M., 2000. Geology of the Wakatipu area, scale 1:250000, Geological Map 18 (GNS Science: Lower Hutt).

# ATTACHMENT A –SELECTED SAMPLES FOR GEOCHEMICAL TESTING

| n | SAMPLEID | HOLEID | FROM | TO | Au_pref_ppm | As_pref_ppm | TOTAL S (ppm) | CLASSIFICATION | GeolUnit | S CATEGORY[2] | As CATEGORY[2] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | MG20754 | MDD081 | 211 | 212 | 0.44 | 885 | | Low-grade Ore | RSSZ | NA | As2 |
| 2 | MG20740 | MDD081 | 200 | 201 | 0.47 | 2,396 | | Low-grade Ore | RSSZ | NA | As3 |
| 3 | MG12535 | MDD044 | 369 | 370 | 0.37 | 1,818 | 414 | Low-grade Ore | RSSZ | S2 | As3 |
| 4 | MG15521 | MDD048R | 219 | 220 | 0.42 | 185 | | Low-grade Ore | TZ4 | NA | As2 |
| 5 | MG11578 | MDD021R | 355 | 356 | 0.45 | 678 | 860 | Low-grade Ore | TZ4 | S3 | As2 |
| 6 | MG16760 | MDD080 | 184 | 185 | 2.69 | 3,762 | 133 | Ore/Tailings | RSSZ | S1 | As3 |
| 7 | MG12577 | MDD044 | 401 | 402 | 2.78 | 233 | 648 | Ore/Tailings | RSSZ | S2 | As2 |
| 8 | MG12518 | MDD044 | 357 | 358 | 28.46 | 7,443 | 809 | Ore/Tailings | RSSZ | S3 | As3 |
| 9 | MG12196 | MDD031 | 301 | 302 | 2.49 | 23,154 | 2069 | Ore/Tailings | RSSZ | S4 | As4 |
| 10 | MG11512 | MDD021R | 298 | 299 | 1.09 | 2,750 | 516 | Ore/Tailings | TZ4 | S2 | As3 |
| 11 | MG13343 | MDD028 | 213 | 214 | 0.06 | 11 | | Waste | RSSZ | NA | As1 |
| 12 | MG13584 | MDD034 | 222 | 223 | 0.07 | 370 | | Waste | RSSZ | NA | As2 |
| 13 | MG14410 | MDD061 | 176 | 177 | 0.2 | 965 | | Waste | RSSZ | NA | As2 |
| 14 | MG15086 | MDD034R | 269 | 270 | 0.2 | 2,681 | | Waste | RSSZ | NA | As3 |
| 15 | MG16971 | MDD083 | 239 | 240 | 0.01 | 75 | 88 | Waste | RSSZ | S1 | As1 |
| 16 | MG18148 | MDD082 | 177 | 178 | 0.09 | 851 | 67 | Waste | RSSZ | S1 | As2 |
| 17 | MG16810 | MDD080 | 219 | 220 | 0.18 | 1,569 | 73 | Waste | RSSZ | S1 | As3 |
| 18 | MG20739 | MDD081 | 199 | 200 | 0.14 | 2,317 | | Waste | RSSZ | NA | As3 |
| 19 | MG20748 | MDD081 | 205 | 206 | 0.21 | 3,477 | | Waste | RSSZ | NA | As3 |
| 20 | MG16985 | MDD083 | 248 | 249 | 0.24 | 4,802 | 143 | Waste | RSSZ | S1 | As3 |
| 21 | MG27052 | MDD084 | 202 | 203 | 0.19 | 3,043 | 144 | Waste | RSSZ | S1 | As3 |
| 22 | MG12618 | MDD044 | 436 | 437 | 0.22 | 226 | 673 | Waste | RSSZ | S2 | As2 |
| 23 | MG17008 | MDD050 | 267 | 268 | 0.03 | 117 | 517 | Waste | RSSZ | S2 | As2 |
| 24 | MG11792 | MDD023R | 334 | 335 | 0.22 | 1,097 | 438 | Waste | RSSZ | S2 | As3 |
| 25 | MG13610 | MDD033 | 253 | 254 | 0.12 | 1,200 | 425 | Waste | RSSZ | S2 | As3 |
| 26 | MG13586 | MDD034 | 224 | 225 | 0.2 | 3,391 | 543 | Waste | RSSZ | S2 | As3 |
| 27 | MG15307 | MDD042 | 201 | 202 | 0.17 | 2,812 | 816 | Waste | RSSZ | S3 | As3 |
| 28 | MG19793 | MDD145 | 5 | 6 | | 9 | <50 | Waste | TZ3 | NA | As1 |
| 29 | MG19795 | MDD145 | 15 | 16 | | 10 | <50 | Waste | TZ3 | NA | As1 |
| 30 | MG19796 | MDD145 | 20 | 21 | | 8 | 430 | Waste | TZ3 | S2 | As1 |
| 31 | MG19801 | MDD145 | 45 | 46 | | 7 | 690 | Waste | TZ3 | S2 | As1 |

| n | SAMPLEID | HOLEID | FROM | TO | Au_pref_ppm | As_pref_ppm | TOTAL S (ppm) | CLASSIFICATION | GeolUnit | S CATEGORY[2] | As CATEGORY[2] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 32 | MG19805 | MDD145 | 65 | 66 | | 11 | 570 | Waste | TZ3 | S2 | As1 |
| 33 | MG19810 | MDD145 | 85 | 86 | | 11 | 690 | Waste | TZ3 | S2 | As1 |
| 34 | MG19817 | MDD145 | 120 | 121 | | 10 | 730 | Waste | TZ3 | S2 | As1 |
| 35 | MG19811 | MDD145 | 90 | 91 | | 10 | 800 | Waste | TZ3 | S3 | As1 |
| 36 | MG19814 | MDD145 | 105 | 106 | | 11 | 1250 | Waste | TZ3 | S3 | As1 |
| 37 | MG19819 | MDD145 | 130 | 131 | | 11 | 1080 | Waste | TZ3 | S3 | As1 |
| 38 | MG19821 | MDD145 | 140 | 141 | | 10 | 1000 | Waste | TZ3 | S3 | As1 |
| 39 | MG19825 | MDD145 | 161 | 162 | | 6 | 800 | Waste | TZ3 | S3 | As1 |
| 40 | MG19820 | MDD145 | 135 | 136 | | 11 | 1610 | Waste | TZ3 | S4 | As1 |
| 41 | MG11251 | MDD019R | 222 | 223 | 0.1 | 18 | | Waste | TZ4 | NA | As1 |
| 42 | MG11454 | MDD020 | 274 | 275 | 0.24 | 78 | | Waste | TZ4 | NA | As1 |
| 43 | MG11527 | MDD021R | 313 | 314 | 0.23 | 448 | | Waste | TZ4 | NA | As2 |
| 44 | MG16057 | MDD056 | 228 | 229 | 0.21 | 433 | | Waste | TZ4 | NA | As2 |
| 45 | MG16948 | MDD083 | 220 | 221 | 0.18 | 205 | | Waste | TZ4 | NA | As2 |
| 46 | MG17636 | MDD066 | 520 | 521 | 0.1 | 19 | 513 | Waste | TZ4 | S2 | As1 |
| 47 | MG20383 | MDD072 | 216 | 217 | 0.01 | 40 | 499 | Waste | TZ4 | S2 | As1 |

*1. – Note: Ore samples are also used as samples for the assessment of tailings (e.g., n= 47 + 5 = 52); historic materials (n=5) and the CRM (n=3) are not included in this table.*

*2. – Sulfur and arsenic categories are explained in Attachment B.*

# ATTACHMENT B – ARSENIC AND SULFUR CONTENTS AND CATEGORIES

**Data Analysis: pXRF**

According to arsenic pXRF analysis of the samples provided, the following can be drawn for each relevant geological unit:

- TZ3: from a group of 360 samples, 98.9 % are below 42 ppm and only 3 are above 100 ppm. (117 – 1,333 ppm).
- TZ4: from a group of 8,008 samples, 36% of the samples are above 100 ppm, 5.5% are above 1,000 ppm and 3 samples are above 10,000 ppm up to 21,000 ppm
- RSSZ: from a group 6,583 samples, 84% are above 100 ppm, almost half of the samples (49%) are above 1,000 ppm and 181 samples (2.75%) are above 10,000 ppm up to 54,417 ppm.

In summary TZ3 is generally low As (<50 ppm) relative to the mineralised geological units (TZ4 and RSSZ). Arsenic content (as measured by pXRF) are shown as a $Log_{10}$ plot in Figure 6. However, this geological unit is under sampled (given that it does not have any mineralisation) compared to the other two geological units. Further testing is recommended.

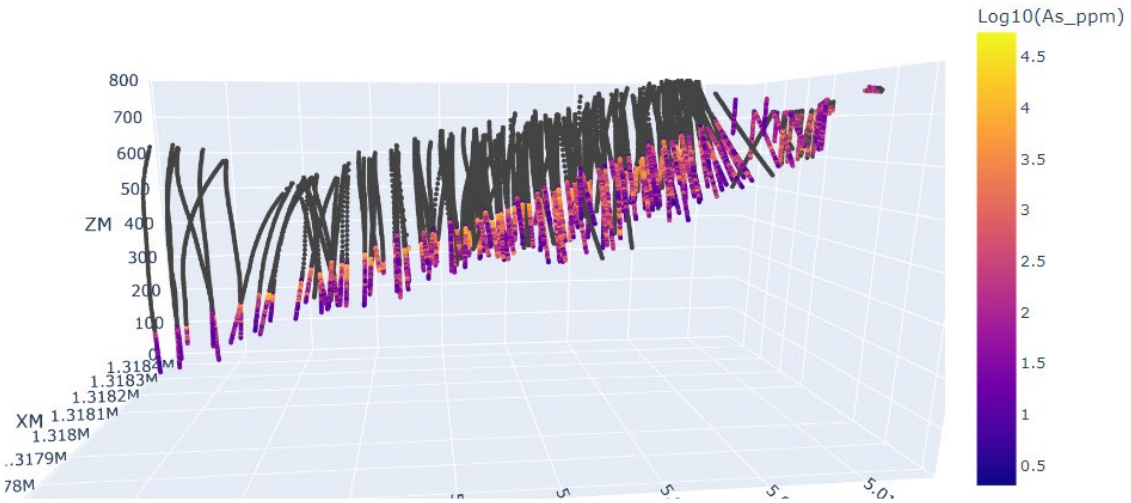


Figure 6. As concentrations $Log_{10}$ for the RAS mineral deposit. (grey colour indicates no data available)

An analysis was undertaken based on the arsenic (As) and sulfur (S) contents to understand the cumulative distributions (Figure 7). This analysis supported the selection of samples for various material types.

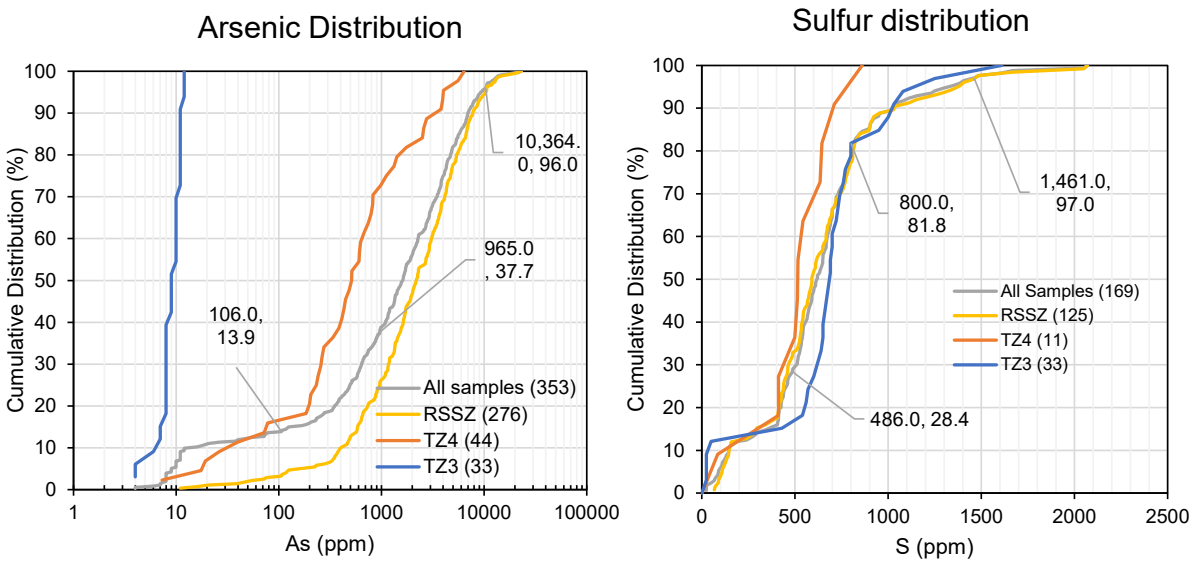


Figure 7. Arsenic and sulfur cumulative distributions.

Based on the total sample population, approximately 14% of the samples have arsenic (As) levels below 100 ppm, about 40% are below 1,000 ppm, and a significant proportion (96%) are below 10,000 ppm.

In regard to sulfur distribution, roughly 25% of the samples have sulfur levels below 400 ppm, while 85.9% are below 860 ppm, and a substantial proportion (97.4%) are below 1,483 ppm.

Arsenic and sulfur categories have been developed and are outlined in Table 2.

Table 2. Arsenic and sulfur categories

| CATEGORY LEVEL | ARSENIC RANGE (ppm) | SULFUR RANGE (ppm) |
|---|---|---|
| 1 – Low | 0 - 100 | 0 - 400 |
| 2 – Moderate | 100 - 1,000 | 400 - 800 |
| 3 – High | 1,000 - 10,000 | 800 - 1,400 |
| 4 – Very High | >10,000 | >1,400 |

*where the prefix As-1 refers to category 1 for arsenic; S-1 refers to category 1 for sulfur, etc*

**Sample Selection for Geochemical Testwork**

The categories are used to assess the different material types for the samples selected as part of this SAP development (Table 3). In instances where no sulfur concentration information was available, 'NA[5]' was used instead.

Key observations include:

- RSSZ:
    - RSSZ rocks are mostly classified as ore.

[5] *Not available*

- The most prevalent ore types are RSSZ-S2-As3 and RSSZ-NA-As3 (although no sulfur concentrations available).
- Waste rock from the RSSZ typically ranges from As3 to As2, suggesting the potential for waste rock from RSSZ to have concentrations typically exceeding 100 and 1,000 ppm As.
- As4 was only identified in ore samples in RSSZ, indicating that tailings could potentially exhibit high arsenic concentrations.

- TZ3:
  - The most common waste rock is TZ3-S2-As1 (n = 21).
  - All the TZ3 samples are classified as As1, however, it is recommended to have more samples tested from this unit, since the TZ3 represents a significant amount of waste rock, and the current sample set are only from one drillhole (MDD145).
- TZ4:
  - The majority of the TZ4 samples are classified as As2 (n =25) followed by As3 (n =12) and As1 (n=7).
  - Most of the samples are classified as S2 (n=9) and 1 sample as S1 and 1 as S3.

It's important to note that the analysed samples are a subset of samples selected for QA/QC purposes for determining ore resources (excluding MDD145). Therefore, the samples may not be representative of the overall composition of the RAS mineral deposit. Consequently, caution is advised when interpreting results, as they specifically relate to this subset of samples.

Table 3. Material Categories for As and S.

| GEOLOGICAL UNIT – AS CATEGORY – S CATEGORY | LOW-GRADE ORE | ORE | WASTE | GRAND TOTAL |
|---|---|---|---|---|
| RSSZ-NA-As1 | 2 | 1 | 3 | 6 |
| RSSZ-NA-As2 | 9 | 37 | 10 | 56 |
| RSSZ-NA-As3 | 17 | 62 | 11 | 90 |
| RSSZ-S1-As1 | | | 1 | 1 |
| RSSZ-S1-As2 | | | 1 | 1 |
| RSSZ-S1-As3 | 2 | 13 | 3 | 18 |
| RSSZ-S2-As1 | | 1 | | 1 |
| RSSZ-S2-As2 | | 5 | 2 | 7 |
| RSSZ-S2-As3 | 9 | 50 | 7 | 66 |
| RSSZ-S2-As4 | | 1 | | 1 |
| RSSZ-S3-As3 | | 13 | 1 | 14 |
| RSSZ-S3-As4 | | 9 | | 9 |
| RSSZ-S4-As4 | | 6 | | 6 |
| TZ3-NA-As1 | | | 3 | 3 |
| TZ3-S1-As1 | | | 1 | 1 |
| TZ3-S2-As1 | | | 21 | 21 |

| GEOLOGICAL UNIT – AS CATEGORY – S CATEGORY | LOW-GRADE ORE | ORE | WASTE | GRAND TOTAL |
|---|---|---|---|---|
| TZ3-S3-As1 | | | 7 | 7 |
| TZ3-S4-As1 | | | 1 | 1 |
| TZ4-NA-As1 | 1 | 1 | 3 | 5 |
| TZ4-NA-As2 | 6 | 10 | 7 | 23 |
| TZ4-NA-As3 | | 5 | | 5 |
| TZ4-S1-As3 | 1 | | | 1 |
| TZ4-S2-As1 | | | 2 | 2 |
| TZ4-S2-As2 | | 1 | | 1 |
| TZ4-S2-As3 | 2 | 4 | | 6 |
| TZ4-S3-As2 | 1 | | | 1 |
| **Grand Total** | **50** | **219** | **84** | **353** |

# ATTACHMENT C – CERTIFIED REFERENCE MATERIALS FOR ACID BASE ACCOUNTING

MINE WASTE MANAGEMENT
GREENROAD GROUP

301E Blenheim Road,
Christchurch 8041, New Zealand

T. +64 3 242 0221
E. admin@minewaste.com.au

# MEMORANDUM

| | |
|---|---|
| ***Document Title:*** | Certified Reference Materials for acid base accounting |
| ***Document Rev:*** | Rev0 |
| ***Date*** | 18 September 2023 |

The potential hazard for acid metalliferous drainage (AMD) typically involves laboratory based static geochemical testing, which includes acid base accounting (ABA) analyses such as acid neutralisation capacity (ANC), maximum potential acidity (MPA) and net acid generating (NAG) tests. These tests are regularly carried out by both mine sites and commercial laboratories. Such testing should include the use of certified reference materials (CRM) as one aspect of the quality assurance / quality control (QA/QC) programme.

CRM are one tool for assessing the accuracy of analyses conducted by laboratories. However, there is an acknowledgment that the development of certified reference materials requires careful consideration to ensure material homogeneity and material stability (Bleeze et al., 2022).

This memorandum provides background information on the use of certified reference materials for QA/QC purposes.

## GEOSTATS REFERENCE MATERIAL

Geostats Pty Ltd (Geostats) (Perth, Western Australia) provides a range of CRM. The CRM possess a nominal 40-micron particle size and are blended to achieve maximum homogeneity within the specific sample matrix. All CRM are tested thoroughly in the Geostats bi-annual laboratory survey, which involves assaying by multiple laboratories. Results are compiled into a comprehensive statistical report for each CRM. Table 1 provides a list of the CRM that has been supplied by Geostats and the referenced parameters.

Table 1. Certified reference materials.

| PRODUCT CODE | REFERENCED PARAMETER (%) | |
|---|---|---|
| GS310-10 | Total S | Total C |
| GS320-10 | Total S | Total C |
| GS917-4 | Total S | Total C |
| GS922-8 | Total S | Total C |

*Source: Geostats Pty Ltd List of certified reference materials (2023).*

Table 3 summarises the analysis data for the CRM samples shown in Table 1 as provided by Geostats. Certification can be found in Attachment A.

**Interlaboratory Testing**

A study conducted by Bleeze et al. (2022) assessed the suitability of six Geostats CRM for ANC and NAG analysis (this work can be found in Attachment B). Two interlaboratory test rounds were conducted on the following CRM: GS312-8, GS310-10, GS918-6, GS911-8, GS917-4, and GS312-3.

The first round of interlaboratory testing requested laboratories to use their usual methods. A second round of testing using the same set of samples, required the participating laboratories to use supplied standardised methods (Bleeze et al., 2022). Results indicated that irrespective of whether participating laboratories used their in-house methods, or the standardised methods, the mean ANC and NAGpH values were the same for both rounds of interlaboratory testing.

Table 2 shows the certification outcomes for ANC and NAGpH. Samples included ores, low-grade ores, and other mine materials covering a range of ANC (11.6 – 516 kg $H_2SO_4$/t) and NAGpH (3.4 – 8.3) values.

Overall, the results showed that interlaboratory reproducibility was favourable, allowing for certified ANC or NAGpH values to be developed. Hence, these materials can provide confidence in laboratory methodologies, which is essential for informed decision making processes in regards to the potential for AMD.

Table 2. ANC and NAGpH reference material properties.

| SAMPLE CODE | REFERENCED PARAMETER | UNITS | REFERENCE VALUE | CERTIFICATION LEVEL |
|---|---|---|---|---|
| GS312-8 | ANC | kg $H_2SO_4$/t | 11.6 | Reference Value |
| GS310-10 | ANC | kg $H_2SO_4$/t | 77.8 | Certified Value |
| GS918-6 | ANC | kg $H_2SO_4$/t | 516 | Certified Value |
| GS911-8 | NAGpH | pH unit | 8.29 | Certified Value |
| GS917-4 | NAGpH | pH unit | 3.43 | Certified Value |
| GS312-3 | NAGpH | pH unit | 4.48 | Certified Value |

*Source: Bleeze et al. (2022).*

*Blue samples have been included in the summary table below, which were used for this project.*

**Summary**

For reporting purposes, the Geostats data and Bleeze et al. (2022) data are presented in Table 3.

Table 3. Reference material properties - summary

| SAMPLE CODE | SULFUR (MEAN) | CARBON (MEAN) | ANC | NAGpH |
|---|---|---|---|---|
| | wt% | wt% | kg $H_2SO_4$/t | pH units |
| GS310-10 | 0.27 | 1.08 | 77.8 | - |
| GS320-10 | 0.27 | 0.59 | - | - |
| GS917-4 | 0.36 | 0.05 | - | 3.43 |
| GS922-8 | 0.08 | 0.45 | - | - |

Table 4. Certified reference material.

| PRODUCT CODE | SULFUR STATISTICS (%) | | | | CARBON STATISTICS (%) | | | | DESCRIPTION OF SOURCE / MATRIX | COLOUR DESIGNATION |
|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | Stdev | Count | 95% CI | Mean | Stdev | Count | 95% CI | | |
| GS310-10[1] | 0.27 | 0.03 | 64 | +/- 0.008 | 1.08 | 0.06 | 40 | +/- 0.019 | Copper gold ore | Very light gray |
| GS320-10[2] | 0.27 | 0.02 | 95 | +/- 0.004 | 0.59 | 0.03 | 75 | +/- 0.007 | High grade gold sulfide | Light gray |
| GS917-4[3] | 0.36 | 0.02 | 90 | +/- 0.004 | 0.05 | 0.01 | 68 | +/- 0.004 | Low grade transitional ore ex Laos | Yellowish gray |
| GS922-8[4] | 0.08 | 0.02 | 80 | +/- 0.004 | 0.45 | 0.03 | 69 | +/- 0.007 | Oxide andesite, Pilbara, WA | Moderate orange pink |

*Source: Geostats Pty Ltd List of certified reference materials (2023).*

*Certified certificate date:*

*1 - April-2010.*

*2 - April-2020.*

*3 - October-2017.*

*4 - October-2022.*

## CLOSING REMARKS

Please do not hesitate to contact Paul Weber at 027 294 5181 or paul.weber@minewaste.com.au should you wish to discuss this memorandum in greater detail.

Attachments: Attachment A – Certified Reference Material Certificates
Attachment B – Interlaboratory Testing Programme Paper

## REFERENCES

Bleeze, B., Qian, G., Romero, S., Stewart, W., and Schumann, R., 2022. Development of Certified Reference Materials for ANC and NAG Test Methods. 12th ICARD. 18-24 September 2022.

Geostats (2023). Information retrieved from http://www.geostats.com.au/. Date accessed: 21 August 2023.

**ATTACHMENT A – CERTIFIED REFERENCE MATERIAL CERTIFICATES**

# GEOSTATS PTY LTD

**Mining Industry Consultants**
**Reference Material Manufacture and Sales**

**Certified Sulphur and Carbon Reference Material Product Code**

# GS310-10

**Certified Control Values**

## Sulphur

| | |
|---|---|
| Sulphur Grade | 0.27 % |
| Standard Deviation | 0.03 % |
| Confidence Interval | +/- 0.008 % |

## Carbon

| | |
|---|---|
| Carbon Grade | 1.08 % |
| Standard Deviation | 0.06 % |
| Confidence Interval | +/- 0.019 % |


**CRM Details**

**Control Statistic Details**

Control statistics were produced from results accumulated in the April-2010 round robin. A total of 64 sulphur results and 40 carbon results were used to certify this material.

**Material Description**

This material is described as a Copper gold ore.

**Usage**

This product is for use in the mining industry as a reference material for monitoring and testing the accuracy of laboratory assaying.

**Preparation and Packaging**

All CRMs are dried in an oven for a minimum of 12 hours at 110°C. The dry material is then pulverised to better than 75 micron (nominal mean of 45 micron) using an air classifier. The material is then homogenised and stored in a sealed, stable container ready for final packaging.

Materials are statistically sampled from stores, then packaged into heat sealed, air tight, plastic or foil lined pulp packets ready for distribution. All packaging has been chosen to ensure minimal contamination from outside sources during shipment, use and storage.

**Assay Testwork**

All standards are tested thoroughly in the Geostats bi-annual laboratory survey. This involves assaying by multiple laboratories from around the world. Results are compiled into a comprehensive report detailing statistics for each standard. Assay distributions are checked and processed statistically, producing monitoring statistics for these standards. Materials are tested regularly to ensure stability and homogeneity.

**Stability**

This product remains stable in its original packaging, away from direct sunlight.

**Material Safety**

This product is not hazardous and non-toxic.

**20 Hines Road, O'Connor, Western Australia 6163**
**Phone : +61 8 9314 2566, Fax : +61 8 9314 3699**
**e-mail : pjh@geostats.com.au, srr@geostats.com.au**
**Website http://www.geostats.com.au**

GS310-10

Geostats Pty Ltd, Certified Sulphur and Carbon Reference Material, Product Code:

# GEOSTATS PTY LTD

**Mining Industry Consultants**
**Reference Material Manufacture and Sales**

**Certified Sulphur and Carbon Reference Material Product Code**

# GS320-10

**Certified Control Values**

## Sulphur

| | |
|---|---|
| Sulphur Grade | 0.27 % |
| Standard Deviation | 0.02 % |
| Confidence Interval | +/- 0.004 % |

## Carbon

| | |
|---|---|
| Carbon Grade | 0.59 % |
| Standard Deviation | 0.03 % |
| Confidence Interval | +/- 0.007 % |


**CRM Details**

**Control Statistic Details**

Control statistics were produced from results accumulated in the April-2020 round robin. A total of 95 sulphur results and 75 carbon results were used to certify this material.

**Material Description**

This material is described as a High grade gold sulphide.

**Usage**

This product is for use in the mining industry as a reference material for monitoring and testing the accuracy of laboratory assaying.

**Preparation and Packaging**

All CRMs are dried in an oven for a minimum of 12 hours at 110°C. The dry material is then pulverised to better than 75 micron (nominal mean of 45 micron) using an air classifier. The material is then homogenised and stored in a sealed, stable container ready for final packaging.

Materials are statistically sampled from stores, then packaged into heat sealed, air tight, plastic or foil lined pulp packets ready for distribution. All packaging has been chosen to ensure minimal contamination from outside sources during shipment, use and storage.

**Assay Testwork**

All standards are tested thoroughly in the Geostats bi-annual laboratory survey. This involves assaying by multiple laboratories from around the world. Results are compiled into a comprehensive report detailing statistics for each standard. Assay distributions are checked and processed statistically, producing monitoring statistics for these standards. Materials are tested regularly to ensure stability and homogeneity.

**Stability**

This product remains stable in its original packaging, away from direct sunlight.

**Material Safety**

This product is not hazardous and non-toxic.

**20 Hines Road, O'Connor, Western Australia 6163**
**Phone: +61 8 9314 2566 | Email: info@geostats.com.au**
**Website: www.geostats.com.au**

GS320-10
Geostats Pty Ltd, Certified Sulphur and Carbon Reference Material, Product Code:

# GEOSTATS PTY LTD

**Mining Industry Consultants**
**Reference Material Manufacture and Sales**

**Certified Sulphur and Carbon Reference Material Product Code**

# GS917-4

**Certified Control Values**

## Sulphur

| | |
|---|---|
| Sulphur Grade | 0.36 % |
| Standard Deviation | 0.02 % |
| Confidence Interval | +/- 0.004 % |

## Carbon

| | |
|---|---|
| Carbon Grade | 0.05 % |
| Standard Deviation | 0.01 % |
| Confidence Interval | +/- 0.004 % |


**CRM Details**

**Control Statistic Details**

Control statistics were produced from results accumulated in the October-2017 round robin. A total of 90 sulphur results and 68 carbon results were used to certify this material.

**Material Description**

This material is described as a Low grade transitional ore ex Laos.

**Usage**

This product is for use in the mining industry as a reference material for monitoring and testing the accuracy of laboratory assaying.

**Preparation and Packaging**

All CRMs are dried in an oven for a minimum of 12 hours at 110°C. The dry material is then pulverised to better than 75 micron (nominal mean of 45 micron) using an air classifier. The material is then homogenised and stored in a sealed, stable container ready for final packaging.

Materials are statistically sampled from stores, then packaged into heat sealed, air tight, plastic or foil lined pulp packets ready for distribution. All packaging has been chosen to ensure minimal contamination from outside sources during shipment, use and storage.

**Assay Testwork**

All standards are tested thoroughly in the Geostats bi-annual laboratory survey. This involves assaying by multiple laboratories from around the world. Results are compiled into a comprehensive report detailing statistics for each standard. Assay distributions are checked and processed statistically, producing monitoring statistics for these standards. Materials are tested regularly to ensure stability and homogeneity.

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**Material Safety**

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**e-mail : pjh@geostats.com.au, srr@geostats.com.au**
**Website http://www.geostats.com.au**

GS917-4

Geostats Pty Ltd, Certified Sulphur and Carbon Reference Material, Product Code:

# GEOSTATS PTY LTD

**Mining Industry Consultants**
**Reference Material Manufacture and Sales**

**Certified Sulphur and Carbon Reference Material Product Code**

# GS922-8

**Certified Control Values**

## Sulphur

| | |
|---|---|
| Sulphur Grade | 0.08 % |
| Standard Deviation | 0.02 % |
| Confidence Interval | +/- 0.004 % |

## Carbon

| | |
|---|---|
| Carbon Grade | 0.45 % |
| Standard Deviation | 0.03 % |
| Confidence Interval | +/- 0.007 % |


**CRM Details**

**Control Statistic Details**

Control statistics were produced from results accumulated in the October-2022 round robin. A total of 80 sulphur results and 69 carbon results were used to certify this material.

**Material Description**

This material is described as an Oxide andesite, Pilbara, WA.

**Usage**

This product is for use in the mining industry as a reference material for monitoring and testing the accuracy of laboratory assaying.

**Preparation and Packaging**

All CRMs are dried in an oven for a minimum of 12 hours at 110°C. The dry material is then pulverised to better than 75 micron (nominal mean of 45 micron) using an air classifier. The material is then homogenised and stored in a sealed, stable container ready for final packaging.

Materials are statistically sampled from stores, then packaged into heat sealed, air tight, plastic or foil lined pulp packets ready for distribution. All packaging has been chosen to ensure minimal contamination from outside sources during shipment, use and storage.

**Assay Testwork**

All standards are tested thoroughly in the Geostats bi-annual laboratory survey. This involves assaying by multiple laboratories from around the world. Results are compiled into a comprehensive report detailing statistics for each standard. Assay distributions are checked and processed statistically, producing monitoring statistics for these standards. Materials are tested regularly to ensure stability and homogeneity.

**Stability**

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**Material Safety**

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**Website: www.geostats.com.au**

GS922-8
Geostats Pty Ltd, Certified Sulphur and Carbon Reference Material, Product Code:

**ATTACHMENT B – INTERLABORATORY TESTING PROGRAMME PAPER**

# Development of Certified Reference Materials for ANC and NAG Test Methods

**Belinda Bleeze[A], Gujie Qian[A], Stuart Romero[B], Warwick Stewart[C], and Russell Schumann[C*]**

[A] College of Science and Engineering, Flinders University, Bedford Park SA 5042, Australia
[B] Geostats Pty Ltd, O'Connor, WA 6163, Australia
[C] Environmental Geochemistry International Pty Ltd, Balmain NSW 2041, Australia
**Presenting author: Russell.Schumann@geochemistry.com.au*

## ABSTRACT

*Current practice in determining potential liability from acid rock drainage (ARD) usually involves static geochemical testing, which frequently includes acid neutralisation capacity (ANC) and net acid generating (NAG) tests. The tests are routinely conducted by mine site and commercial laboratories providing services to the mining industry and consultants. However, unlike many analytical methods, ANC and NAG tests often lack appropriate quality control (QC) measures, including routine analysis of reference materials.*

*There have been numerous methods or modifications for the determination of ANC. Each modification to the procedure may result in a different measured ANC value for a particular sample. While it appears there is less variation in the methods used for the NAG test, there are numerous factors which may affect the result and lead to variations between laboratories. These circumstances suggest that reference materials should be developed and routinely used for QC purposes in ANC and NAG testing.*

*In this study, we examined commercially available reference materials to see if they would be suitable for ANC and NAG analysis. Samples included ores, low-grade ores and other mine materials covering a range of ANC (12 – 516 kg $H_2SO_4$/t) or NAGpH (3.4 – 8.3) values. Two interlaboratory test programmes were conducted to assess their suitability as reference materials for ANC and NAG analysis. The first round of interlaboratory testing requested laboratories to use their usual methods. A second round of testing using the same set of samples, required the participating laboratories to use supplied "standardised" methods.*

*The results showed that whether participating laboratories used their in-house methods, or the standardised methods, mean ANC and NAGpH values were the same for both rounds of interlaboratory testing. However, when all laboratories used the same test methods, the variation of results was reduced.*

*The test programme enabled us to apply certified NAGpH values (3.4, 4.5 and 8.3) and certified ANC values (78 and 516 kg $H_2SO_4$/t) to five reference materials. Results for a sixth sample gave higher interlaboratory variation in the measured ANC and provided a reference value of 12 kg H2SO4/t as guide, but the variation (RSD 23%) was too high to certify this value.*

*These certified reference materials (CRM) will be available for laboratories undertaking ANC and NAG tests to improve QC protocols and increase end user confidence in the results from laboratories using these materials.*

**Keywords:** ANC; NAG, interlaboratory testing, certified reference materials

## 1.0 INTRODUCTION

The development of any mining project will invariably include an assessment of the environmental impact of the project. A major component of this assessment is to determine if any acid rock drainage (ARD) is likely to result from the project and to investigate management options. Current practice in determining ARD liability usually includes static geochemical tests, which essentially assess the balance between potential acid generating processes in materials (waste rock, ore and tailings) handled during the mining/processing operations and the acid neutralising potential of these materials.

A number of static geochemical test methods are routinely used to assess this balance between acid generating and acid neutralising capacity, including acid neutralisation capacity (ANC), or neutralising potential (NP), and the net acid generating (NAG) test. These methods are now widely used by mining operations and consultants for ARD assessment. The tests are routinely conducted by mine site laboratories, and commercial laboratories providing services to the mining industry and consultants. Additionally, regulatory bodies frequently recommend the use of these methods as a part of any ARD assessment, further broadening their use by the industry.

A number of methods have been proposed over the years to assess the ANC of mine rock samples. Unlike the concentration of a particular element in a sample, e.g., total sulphur content, the measured neutralising capacity may vary, depending on how the measurement was conducted. Laboratory analyses of ANC should be viewed as a guide to the magnitude of the effective acid neutralisation potential rather than a precise and accurate measurement. Consequently, there have been numerous methods or modifications of various methods reported in the literature for the determination of ANC. Each modification to the procedure is likely to result in a different measured ANC value for a particular sample. Consequently, laboratories and consultants often make errors in analysis and interpretation of the results. The most common error made in the Sobek or modified Sobek ANC test is the incorrect addition of acid, usually because of improper interpretation of the Fizz test (Price 2009). There may also be problems with the relationship between laboratory ANC measurements and effective neutralising potential if different methods are used for different phases of the ARD programme.

Unlike ANC tests, reported methods for NAG testing appear to be restricted to that specified in the ARD Test Handbook (AMIRA 2002). Despite the uniformity of the method used for evaluation of NAG, several authors have identified areas of concern about the reproducibility of the measurement. Charles et al. 2015 noted that for samples with excess of carbonate, very high pH can be measured post boil often 1.5 – 2 pH units above the pre-boil pH. Results showed that any inconsistency in the timing of pH measurement could change the NAGpH

value for this type of sample. The authors also noted that the change in pH could also impact the solubility of certain elements, potentially affecting results of NAG liquor analysis.

Parbhaker-Fox et al. 2018 examined the NAGpH test using a number of samples from Savage River mine, Tasmania. They examined several variables in the test and how they affect the final NAGpH value. Variables included reaction time, heating time, heating temperature, cooling time and peroxide strength. They noted all these factors can affect the final NAGpH. They also recommended that a standard reference material should be developed and used for QC purposes during NAGpH testing.

These studies suggest that both the ANC and NAG procedures used to obtain any set of reported results need to be described in some detail to enable users to fully interpret results. They also suggest that reference materials covering a range of ANC and NAG values and based on specific and detailed methods, would be useful to enable laboratories to develop appropriate QC procedures which are currently lacking for many ARD methods.

This paper describes results from a research programme designed to develop method specific reference standards for ANC and NAG test methods which cover the range of ANC and NAG values and material types required by laboratories undertaking ARD geochemical analyses.

## 2.0 METHODOLOGY

### 2.1 Project Outline

It is generally recognised that important aspects of development of reference materials which should be considered are characterisation of material homogeneity, material stability and determination of reference values, usually through interlaboratory studies (Ellison et al. 2001). To meet these criteria, it was thought prudent to investigate the use of existing reference materials which had demonstrated homogeneity and stability, so that the programme could progress immediately to the interlaboratory study stage. To this end, reference materials available through Geostats Pty Ltd (Perth Western Australia), which had been certified for Total S and Total C content, and which represented relevant matrices for ARD characterisation i.e., mining ores and rock, were selected for use in development of ARD reference materials.

The process of development of reference materials for ANC and NAG testing was undertaken using the following steps:

1. Twelve certified reference materials were selected from the Geostats catalogue based on Total S and C values to cover the range of likely ANC and NAGpH values required. These materials were characterised (ANC, NAG, Quantitative X-ray Diffraction (QXRD), multi-element bulk assay) and from these results, six were selected for interlaboratory testing.
2. Round 1 interlaboratory study using in-house methods.
3. Analysis of Round 1 interlaboratory study including variations in the methods employed.

4. Analysis of parameters in ANC and NAG test methods (sensitivity analysis) to assess sources of variability in Round 1 results.
5. Development of "standardised" methods based on the results of sensitivity analysis.
6. Round 2 interlaboratory study using "standardised" methods.
7. Analysis of results to assign reference values.

### 2.2 Interlaboratory Test Programme

The interlaboratory test programme consisted of two rounds of testing, with inhouse methods used for the first round and standardised methods in the second. Each laboratory was provided with six different certified reference materials (CRM) supplied by Geostats. 60 samples (3 x 10 replicates for ANC testing and 3 x 10 replicates for NAG testing) were dispatched to each participating laboratory. The sample numbering schema was randomised. The participating laboratories comprised a combination of domestic and international commercial laboratories, all of which were assigned a reference number to ensure confidentiality when reporting results.

Statistical analysis was conducted on the results reported in both rounds of the interlaboratory testing. ANC results were converted to the universal unit of kg $H_2SO_4$/t prior to statistical analysis. The data was analysed using a one-way ANOVA function in Excel, to test for variation and significance in the data set. Outliers were identified using the inter-quartile range (IQR) with the upper and lower limits and confirmed through a GRUBBS analysis. Analysis included the calculation of the mean, standard deviation, 95% confidence interval (CI) and the relative standard deviation (RSD).

The inhouse methods reported by participating laboratories were used to highlight discrepancies between different methods and the potential impact of these differences on the final result. Round one had twelve laboratories participate, while round two had nine participating laboratories.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Test Material Characterisation

Following testing of the 12 Geostats CRMs, 3 samples were selected which covered a range of ANC values (17 - 536 kg $H_2SO_4$/t) and another 3 samples which covered a range of NAGpH values (3.4 – 8.4) (Table 1). XRD analysis of GS312-8 showed the presence of trace calcite, supported by a total carbon assay of 0.03% (carbonate ANC = 2 kg $H_2SO_4$/t) suggesting that silicate minerals provide most of neutralising capacity in this material. XRD and carbon analysis indicate the majority of ANC in GS310-10 and GS918-6 is derived from dolomite in these materials. Acid-base analysis results for sample GS911-8 reveals an excess of neutralising capacity, which is supported by NAG test results which gave a high NAGpH indicative of excess carbonate. XRD analysis showed the presence of pyrite, but also significant dolomite and calcite. XRD and sulphur speciation analysis of sample GS917-4 showed that all the sulphur present in this material was present as pyrite. Carbon analysis, supported by XRD indicated a lack of carbonate minerals in this material, consistent with the low ANC and low

NAGpH. Carbon and sulphur analysis together with XRD analysis demonstrated a lack of carbonate minerals in GS312-3, with almost all the total S present as chalcopyrite. The moderately low NAGpH (4.9) of this sample probably reflects the lack of carbonate neutralising minerals and the presence of chalcopyrite rather than pyrite as the dominate sulphide. Oxidative dissolution of chalcopyrite will generate only half the acidity of pyrite to pH 4.5, with the remaining acidity arising from copper hydrolysis when titrated to pH 7 (Stewart et al. 2003).

**Table 1. Acid-base analysis and NAG test results for materials used in interlaboratory testing**

| Sample Code | Acid-Base Analysis | | | | NAG Test | | |
|---|---|---|---|---|---|---|---|
| | Total S (%) | ANC (kg $H_2SO_4$/t) | NAPP (kg $H_2SO_4$/t) | ANC/MPA | NAGpH | $NAG_{(pH\ 4.5)}$ (kg $H_2SO_4$/t) | $NAG_{(pH\ 7.0)}$ (kg $H_2SO_4$/t) |
| GS312-8 | 0.75 | 17 | 6 | 0.7 | 4.3 | 0.4 | 8 |
| GS310-10 | 0.27 | 77 | -69 | 9.3 | 9.6 | 0 | 0 |
| GS918-6 | 0.31 | 536 | -527 | 57.0 | 8.9 | 0 | 0 |
| GS911-8 | 1.76 | 98 | -44 | 1.8 | 8.4 | 0 | 0 |
| GS917-4 | 0.36 | 3 | 8 | 0.3 | 3.4 | 5 | 10 |
| GS312-3 | 0.47 | 11 | 3 | 0.8 | 4.9 | 0 | 3 |

### 3.2 Round 1 Interlaboratory Test Results

Twelve laboratories participated in the initial interlaboratory study. These included 8 commercial laboratory services with 7 of these located within Australia and one laboratory in Canada. In addition to the commercial laboratories, there was one specialised ARD-laboratory and one University-based laboratory (both Australian), and two mine laboratories (Indonesia and PNG) which also participated in the test programme.

The results for ANC and NAG testing are summarised in Tables 2 and 3 respectively. For ANC testing, the two samples with higher ANC, almost exclusively contributed by carbonates (principally dolomite), provided good interlaboratory reproducibility with 5% RSD in each case. However, for the material with the lowest ANC, principally derived from dissolution of silicate minerals, the interlaboratory reproducibility was significantly poorer (RSD of 27%).

Interlaboratory reproducibility for NAGpH was acceptable (<10%) for the two samples where the final NAGpH was either acidic (3.4) or alkaline (8.4). However, for the material where the final NAGpH was close to 4.5, the RSD increased to 15%, suggesting that where there is a more even balance between the acid-generating and acid-neutralising properties of the sample, it is likely that greater variance in the NAGpH values reported by different laboratories will occur.

**Table 2. Results for Round 1 interlaboratory ANC testing**

| Sample Code | Mean ANC (kg $H_2SO_4$/t) | Std Dev (kg $H_2SO_4$/t) | RSD (%) | 95% CI (kg $H_2SO_4$/t) | Ave. Intra-Laboratory RSD (%) | Count[1] |
|---|---|---|---|---|---|---|
| GS312-8 | 10 | 2.7 | 27 | 0.54 | 7 | 103 |
| GS310-10 | 78 | 4.2 | 5 | 0.83 | 2 | 102 |
| GS918-6 | 519 | 25 | 5 | 4.8 | 1 | 108 |

1. Number of results used in the analysis after exclusion of outliers. A total of 113 results were received for GS312-8 and GS918-6 and 112 results for GS310-10.

**Table 3. Results for Round 1 interlaboratory NAG testing**

| Sample Code | Mean NAGpH | Std Dev | RSD (%) | 95% CI | Ave. Intra-Laboratory RSD (%) | Count[1] |
|---|---|---|---|---|---|---|
| GS911-8 | 8.4 | 0.6 | 7 | 0.11 | 2 | 113 |
| GS917-4 | 3.4 | 0.3 | 9 | 0.06 | 4 | 103 |
| GS312-3 | 4.4 | 0.6 | 15 | 0.13 | 3 | 103 |

1. Number of results used in the analysis after exclusion of outliers. A total of 113 results were received for each sample.

### 3.3 Sensitivity Analysis and Method Refinement

As a part of the first round interlaboratory test programme, participating laboratories were asked to provide details of the in-house method used for each analysis. Tables 4 and 5 provide summaries of the main test parameters used for ANC and NAG testing respectively. Given the apparent considerable variability in the way the ANC and NAG tests were conducted, the results showed surprisingly good interlaboratory reproducibility. However, for some samples (low silicate-based ANC, NAGpH close to 4.5) interlaboratory reproducibility was not satisfactory. Consequently, testing was conducted whereby certain test parameters were varied, and the effect of these variations on the measured ANC or NAGpH were evaluated. For ANC, these parameters included fizz rating assignment (including the final pH after digest), digestion/heating time, digestion/heating temperature, and the cooling time. For NAG testing, the initial pH of hydrogen peroxide, reaction time, heating temperature and cooling time were examined for their influence on the measured NAGpH.

Tables 6 and 7 show the results of experiments used to investigate the influence of test parameters on the measurement of ANC and NAGpH/NAG values respectively. The results of these tests suggest that for determination of ANC, the amount of acid added (evaluated by the final digest solution pH) and digest temperature appear to have the most influence on the result. The NAG test appears to be more robust, except for specific samples where a NAGpH near to 4.5 can be influenced by initial pH of the peroxide used for the test, or where the sample contains organic substances for which changes in the post-reaction heating temperature and time can significantly alter the result.

**Table 4. Test parameters reported for Round 1 interlaboratory ANC testing**

| Parameter | Range of values |
|---|---|
| Sample weight | 1 – 5 g |
| HCl used for digest | 0.1 – 1 M, 4 – 75 mL |
| Digest temperature | 80 – 140 °C |
| Digest time | 2 minutes – 3 hours |
| Fizz rating | 0 - 4, 1 - 5 |
| Final pH control[1] | 0.8 – 1.5, <1.9, <3 |

1. These represent the pH range or upper limit at which the test result is accepted. If these values are not met, the test is repeated using a different fizz rating.

**Table 5. Test parameters reported for Round 1 interlaboratory NAG testing**

| Parameter | Range of values |
|---|---|
| Sample weight | 1 – 2.5 g |
| $H_2O_2$ used for digest | 15%, 100 – 250 mL |
| Digest temperature | Ambient and then 150 – 250 °C |
| Digest time | Typically, overnight at ambient temperature and then 30 minutes to 2 hours at elevated temperature |
| Initial peroxide pH control[1] | None, adjust to pH 4.5, 4.6, 4.8 – 5.1, 4.9 – 5.2 |

1. Hydrogen peroxide is often stabilised by addition of various stabilisers some of which are acidic.

**Table 6. Results of sensitivity tests for ANC analysis**

| Parameter | Range of values evaluated | Result |
|---|---|---|
| Final pH | 0.8 – 3.3 | When the final pH was <2, ANC measurements were similar. Where the final pH was 3 or above, there was a significant decrease in ANC. |
| Digest time | 1 – 3 h | Negligible effect |
| Digest temperature | 80 – 100 °C | The effect seems to be sample dependent. Measured ANC was constant across this temperature range for some samples and increased with temperature for others. |
| Cooling time | 2 – 60 h | Negligible effect |

**Table 7. Results of sensitivity tests for NAG analysis**

| Parameter | Range of values evaluated | Result |
|---|---|---|
| Peroxide pH | 2.8 – 5.5 | The effect seems to be sample dependent. For a sample with a NAGpH near 4.5 the low peroxide pH sample gave lower measured NAGpH and slightly higher NAG values |
| Reaction time | 8 – 48 h at ambient temperature | Negligible effect |
| Post reaction heating temperature | 100 °C for 2 h – 250 °C for 2 h | The effect seems to be sample dependent. There was negligible effect on a sample lacking organic C, but for a sample with significant organic C, NAGpH increased and NAG values decreased with temperature likely because of mineralisation of organics by reaction with peroxide. |
| Cooling time | 24 and 48 h | Negligible effect |

### 3.4 Round 2 Interlaboratory Test Results

Participating laboratories from round 1 of the interlaboratory test programme were invited to participate in a second round of testing using "standardised" methods derived from the results of the sensitivity analysis experiments described above. In summary, the ANC methodology used for this round of interlaboratory testing included:

- 2 g of sample digested for 2 h at 80 °C
- The final pH of the digest solution should be ≤2, adjust fizz rating to achieve this as required
- Titrate to pH ≈5, add 2 drops 30% $H_2O_2$ and then titrate to pH 7

For NAG testing, the method used for this round of interlaboratory testing included:

- 2.5 g of sample reacted with 250 mL of 15% $H_2O_2$ adjusted to pH 4.6 – 5.5
- React at ambient temperature for a maximum of 24 h
- Heat for 2 h at a gentle simmer/boil
- Cool for a maximum of 16 h and titrate to pH 4.5 and then 7

Nine of the 12 labs that participated in the first round of interlaboratory testing also contributed to the second-round test programme. The results for ANC and NAG testing are summarised in Tables 8 and 9 respectively.

There was little variation observed between the two rounds for low ANC material. The absolute standard deviation is consistent between both rounds, with the RSD 3% smaller in the second round. Despite the small reduction in RSD between the first and second rounds, at 23% RSD, the variation in interlaboratory test results is still significant. Participating laboratories typically reported a limit of detection of 1 kg $H_2SO_4$/t, although this may overestimate method sensitivity. Nevertheless, a value of 12 kg $H_2SO_4$/t is sufficiently above the method detection limit, such that measurement reproucibility should be less than 10% RSD. The measured Total C in this sample is 0.03 % and, assuming all of this carbon is present as carbonate C, suggests a carbonate ANC of 2 kg $H_2SO_4$/t. This indicates that the majority of the ANC of approximately 12 kg $H_2SO_4$/t is likely to be derived from silicate minerals. Dissolution of silicate minerals, unlike carbonate minerals, is unlikely to be quantitative during the ANC digest procedure. As such, the measured ANC is expected to be relatively sensitive to the method parameters used. Under these circumstances, an absolute standard deviation in interlaboratory results of under 3 kg $H_2SO_4$/t is reasonable and, in the context of acid base accounting, unlikely to be significant.

For the other two samples, interlaboratory reproduciblity using the “standardised” ANC method was excellent with RSD of 3% for both samples.

Using the “standardised” NAG procedure, the interlaboratory reproducibility for analysis of NAGpH of the three samples examined gave RSD of less than or equal to 6%, indicating excellent reproducibility. The use of hydrogen peroxide in which the pH has been standardised to between 4.6 and 5.5, appears to have resulted in significant improvement in the reproducibility of the NAGpH for sample GS918-6, which gave a NAGpH of 4.5. The result was similar to the round 1 results, but with the RSD reduced from 15% in the first round to 4% in the second round.

**Table 8. Results for Round 2 interlaboratory ANC testing**

| Sample Code | Mean ANC (kg $H_2SO_4$/t) | Std Dev (kg $H_2SO_4$/t) | RSD (%) | 95% CI (kg $H_2SO_4$/t) | Ave. Intra-Laboratory RSD (%) | Count[1] |
|---|---|---|---|---|---|---|
| GS312-8 | 12 | 2.7 | 23 | 0.68 | 5 | 66 |
| GS310-10 | 78 | 2.7 | 3 | 0.61 | 1 | 76 |
| GS918-6 | 516 | 15 | 3 | 3.4 | 0.5 | 76 |

1. Number of results used in the analysis after exclusion of outliers. A total of 76 results were received for each sample.

**Table 9. Results for Round 2 interlaboratory NAG testing**

| Sample Code | Mean NAGpH | Std Dev | RSD (%) | 95% CI | Ave. Intra-Laboratory RSD (%) | Count[1] |
|---|---|---|---|---|---|---|
| GS911-8 | 8.3 | 0.3 | 4 | 0.08 | 2 | 76 |
| GS917-4 | 3.4 | 0.2 | 6 | 0.05 | 2 | 76 |
| GS312-3 | 4.5 | 0.2 | 4 | 0.04 | 1 | 76 |

1. Number of results used in the analysis after exclusion of outliers. A total of 76 results were received for each sample.

### 3.5 Comparison of Round 1 and 2 Interlaboratory Test Results

Figure 1 shows a comparison between the average ANC values measured during the first and second rounds of interlaboratory testing. The error bars represent the 95% CI calculated from all values obtained for the sample, excluding outliers. This comparison shows minimal difference of the average value and 95% CI obtained for both rounds. These results suggest that the measurement of ANC for these materials is not particularly method dependent, which is important for reference materials and supporting their use in QC for ANC analysis.

Figure 2 shows the average NAGpH values obtained from the Round 1 and Round 2 interlaboratory studies for the three NAG materials tested. The values presented exclude outliers and the error bars represent the 95% CI of the means. These figures show that there was minimal difference in the average NAGpH measured in the two rounds of testing. These results suggest that the NAG test is reasonably robust, so that any minor differences in the way the test was conducted by the various participating laboratories, did not appear to result in significant variation in the measured NAGpH. However, **these results do suggest adjusting the pH of the hydrogen peroxide prior to reaction will likely improve method reproducibility.**

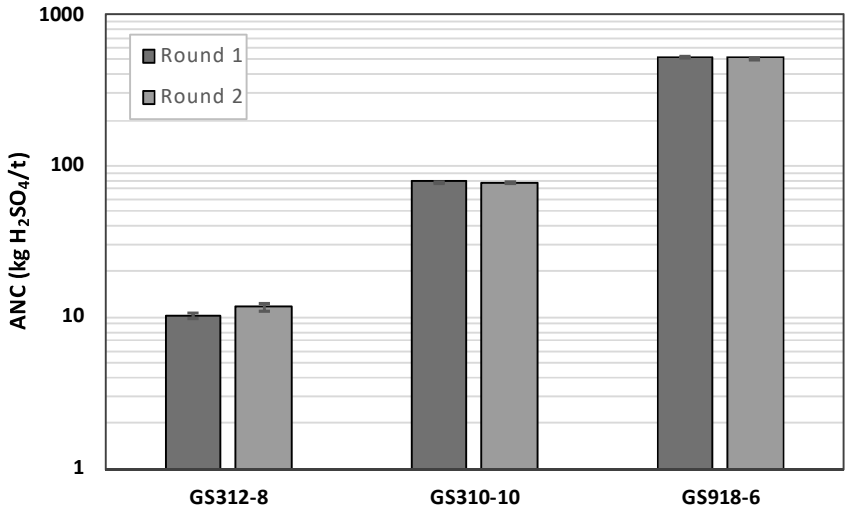


**Figure 1. Average ANC values obtained from round one and round two of interlaboratory testing. Error bars show the 95% confidence interval.**

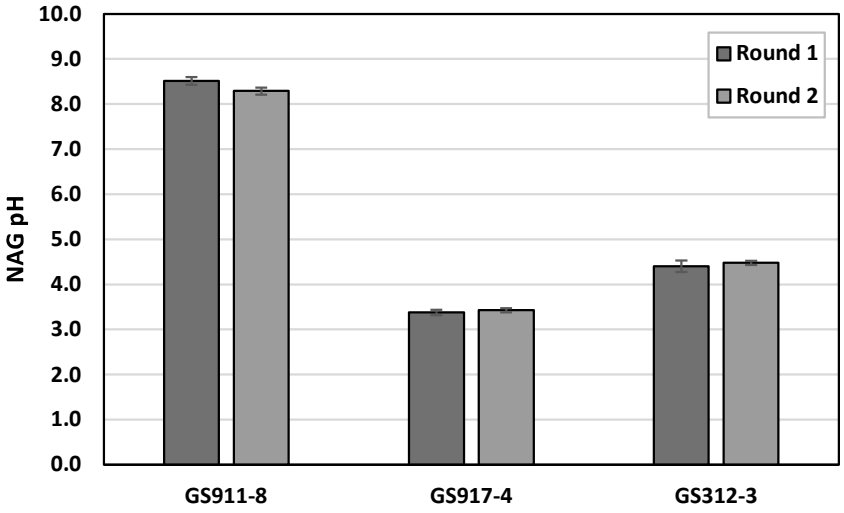


**Figure 2. Average NAGpH values obtained from round one and round two of interlaboratory testing. Error bars show the 95% confidence interval.**

## 4.0 CONCLUSIONS

The certification outcomes for the three ANC and three NAG materials tested are shown in Table 10 below. For all but one of the samples evaluated, interlaboratory reproducibility was sufficiently good to provide certified values for ANC or NAGpH. For the lowest ANC sample GS312-8, the interlaboratory variance was such that a certified value was not assigned and for this material a reference value was assigned.

These materials will now be made available to analysts wishing to improve QC protocols for ANC and NAG analyses, and their use should add to the reliability of these measurements which form an important part of ARD risk assessment of mined materials.

**Table 10. Properties of reference materials**

| Sample Code | Referenced Parameter | Units | Reference Value | Certification Level |
|---|---|---|---|---|
| GS312-8 | ANC | (kg $H_2SO_4$/t) | 11.6 | Reference Value |
| GS310-10 | ANC | (kg $H_2SO_4$/t) | 77.8 | Certified Value |
| GS918-6 | ANC | (kg $H_2SO_4$/t) | 516 | Certified Value |
| | | | | |
| GS911-8 | NAGpH | pH unit | 8.29 | Certified Value |
| GS917-4 | NAGpH | pH unit | 3.43 | Certified Value |
| GS312-3 | NAGpH | pH unit | 4.48 | Certified Value |

## 5.0 ACKNOWLEDGEMENTS

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