

TECHNICAL MEMORANDUM

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TO Melinda Brand, Rio Tinto Iron Ore

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MESA H – GEOCHEMICAL CHARACTERISATION

1.0 INTRODUCTION

Golder Associates Pty Ltd (Golder) was engaged by Rio Tinto Iron Ore (RTIO) to assist with geochemical characterisation of tailings material from the Mesa H project. Mesa H is a pisolitic Channel Iron Deposit (CID) within the RTIO Robe Valley operations, in the Hamersley Ranges area of the Pilbara Region of Western Australia.

RTIO (2016a, 2016b) analysed the S distribution of Mesa H ore (TP, geozone 50, 51, 53, 56, and 59) from the drill hole assay data of over 18,500 intervals located within the proposed final pit shell. The assessment showed that 0.2% of the ore samples had S > 0.1wt% and only 0.05% of the samples had S > 0.3wt%, suggesting that ore, and by extension the tailings, would be unlikely to be a source of acid and metalliferous drainage (AMD).

A metallurgical tailings slurry sample representative of the tailings to be produced by the processing of the Mesa H ore was provided by RTIO for a geochemical characterisation program, to provide information of use in facility design and closure planning, as well as the regulatory approvals process.

2.0 GEOCHEMICAL CHARACTERISATION TEST PROGRAM

RTIO provided a Mesa H tailings slurry sample, which was characterised using the following test program:

- Sulfur speciation (total S, sulfide S using the chromium reducible sulfur (S_{Cr}) method, and SO_4 by the hydrochloric acid (HCl) digestion method)
- Acid neutralising capacity (ANC)
- Net acid generation (NAG) testing
- Carbon speciation (total C, inorganic C, organic C)
- Multi-element solid assay including forms of nitrogen.

The tailings solids also underwent the following extraction test work and associated multi-element assays:

- Australian standard leaching procedure (ASLP) with deionised water at a solid to liquid (S:L) ratio of 1:20 using a bottle roll procedure (12 h contact time)
- Deionised water leach at a S:L ratio of 1:2 using a bottle roll procedure (12 h contact time)

- Deionised water leach at a S:L ratio of 1:2 using a bottle roll procedure (12 h contact time) with leachate filtered through a 0.2 µm filter
- Deionised water low contact leach at a S:L ratio of 0.75:1 using a bottle roll procedure (12 h contact time). A low contact ratio was achieved by conducting a series of bottle roll leaches. In the initial leach, deionised water and solids were mixed at a S:L ratio of 1:2 and agitated for a period of 12 hours. On completion of this first step, the leachate was separated and used in a second 12-hour leach on a fresh split of the sample material (again at an S:L ratio of 1:2). The process was repeated for four cycles. At the end of multiple steps, the same volume of liquid had been in contact with a larger mass of the solid than would have been practicable in a single test.
- Saline leach using a low salinity (2 g/L) and a high salinity (10 g/L) at a S:L ratio of 1:2 using a bottle roll procedure (12 h contact time)
- Hydrogen peroxide solution at a S:L ratio of 1:100.

The leaching test work was designed to provide insights into the relative solubility of elements of environmental concern under variable scenarios, with the saline leaching and the low contact leaching tests likely most relevant to field conditions likely to prevail at Mesa H.

The tailings liquid fraction underwent the following tests:

- pH/EC determination
- Acidity/alkalinity testing
- Multi-element analysis.

All test work was conducted by Australian Laboratory Services (ALS).

3.0 GEOCHEMICAL CHARACTERISATION RESULTS

3.1 Tailings Solids General Characterisation

Acid base accounting test work results together with S and C speciation data are presented in Table 1. The data show that the sample can be classified as non-acid forming (NAF) due to the negligible total S concentration of <0.01 wt%S, and NAG pH > 4.5. The paste pH was circum-neutral and the sample was non-saline, with an EC of 78 µS/cm. A small amount of C was detected in the sample (0.33 wt%C), with C speciation suggesting that all the carbon was associated with organic material (potentially lignite, which is occasionally associated with the ore at Robe Valley operations).

Table 1: Static testwork results for Mesa H tailings solid sample

Static Testwork ABA Results		
pH Value (1:5)	pH Unit	7.7
Electrical Conductivity (1:5)	µS/cm	78
NAG pH	pH Unit	7.6
ANC as kg H ₂ SO ₄ /t	kg H ₂ SO ₄ /t	6.8
Sulfur – Total as S (LECO)	%	<0.01
Chromium Reducible Sulfur	%	<0.005
Sulfate as SO ₄ ²⁻	mg/kg	<100
Total C	%	0.33
Organic C	%	0.31
Inorganic C	%	0.02

Based on results from the sample analysed, Mesa H tailings are unlikely to pose a hazard with respect to AMD generation.

The results of the multi-element assay on the tailings solids are presented in Table 2. The geochemical abundance index (GAI) compared to typical background concentration reported for median soil abundance (Bowen, 1979) is also included in the table, for reference. In general, a GAI value > 3 is considered a significant enrichment, and a GAI value ranging from 1-2 suggests a minor enrichment, while a GAI of <1 represents little or no enrichment with respect to median soil values. The results indicate that the Mesa H tailings sample was significantly enriched in Ag, Be, and Fe and slightly enriched in As, Co, Mo, Se, and W. These results are consistent with those of EGi (2014), for tailings from the adjacent Mesa J deposit.

Total N was present at a concentration of 80 mg/kg, with the majority of nitrogen associated with Total Kjeldahl Nitrogen (TKN representing organic and NH₃/NH₄⁺ nitrogen). Soluble nitrate (NO₃) was also detected in the tailings solids at a concentration of 4.2 mg/kg NO₃-N (~18.6 mg/kg NO₃).

Table 2: Multi-element assay for the Mesa H tailings solid and associated GAI value

Element	Unit	Concentration	GAI*
Silver – Ag	mg/kg	0.44	3
Aluminium – Al	%	2.64	-
Arsenic – As	mg/kg	14.8	1
Barium – Ba	mg/kg	100	-
Beryllium – Be	mg/kg	4.04	3
Bismuth – Bi	mg/kg	0.13	-
Calcium – Ca	%	0.1	-
Cadmium – Cd	mg/kg	0.06	-
Chloride – Cl	%	0.109	
Cobalt – Co	mg/kg	24.3	1
Chromium – Cr	mg/kg	38	-
Copper – Cu	mg/kg	13.2	-
Iron – Fe	%	47.3	3
Mercury – Hg	mg/kg	0.119	-
Potassium – K	%	0.02	-
Magnesium – Mg	%	0.15	-
Manganese – Mn	mg/kg	1310	-
Molybdenum – Mo	mg/kg	3.4	1
Sodium – Na	%	0.02	-
Nickel – Ni	mg/kg	32.3	-
Phosphorus – P	mg/kg	430	-
Lead – Pb	mg/kg	10.2	-
Antimony – Sb	mg/kg	0.67	-
Selenium – Se	mg/kg	1	1
Silica – Si	mg/kg	50	
Tin – Sn	mg/kg	1	-
Sulfur – S	%	0.02	-
Strontium – Sr	mg/kg	11.3	-
Thallium – Tl	mg/kg	4.73	-
Titanium – Ti	%	0.194	-
Uranium – U	mg/kg	1.7	-
Tungsten – W	mg/kg	3.3	1

Element	Unit	Concentration	GAI*
Zinc – Zn	mg/kg	96	-
Zirconium – Zr	mg/kg	59.5	-
Nitrite as N (Soluble) (NO ₂ as N)	mg/kg	<0.1	-
Nitrate as N (Soluble) (NO ₃ as N)	mg/kg	4.2	-
Total Kjeldahl Nitrogen as N (TKN as N)	mg/kg	80	-
Total Nitrogen as N	mg/kg	80	-

Notes: *In the table the symbol “-” denotes that the element is not enriched compared to the median soil value

3.2 Leach extracts at variable solid:liquid ratios

The test results show that the pH of samples remained relatively unchanged irrespective of the dilution ratio while, as expected, salinity, alkalinity and major ion (i.e. Ca, Mg, SO₄, K, Na) concentrations decreased with increasing dilution. For example, salinity decreased from 455 µS/cm in the deionised water 0.75:1 sample to 54 µS/cm in the deionised water 1:20 samples (Table 3, Figure 4).

With the exception of the low-contact water sample, bicarbonate was the dominant anion followed by Cl. The dominant cations in solution were Na and Ca in that order in all extracts.

The trend in trace element concentrations was complex, with some metals decreasing, other increasing, and others showing no clear trend as a function of dilution ratio. Elements that showed increasing concentrations as a function of increasing dilution ratio included Ba, Mn, and Zn, while for Si and Sr the opposite trend was observed. Al, Fe, and Mn were particularly elevated in the deionised water 1:2 sample, potentially associated with colloidal particulates in the leachate.

Al, Cu, Pb, Fe, and Ti were mobilised in the deionised water 1:2 and 1:20 samples with concentrations decreasing as a function of increasing dilution ratio but were not detected in the low contact water sample (0.75:1). The low contact water sample (0.75:1) mobilised several trace analytes (Cu, Pb, Mn, Al, Zn, Ba, and Fe) at the lowest concentrations and major analytes (Sr, K, K, Ca, Mg, Na, Cl, Si, SO₄, and alkalinity) at the highest concentrations when compared to higher dilution ratio samples.

Nitrates were detected in all leachates with concentrations not showing a specific trend as a function of water contact ratios.

Mesa H - Variable contact ratio leach tests

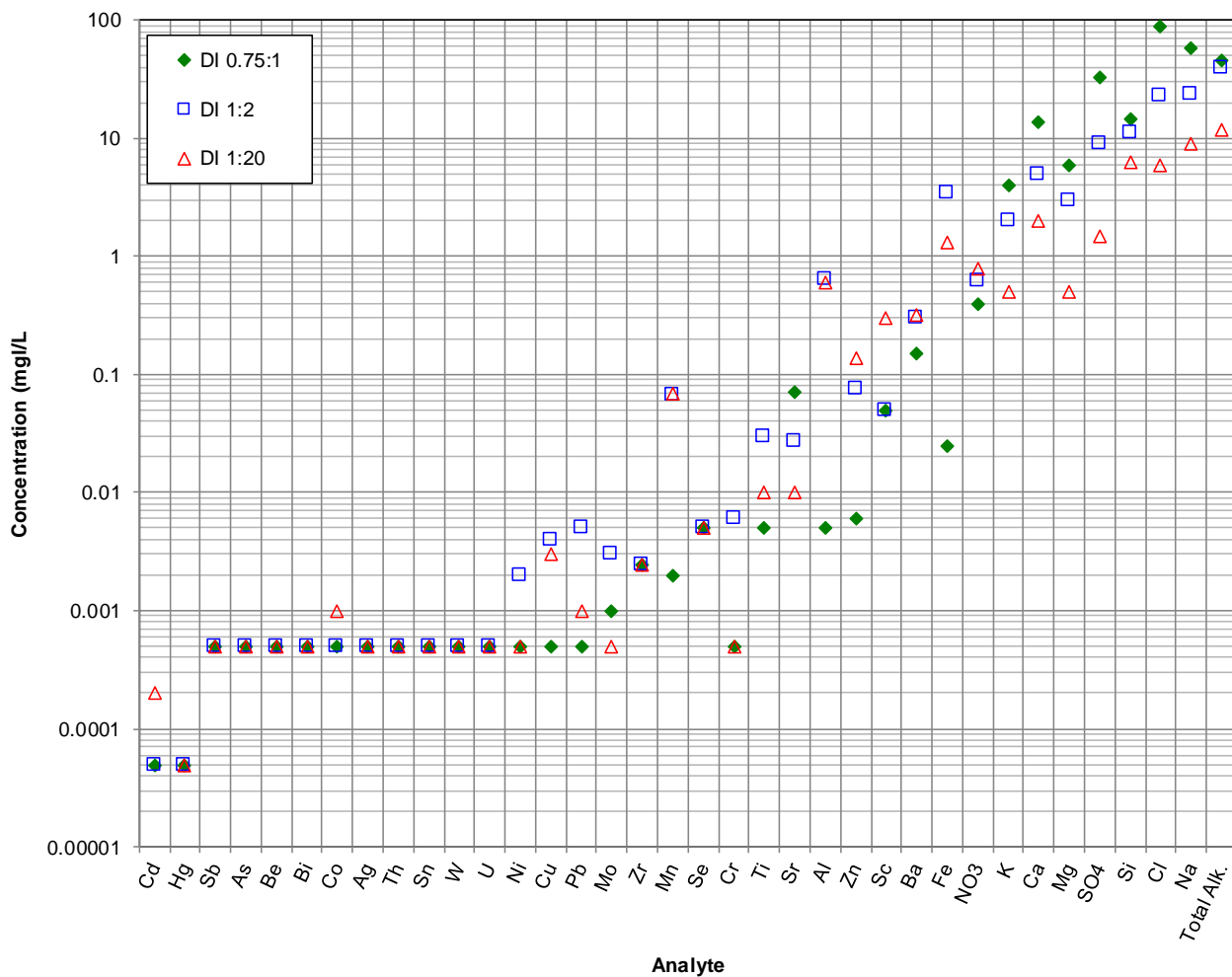


Figure 1: Elemental composition of Mesa H tailings deionised water extractions as a function of S:L contact ratio (DI = deionised water). Values below detection limit were reset at 1/2 LOR for illustration purposes.

3.3 Leach extracts at variable filter sizes

Table 3 compares the water quality for deionised water extract at a 1:2 (S:L) contact ratio filtered using a standard 0.45 µm filter and a 0.20 µm filter. Results are illustrated in Figure 5.

As expected, the concentrations of several elements are lower when a 0.20 µm filter is used, with the greatest decrease (more than one order of magnitude) being for Fe, Al, and Mn. Other trace metals (Cu, Mo, Pb, and Ti) showed a decrease in concentration by up to an order of magnitude. For example, Fe decreased from 3.5 mg/L to 0.28 mg/L and Cu decreased from 0.004 mg/L to <0.001 mg/L.

The marked decrease in concentrations for Fe, Al, and Mn is likely due to the fact that the Fe, Al, and Mn are not truly dissolved but are present as colloidal particulates which are not readily filtered by a standard 0.45 µm filter. Colloids can provide sorption sites for several metals, thus decrease in concentration observed for some metals (and particularly Cu) in the 0.2 µm filter leachate may be associated with removal of colloidal matter.

Mesa H - Effect of filter size of water quality results

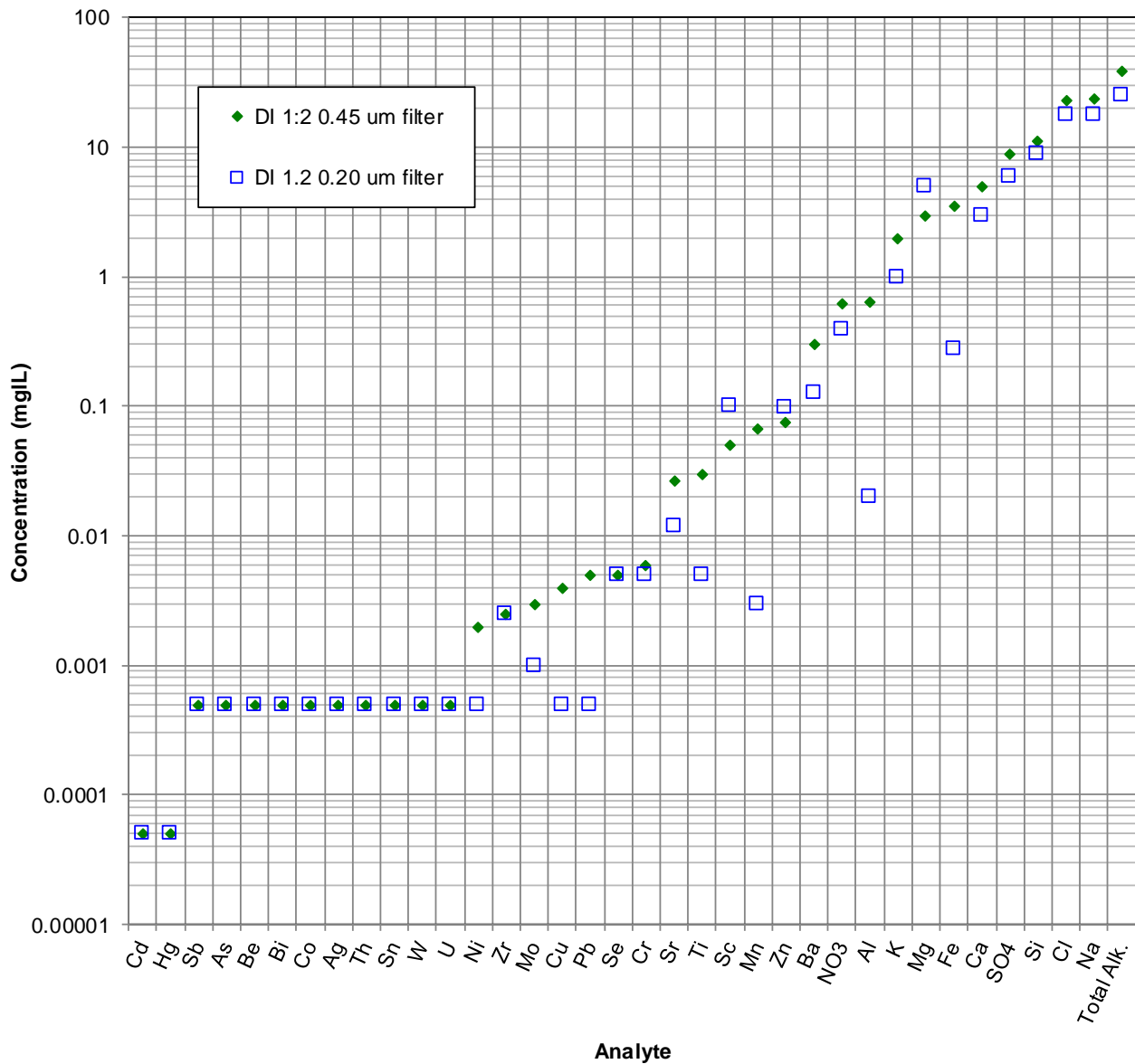


Figure 2: Elemental composition of Mesa H tailings deionised water extractions as a function of filter size for the deionised water 1:2 leach extract. Values below detection limit were reset at ½ LOR for illustration purposes.

3.4 Saline leach extracts

The test results show that the pH values of the samples were circum-neutral to alkaline with pH decreasing with increasing salinity (Table 3), while, as expected, electrical conductivity (EC) increased with increased salinity. Major ions such as Mg, Ca, and K increased as a function of increasing salinities, while SO₄ was relatively unaffected (Cl and Na increased due to the use of sodium chloride to increase the salinity of the leach solution).

Figure 6 illustrates the results of the saline extraction compared to the deionised water leach results. For several elements there was no or minimal change in concentration as a function of salinity with Ag, As, Be, Bi, Co, Hg, Sb, Se, Sn, Ti, Th, U, W, and Zr remaining below detection limit irrespective of the salinity of the solution, while Cu, Cr, Mo, and Pb showed minimal changes in concentrations with changing salinity. Those elements that showed increasing concentration with increasing salinity were Al, Ba, Ca, Cd, Cl, K, Mg, Mn, Ni, Si, Sr, and Zn.

These trends are consistent with those observed by EGi (2014) and SRK (2017) amongst others. It is postulated that changes in major ions and pH as a function of salinity are associated with cation exchange, with Na+ in solution exchanging for H+, Ca+, Mg+ and K+, while changes in concentrations in trace metals may be associated with desorption, enhanced dissolution and/or precipitation reactions enhanced and/or inhibited by the saline environment (SRK, 2017).

Mesa H - Variable salinity leach test

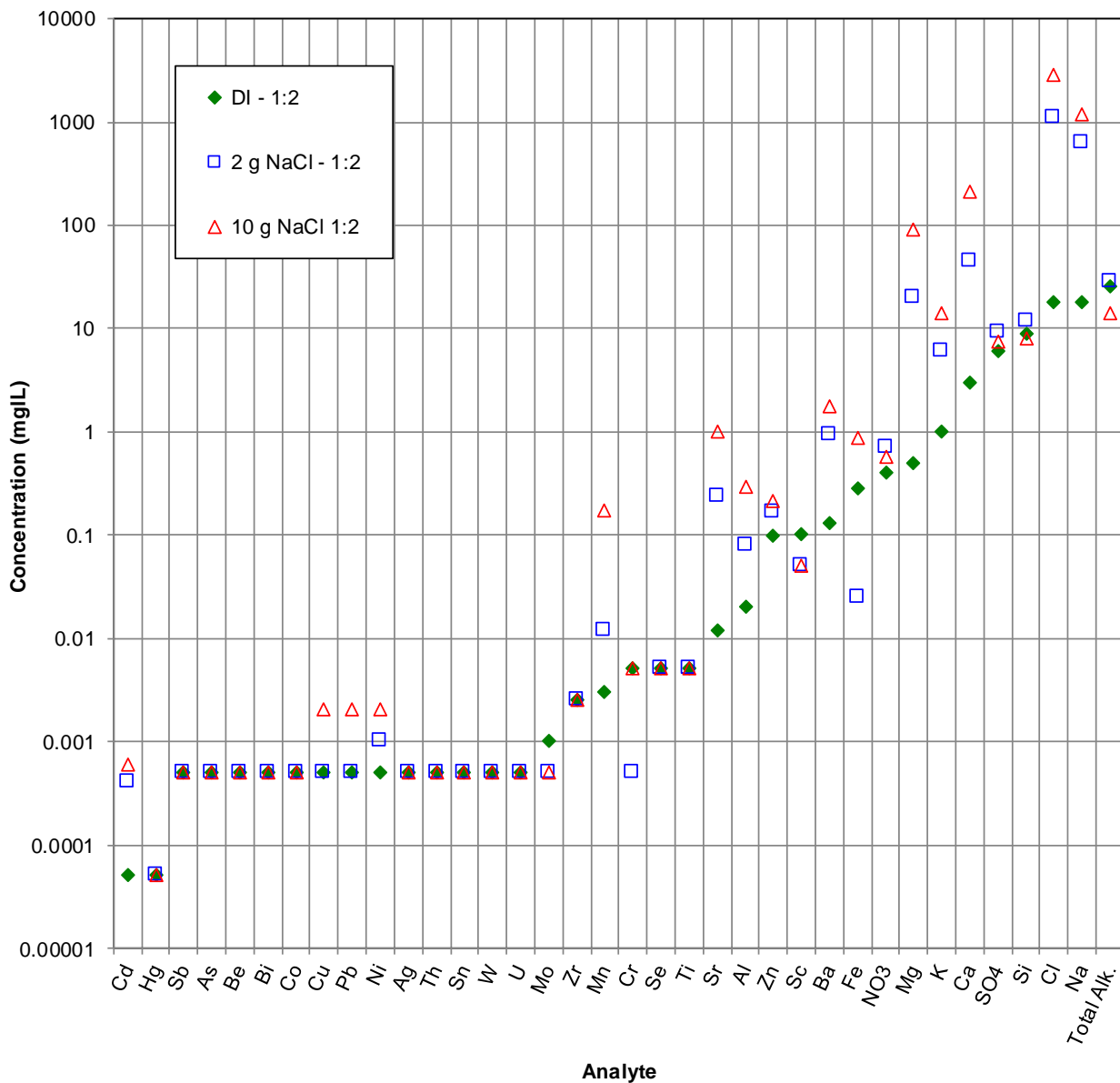


Figure 3: Elemental composition of Mesa H tailings water extractions as a function of salinity. Values below detection limit were reset at 1/2 LOR for illustration purposes.

3.5 Hydrogen peroxide extract

Table 3 lists the water quality results for the peroxide extraction. For this test, a solid sample was reacted with peroxide to induce aggressive oxidation conditions, which are unlikely to be encountered in the field. However, the test was conducted to investigate the effect of aggressive oxidation on key metal species.

Compared to the deionised water 1:20 extract results, the peroxide extraction generated a leach with higher concentrations for several analytes, for example Al, Cr, Fe, Mn, Mo, Ni, Sn, and Ti. Major ions, pH, and EC remained relatively unaffected by leaching with peroxide, and with the exception of Sn it mobilised the same elements which were observed in the deionised water and saline leach extractions but often at higher concentrations.

Elevated concentrations of Fe (57 mg/L) and Al (13 mg/L) may be indicative of colloids, and elevated total C (22 mg/L) is likely indicative of the presence of some organic matter within the tailing's sample.

As peroxide extraction tests subject samples to a chemically harsh oxidising environment that is not representative of normal environmental conditions, results from these tests are not representative of concentration ranges of these constituents under field conditions.

3.6 Tailings Liquid Fraction

Table 3 presents the water quality results for the Mesa H tailings liquid fraction submitted for analysis as part of this study. The Mesa H tailings liquor had a mildly alkaline pH of 8.02 and was slightly saline (EC of 699 $\mu\text{S}/\text{cm}$). The major ion chemistry was dominated by Na and Cl. The dominant cations in solution were Na and Ca, and the major anions were Cl and bicarbonate. Elemental determination indicated that the majority of the metals and metalloids were at low concentrations, many being below the detection limit. Trace analyte concentrations detected included Ba (0.03 mg/L), Mn (0.001 mg/L), Sr (0.11 mg/L), and Zn (0.006 mg/L). Additionally, the Mesa H tailings liquid fraction contained approximately 2.5 mg/L of NO_3 . Results are generally consistent with the chemistry of tailings liquor from the neighbouring Mesa J mine, reported by EGi (2014).

Table 3: Mesa H: water quality for tailings contact water and leach testwork results

Parameter	Unit	Tailings Liquid Fraction	Leach Testwork						
			Deionised Water 0.75:1 (S:L)	Deionised Water 1:2 (S:L)	Deionised Water 1:2 (S:L) 0.2 µm filter	Deionised Water 1:20 (S:L)	Saline 2 g/L NaCl 1:2 (S:L)	Saline 10 g/L NaCl 1:2 (S:L)	Peroxide 1:100 (S:L)
pH Value	pH Unit	8.02	7.5	7.6	6.7	7.3	7.1	6.9	7.5
Electrical Conductivity	µS/cm	699	445	168	154	54	3420	8170	80
Total Alkalinity as CaCO ₃	mg/L	82	46	39	25	12	28	14	31
Chloride	mg/L	155	88	23	18	6	1080	2870	6
Sulfate	mg/L	45	33	9	6	<3	9	<15	<15
Calcium	mg/L	20	14	5	3	2	45	208	2
Magnesium	mg/L	10	6	3	<1	<1	20	91	1
Potassium	mg/L	4	4	2	1	<1	6	14	3
Sodium	mg/L	67	59	24	18	9	613	1160	15
Aluminium	mg/L	<0.01	<0.01	0.64	0.02	0.61	0.08	0.29	12.5
Antimony	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.005
Arsenic	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.005
Beryllium	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.005
Barium	mg/L	0.03	0.152	0.304	0.13	0.32	0.922	1.74	0.29
Bismuth	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.005
Cadmium	mg/L	<0.0001	<0.0001	<0.0001	<0.0001	0.0002	0.0004	0.001	<0.0005
Chromium	mg/L	<0.001	<0.001	0.006	0.01	<0.001	<0.001	0.005	0.018
Cobalt	mg/L	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	0.005
Copper	mg/L	<0.001	<0.001	0.004	<0.001	0.003	<0.001	0.002	<0.005
Lead	mg/L	<0.001	<0.001	0.005	<0.001	0.001	<0.001	0.002	<0.005
Iron	mg/L	<0.05	<0.05	3.51	0.28	1.33	<0.05	0.87	56.9
Manganese	mg/L	0.001	0.002	0.067	0.003	0.07	0.012	0.17	0.27
Molybdenum	mg/L	<0.001	0.001	0.003	0.001	<0.001	<0.001	<0.001	0.012
Mercury	mg/L	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Nickel	mg/L	<0.001	<0.001	0.002	<0.001	<0.001	0.001	0.002	0.011

Parameter	Unit	Tailings Liquid Fraction	Leach Testwork						
			Deionised Water 0.75:1 (S:L)	Deionised Water 1:2 (S:L)	Deionised Water 1:2 (S:L) 0.2 µm filter	Deionised Water 1:20 (S:L)	Saline 2 g/L NaCl 1:2 (S:L)	Saline 10 g/L NaCl 1:2 (S:L)	Peroxide 1:100 (S:L)
Scandium	mg/L	<0.1	<0.1	<0.1	0.1	0.3	<0.1	<0.1	0.4
Selenium	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.05
Silver	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.005
Silicon	mg/L	12	15	11	8.9	6.41	12	8	13
Strontium	mg/L	0.106	0.072	0.027	0.012	0.01	0.238	1.01	0.017
Thorium	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.005
Tin	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.006
Titanium	mg/L	<0.01	<0.01	0.03	<0.01	0.01	<0.01	<0.01	0.42
Tungsten	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.005
Uranium	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.005
Zinc	mg/L	0.006	0.006	0.076	0.098	0.14	0.164	0.209	0.168
Zirconium	mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.025
Nitrite as N	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Nitrate as N	mg/L	0.58	0.09	0.14	0.09	0.18	0.16	0.13	0.32
Nitrate as NO ₃	mg/L	2.57	0.4	0.62	0.4	0.8	0.71	0.58	1.42
Nitrite + Nitrate as N	mg/L	0.58	0.09	0.14	0.09	0.18	0.16	0.13	0.32
Total Kjeldahl Nitrogen as N	mg/L	0.3	0.2	0.1	0.1	0.7	<0.1	0.1	1.2
Total Nitrogen as N	mg/L	0.9	0.3	0.2	0.2	0.9	0.2	0.2	1.5
Phosphorus	mg/L	<0.01	<1	<1	<1	<1	<1	<1	<1
Total Carbon	mg/L	16	215	8	15	4	6	5	22

4.0 CONCLUSIONS

Mesa H tailings solids are unlikely to generate AMD as they contain no detectable sulfur in any form and classify as NAF.

Although analytes such as Ag, As, Be, Co, Fe, Mo, Se, and W were enriched in the tailings solids, the solubility of these and other environmentally sensitive elements was generally low.

In particular, Ag, As, Be, Bi, Hg, Sb, Se, Th, W, U, and Zr were not observed above their detection limit regardless of the experimental conditions. Cd, Cr, Co, Cu, Pb, and Ni were occasionally mobilised but only at low concentrations (generally not higher than a few µg/L). Elevated concentrations of Fe, Al, and Mn observed in Mesa H leach extracts were likely associated with colloidal materials (particulate), but their true dissolved concentrations are likely to be substantially lower.

Zn and NO₃ were leached under all experimental conditions for Mesa H tailings, at variable concentrations ranging from 0.006 mg/L to 0.21 mg/L for Zn, and from 0.4 mg/L to 2.6 mg/L for NO₃. Ba and Sr were also mobilised in all leach extracts averaging (excluding the peroxide extract) 0.6 mg/L for Ba and 0.23 mg/L for Sr. These data suggest that Zn, NO₃, Ba, and Sr may be readily mobilised under a range of environmental conditions.

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[https://golderassociates.sharepoint.com/sites/27376g/documents/06 deliverables/040 mesa h tailings geochemistry/1895943-040-m-rev0-geochem_mesa_h.docx](https://golderassociates.sharepoint.com/sites/27376g/documents/06%20deliverables/040%20mesa%20h%20tailings%20geochemistry/1895943-040-m-rev0-geochem_mesa_h.docx)

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SRK (2017) Robe Valley geochemical characterisation – forms of acidity and supplemental leach testing