

# Characterisation of arsenic geochemistry in mine tailings from a mesothermal Au deposit

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## Abstract

Macraes mine was opened in 1989, and extracts mesothermal gold from a shearing zone in the Otago schist. The gold occurs in pyrite and arsenopyrite, which comprise 1 % of the ore. The sulfide rich fraction is separated by flotation, and is processed to approximately 15  $\mu\text{m}$  before autoclave oxidation to release gold for carbon in pulp cyanide extraction of the gold. The Mixed Tailings Facility (MTF) received flotation and sulfide concentrate tailings for 25 years, under changing processing and management regimes.

In September 2015 an 80 m core was drilled through the northern end of the MTF. The core encompasses tailings deposited over much of the lifetime of Macraes mine including the changes that have occurred in gold extraction and tailings management, such as the introduction of pressure oxidation of sulfide concentrate in 1999. This paper presents initial results from the core, as part of an overall project investigating the speciation and phase associations of arsenic in the MTF.

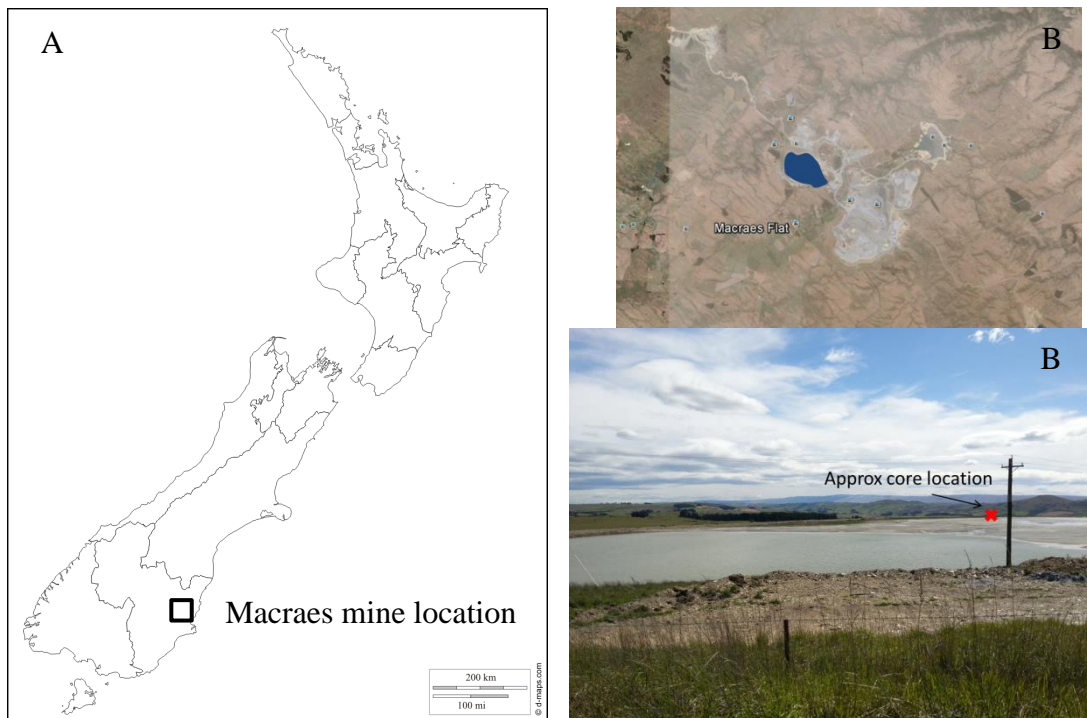
Preliminary study of the core has involved characterisation of a section at 44 m depth, and a section at 77 m depth. The shallower sample has brown tailings, indicative of iron oxide minerals produced during pressure oxidation. The deep sample is grey, consistent with the persistence of sulfide minerals. The tailings pore water at both depths contains 2 ppm As. Arsenic in the tailings is associated predominantly with iron oxide minerals at 44 m depth, and with sulfide minerals at 77 m depth. The sequential extraction showed promise as a way to investigate mineral associations in the MTF, and we propose geochemical modelling be used together with sequential extractions to assess controls on the As concentrations in pore water of the tailings dam.

**Keywords:** tailings, mesothermal gold, arsenic, sequential extraction, pressure oxidation

## Introduction

The Macraes mine extracts mesothermal gold from a mineralised shear zone in the Otago Schist (Figure 1). The ore typically has 1 % pyrite and arsenopyrite which contain encapsulated gold, in the order of 1.6 grams of gold per tonne (Milham and Craw 2009). The mine was opened in 1989, and has undergone several changes to the ore processing regimes over its lifetime (Figure 2). This has led to variations in the chemistry and composition of the mine wastes over this time.

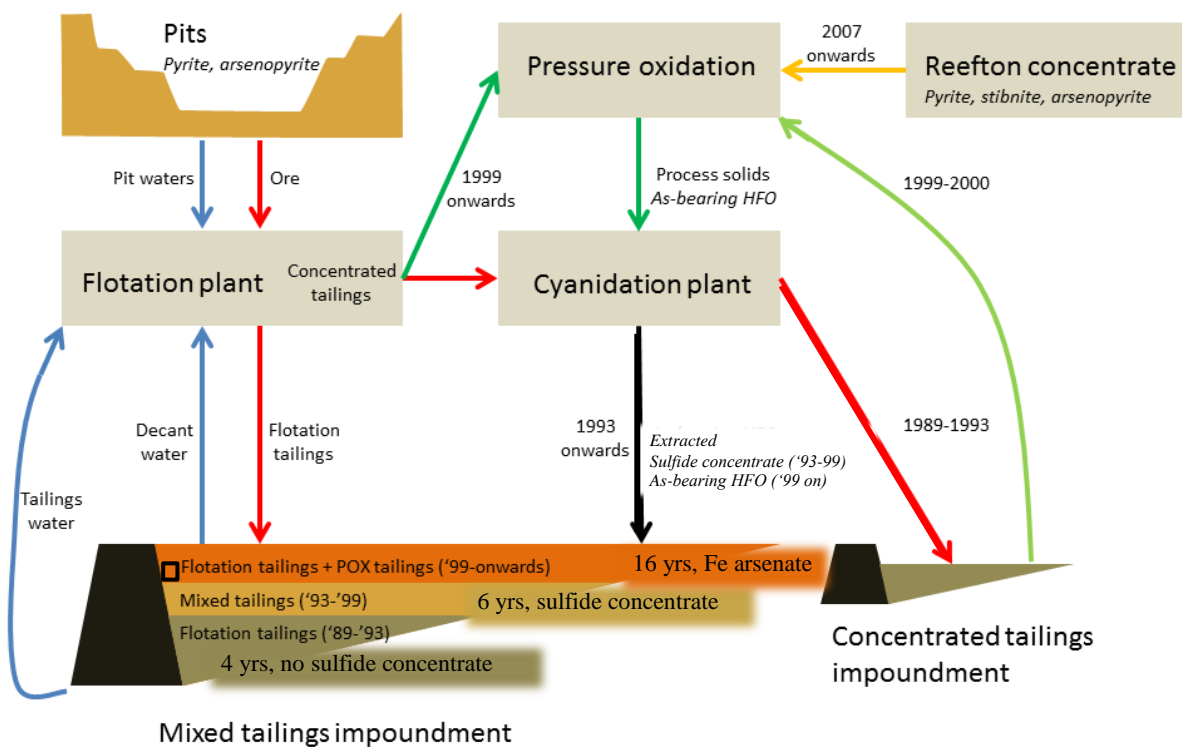
The ore processing regimes use a combination of physical and chemical processes to extract the gold. The ore is crushed and ground to sand and the sulfide rich fraction is concentrated using froth flotation. The gangue is deposited into the Mixed Tailings Facility (MTF), while the concentrate is further milled to  $15 \pm 10 \mu\text{m}$  prior to oxidation and gold extraction. The gold is extracted from the sulfide fraction by carbon-in-pulp cyanidation (Craw et al. 1999). When the mine opened in 1989 this extraction was performed directly on the sulfide concentrate, without the oxidation step. Between 1989 and 1993, the arsenopyrite-bearing concentrate tailings were stored in a separate facility to the flotation tailings (Craw et al. 1999), however from 1993 onwards the concentrate tailings were also sent to the MTF.



**Figure 1.** The location of the macraes mine (A), tailings dam (B, blue shading) and core site (C) in Otago. Images A and B adapted from d-maps and Google Earth respectively.

In order to maximise gold extraction, a pressure oxidation plant was commissioned in 1999 which treated the sulfide concentrate prior to cyanidation (Craw 2003). The concentrate is roasted in an oxygen rich autoclave (225 °C, 3800 kPa O<sub>2</sub>) for 1 hour which causes nearly complete oxidation of the sulfides (Craw 2006). The oxidation process generates sulfuric acid, which is managed via limestone addition to maintain a solution pH between 1 and 2. The principal wastes formed in the pressure oxidation plant are calcium sulfate (as anhydrite and/or gypsum), jarosite, iron (oxyhydr)oxide (as hematite or ferrihydrite), and amorphous iron arsenate. The discharge from the pressure oxidation plant is treated by carbon-in-pulp cyanidation and then deposited in the MTF with the flotation tailings. Between 1999 and 2000, the concentrate tailings collected between 1989-1993 were reprocessed through the oxidation plant and sent to the MTF. In 2007, the plant also started processing concentrate from the Globe mine near Reefton, which has 4% stibnite in addition to pyrite and arsenopyrite (Milham and Craw, 2009).

Arsenic is an environmentally relevant element that is present in the MTF at Macraes mine. Consent conditions for Macraes set As limits and monitoring requirements for the mine and associated facilities. Seepage from the tailings is captured in a dedicated drainage system and returned to the processing plant as part of the process water circuit. Release of As from the MTF is an environmental risk, the magnitude of which is dependent on the geochemistry of the tailings and the in situ processes occurring in the impoundment. The changes in ore processing over the lifetime of Macraes mine has altered the geochemistry of the As bearing phases in the tailings. Characterisation of the tailings and processes controlling As mobility will help to inform management practices required into the future. In 2015, a core was taken through 80 m of the MTF. This paper tests a sequential extraction to investigate the association of As with minerals in tailings from two sections of the core that have undergone different gold extraction processes.



**Figure 2.** A schematic detailing changes to the processing system at Macraes mine, modified from Milham and Craw (2009).

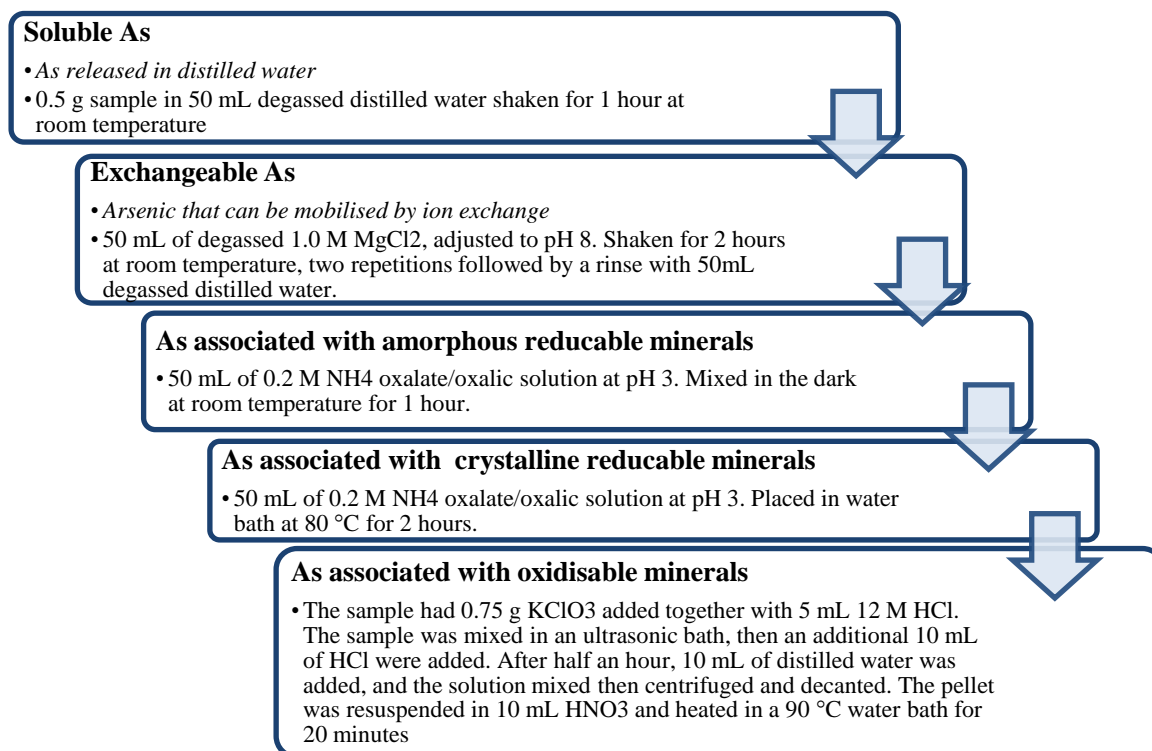
## Methods

The core was extracted from the MTF in September 2015, and was cut into sections, wrapped in cling film, and frozen. The frozen sections were stored at  $-18^{\circ}\text{C}$  prior to analysis. Two core depths were selected for provisional study; one at 77 m depth near the base of the core, and one at 44 m depth. Ten centimetre subsamples were cut from the frozen sections with a saw, and thawed in a nitrogen atmosphere in a glove box. A plastic knife was used to remove sample that had been in contact with the metal saw. The 10 cm sub-sample was homogenised by mixing, and then placed into 50 mL centrifuge tubes. The tubes were centrifuged for 16 hours and pore water that pooled on top was collected. The pH of the pore water was measured with a calibrated pH meter. Subsamples of the pore water were then diluted with degassed distilled water prior to analysis.

Arsenic speciation in the pore waters was measured using the spectrophotometric method of Johnson and Pilson (1972). This method takes advantage of the reactivity of arsenate and phosphate with molybdenum blue complexes, and manipulates arsenic oxidation state to determine the arsenate and arsenite concentrations by difference.

The phase associations of arsenic in the tailings were investigated using sequential extraction techniques. These techniques use increasingly aggressive chemical reagents to target dissolution of mineral groups in solid samples depending on their reactivity. This results in operationally defined fractions that are intended to represent elemental relationships with particular mineral constituents of the tailings. In this study an extraction scheme used by Nieva et al. (2016) was adapted to target soluble, exchangeable, amorphous and crystalline iron and manganese oxide bound, and sulfide bound arsenic phases (Fig. 3.). After each

extraction step the sample was centrifuged for 15 minutes and the supernatant filtered and collected for analyses. The next reagent was added to the remaining solid in the centrifuge tube. In addition, an extraction was performed in aqua regia to determine the total concentration of arsenic present in the tailings. A certified reference material (CRM-RTS 3a from Canmet Mining) comprised of sulfide ore mill tailings, was extracted alongside the tailings extracts. The pore water, sequential extraction and aqua regia extracts were analysed for Al, As, Fe, Mn, P, S and Sb by ICP-MS and ion chromatography methods at an accredited laboratory. Pore water solute concentrations were entered into Visual Minteq modelling software.



**Figure 3.** A summary of the sequential extraction technique modified from Nieva et al. (2016).

## Results

The tailings from 77 m depth in the MTF were grey, with a clay-like texture (Fig. 4). The grey colouring is similar to that of the schist that is visible around the Macraes area. A few millilitres of pore water were able to be extracted from the tailings, and the pore water pH was 8.58. Unfortunately the volume was too small to allow for speciation analyses to be performed, however ICP-MS revealed 2 ppm of arsenic is present in the pore water. The tailings from 44 m depth were brown in colour (Fig. 4.), and had some coarser material mixed in with the clay-like textured material. A greater volume of pore water was able to be extracted from the 44 m tailings. Pore water pH was 8.14, and the 2 mg/L of arsenic present was speciated entirely as As V. Provisional modelling indicated that at both depths the tailings were saturated with respect to aluminium hydroxide phases, and that the tailings at 44 m depth were close to saturation with respect to gypsum and anhydrite.

The sequential extraction results show markedly different As chemistry in the tailings at the two depths (Fig. 5.). At 77 m depth, arsenic was predominantly associated with sulfide minerals, and at 44 m depth, arsenic was predominantly associated with reducible metal oxide minerals. There were higher concentrations of soluble and exchangeable As in the

tailings from 77 m depth. In the CRM and the 44 m depth tailings sample, the sum of the sequential extraction concentrations was very similar to the concentration from the aqua regia digest. The 77 m sample had significantly lower concentrations extracted with aqua regia than in the sequential extraction.



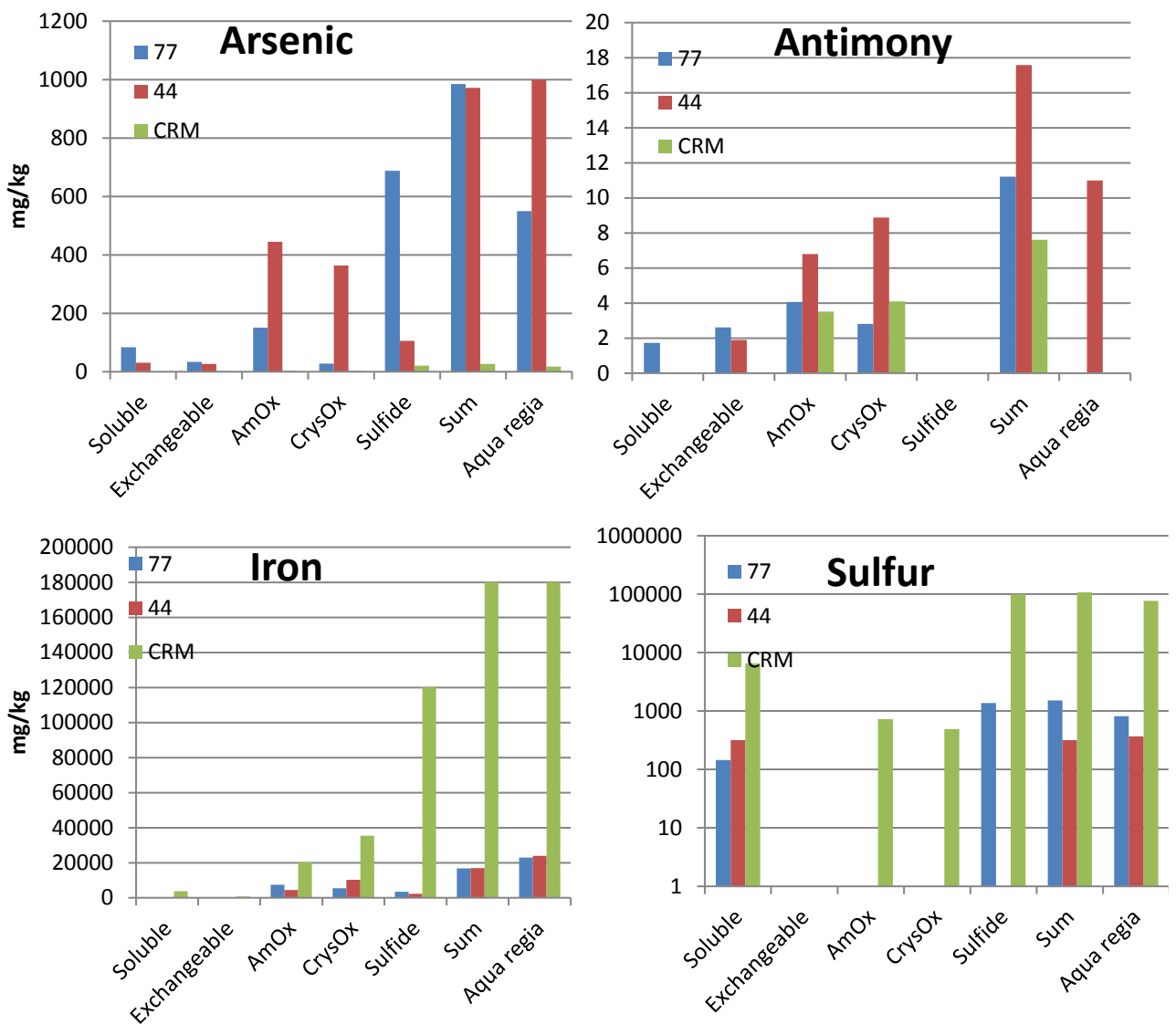
**Figure 4.** Subsamples of tailings from 77 m depth (grey, above) and 44 m depth (brown, below) showing the colour difference between the samples.

Antimony was predominantly associated with reducible metal oxide minerals in both of the tailings samples, and no sulfide associated Sb was detected (Fig. 5.). The deep tailings sample had greater concentrations of soluble and exchangeable Sb than the shallower tailings that have undergone pressure oxidation. For the aqua regia digestion, the detection limit of the method was 10 mg/kg of tailings. The 44 m depth tailings had a lower aqua regia extractable Sb concentration than the sum of the sequential extracts. The sum of sequential extraction extracts was close to or less than the aqua regia 10 mg/kg detection limit in the 77 m sample and the CRM, and no detectable Sb was found using the aqua regia method.

Iron in the tailings was predominantly in an oxidised form. The mineral forms were not identified, but in the deep tailings a greater proportion of Fe was mobilised in the extraction phase targeting amorphous metal oxides. In the shallow tailings more than twice as much iron was present in a crystalline rather than amorphous iron oxide form. There was more sulfide associated iron in the deep tailings from 77 m than the shallow tailings at 44 m, however some sulfide associated iron persisted in the shallow sample.

There was considerable soluble sulfur present in the tailings, 145 and 318 mg/kg in the 77 m and 44 m depth samples respectively. No detectable ( $> 100$  mg/kg) sulfur was released during the reducing steps indicating that little, if any, sulfur is present in oxy or hydroxyl sulfate minerals. In the 77 m depth sample, an additional 1376 mg/kg of S was released during the extraction step targeting sulfide minerals, indicating persistence of sulfide minerals in the deep tailings. The CRM had high sulfur concentrations, mostly in the form of sulfide minerals.

Comparison of the aqua regia results for the CRM with the certified concentration values indicates 99% recovery of arsenic (Table 1). For phosphorous and iron, recovery was  $100 \pm 12\%$ . Only 80 % of sulfur was recovered from the sample, and for the other analytes, much lower recoveries were achieved. The aqua regia extraction does not dissolve silicate phases. An interesting occurrence with this data set is that the sum of sequential extracts often exceeded the concentration indicated by aqua regia digestion (Fig. 5.).



**Figure 5.** Concentrations of elements dissolved in each step of the sequential extraction, together with the sum of concentrations, and the concentration dissolved in aqua regia. The CRM had more than an order of magnitude more sulfur present than the tailings samples, and so this graph is displayed with a logarithmic scale on the y axis. Results that were below detection are not shown on the graphs.

**Table 1.** Recovery efficiency of aqua regia digestion of CRM-RTS3a

Recovery using AqReg extraction of CRM	
Phosphorus	112%
Silicon	0.04%
Sulfur	80%
Calcium	56%
Magnesium	69%
Potassium	39%
Sodium	6%
Aluminium	43%
Antimony	0%
Arsenic	99%
Iron	88%
Manganese	40%

## Discussion

The concentration of arsenic in both the pore water of the tailings, and the tailings themselves was similar at the 44 m and 77 m sample depths. However, the phase associations of arsenic in the tailings were distinct. Arsenic in the ore occurs predominantly in pyrite and as arsenopyrite, and it is apparent the changes in gold extraction practises used at the mine have altered the distribution of arsenic between the operationally defined mineral fractions in the tailings.

Preliminary modelling of pore waters showed no arsenic minerals close to saturation at either depth, and so it seems likely sorption equilibria may be more important for determining pore water As concentrations than solubility equilibria. It was interesting however that despite identical As concentrations in the pore water, the soluble and exchangeable As fractions in the tailings was substantially larger in the 77 m depth tailings. This is likely a result of greater solubility of the As containing minerals at depth, for instance arsenopyrite is more soluble than iron arsenate. Other possible reasons may include pH and arsenic speciation. The 77 m depth pore water sample was not analysed for As III/V speciation, however if there was a proportion of As present as As III, it may be more easily mobilised by the extractions than As V due to its typically lower affinity for iron oxide surfaces at pH ~8. The pore water pH was 8.58 at 77 m depth, compared to 8.14 at 44 m.

If adsorption equilibria are a primary control on As mobility, comprehensive modelling of the pore water solutions and the adsorbing phases may improve understanding on the processes controlling pore water As concentrations in the system. This will be performed as this project progresses. As part of this further assessment methods such as those employed by Keon et al. (2001), using a phosphate solution to competitively desorb As from iron oxides may be employed. This will allow some distinction to be made between adsorbed versus co-precipitated As species, which may have different mobilities.

At 44 m depth 83% of the arsenic present was associated with iron oxides, with 45 % associated with amorphous iron oxides and 38 % associated with crystalline iron oxides. At the Giant mine in Canada, milled concentrate showed a similar distribution of As association to those observed in the tailings at Macraes mine. Prior to roasting, As was principally associated with sulfide minerals in the mill product, while the roasted product had As predominantly associated with amorphous metal oxides (Walker et al. 2015). The arsenic distribution is contrasting to that of the iron itself, which had a greater proportion present in crystalline forms in the pressure-oxidation tailings at Macraes mine. These results are consistent with papers interpreting mineralogy of pressure oxidation tailings from Macraes, which contain amorphous iron arsenate, jarosite, amorphous iron oxy-hydroxide and hematite (Craw 2003; Craw 2006). At 77 m depth, 70 % of the arsenic present was associated with sulfide minerals. It seems little alteration of the As containing minerals in the ore occurred during processing. A small proportion of sulfide bound As persists in the pressure oxidation tailings from 44 m as well, which may be due to incomplete oxidation of the sulfide concentrate, and/or incomplete removal of the sulfide fraction during flotation.

The sequential extraction technique showed some interesting and coherent results, however other results indicate some further method development will be required. The aqua regia extraction targets most non-silicate phases, however concentrations of Sb, As and S were at times lower in the aqua regia extract than the sum of extracts from the sequential extraction. For As, this only occurred in the 77 m depth tailings sample, which had a sum of 984 mg/kg

As as opposed to 550 mg/kg As by aqua regia extraction. The values extracted by sequential extraction and aqua regia were within a few percent of each other for the 44 m and CRM samples, and equated to 99% recovery of As in the CRM (Table 1.). Unfortunately the liquid:solid ratios used for the aqua regia extraction meant that the a detection limit equivalent to 10 mg/kg Sb was achieved. The CRM Sb concentration was below this, and although the sum of extracts for the 44 m depth sample was nearly 18 mg/kg, no Sb was detected in the aqua regia extract. The results for sulfur were within 15% of each other for the 44 m and CRM samples, however the 77 m sample had nearly double S by sum of extracts than what was measured in the aqua regia extraction. This is the same sample that showed low As in the aqua regia extraction. This may point to incomplete sulfide oxidation, except that the CRM had far greater sulfide concentrations, so we propose subsample heterogeneity may be responsible for these results. Going forward there will be greater repetition of samples to ensure we understand the capabilities of the method.

## Conclusions

The As chemistry in the MTF at Macraes mine is influence by gold extraction techniques. Tailings that were directly extracted have As predominantly associated with sulfide minerals, whereas tailings that have undergone pressure oxidation have As associated with predominantly crystalline metal oxides. The solid tailings contain close to 1000 mg/kg of As, though pore water concentrations are 2 mg/L at both tailings depths. It is likely that sorption equilibria are important regulating As concentrations than solubility equilibria, at both depths studied.

Continuing study of the core will characterise pore water and tailings chemistry throughout the length of the core, and geochemical modelling will be applied to assess the processes controlling pore water arsenic concentrations.

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