

# Storage of arsenic-rich gold mine tailings as future resources

Dave Craw, Gemma Kerr, Kirstine Malloch, Christine McLachlan

*Geology Department, University of Otago, Dunedin 9010, New Zealand*

**Abstract** Arsenic-bearing gold mine tailings in New Zealand have been stored at mine sites for up to 100 years. Primary arsenopyrite remains largely unaffected by oxidation in water-saturated tailings on a time scale of years to decades. Tailings that have been roasted to release encapsulated gold contain ferric iron oxide and ferric arsenate minerals that are stable on a time scale of decades. Waters leaving these tailings storage sites have low dissolved As (<0.1 mg/L). Arsenolite,  $\text{As}_2\text{O}_3$ , is a highly soluble intermediate oxidation product of arsenopyrite during roasting and under surficial conditions, and can contribute to localised elevated dissolved As concentrations. However, under most conditions, dissolved As is adsorbed by iron oxyhydroxides. Long-term storage of As-bearing gold mine tailings can be managed to limit As discharges, and is desirable to retain potential resources that can be more efficiently reprocessed in the future.

**Key words** arsenic, arsenopyrite, hematite, scorodite, tailings, decant water, circumneutral

## Introduction

Gold extraction from ore is never 100% efficient, so some Au remains in most mine wastes. Most residual gold typically remains in tailings that have been excavated, crushed, ground, and commonly concentrated during processing. These tailings represent potential resources from which the residual gold may be extracted at some time in the future when better processing techniques have been developed. In the meantime, the tailings need to be stored in an environmentally benign manner so that any discharging waters have low contents of potentially toxic dissolved load. Dissolved arsenic is the most significant potential discharge issue around such tailings storage sites.

Historic and modern mine sites in New Zealand provide insights into the key mineralogical and geochemical features of orogenic gold deposits in mine tailings from several ore processing techniques. Arsenopyrite ( $\text{FeAsS}$ ) is the principal As-bearing mineral, which contains significant encapsulated gold. Many mines have created sulphide concentrates during gold extraction, and tailings are rich in arsenopyrite. Some mines have oxidised sulphides during processing, and residues contain As-rich oxide minerals including arsenolite ( $\text{As}^{\text{I}}_2\text{O}_3$ ), and a range of oxidised  $\text{Fe}^{\text{III}}$ -bearing minerals with high arsenate contents including scorodite ( $\text{FeAs}^{\text{V}}\text{O}_4 \cdot 2\text{H}_2\text{O}$ ).

## Methods

Data for this study were collected at the active Macraes gold mine in southern New Zealand, where routine water quality monitoring is carried out for processing and environmental purposes. Mineralogical studies were carried out on sulphide concentrate tailings to augment the water monitoring programme. Mineralogical characteristics of historic mine tailings were determined by scanning electron microscopy (SEM) with energy dispersive

analytical capability. Associated water runoff was analysed by Hill-Laboratories, Hamilton, New Zealand. Details of methods are contained in the appended references.

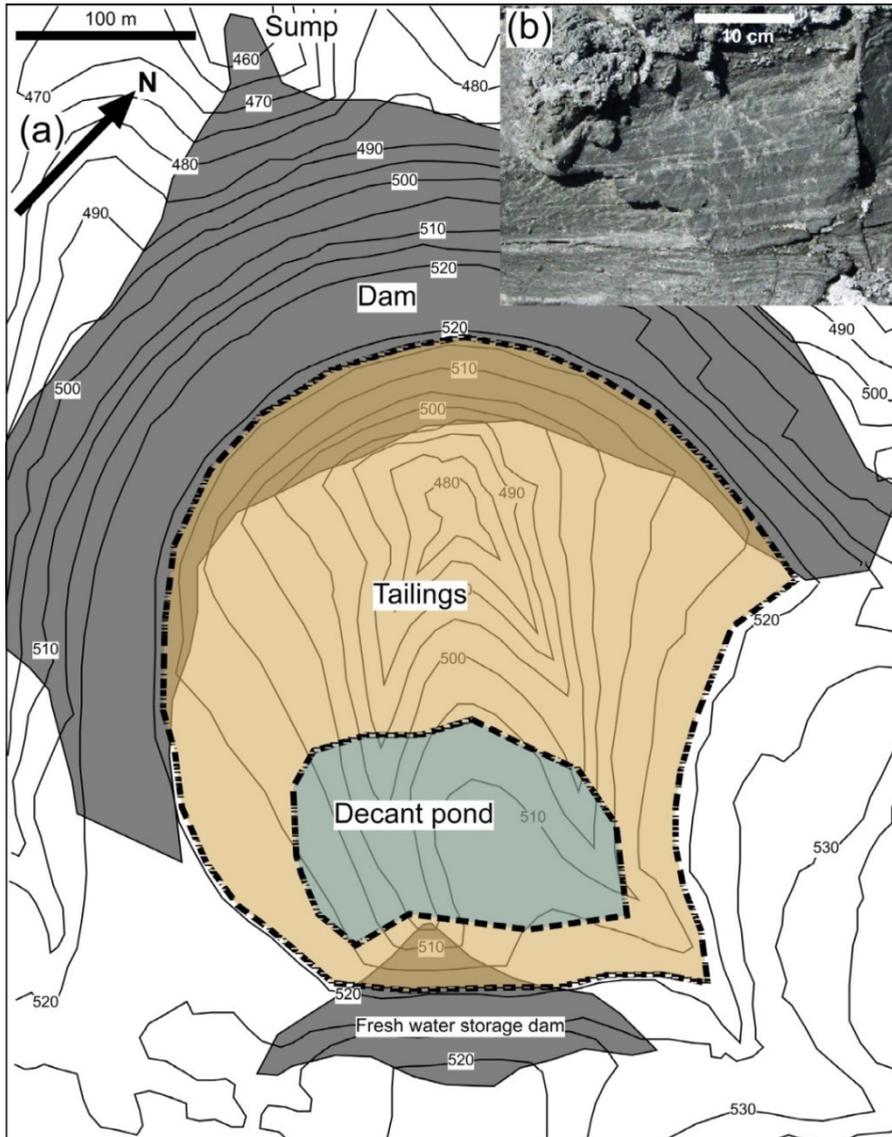
### **Macraes gold mine**

The Macraes gold mine is a world-class orogenic deposit that has been in operation since 1990 (MacKenzie and Craw 2016). Gold is encapsulated in pyrite and arsenopyrite, and processing involves production of a sulphide concentrate via flotation of crushed and ground ore, and gold is extracted by carbon-in-pulp cyanidation. When the mine first opened, the sulphide concentrate was reground to 15  $\mu\text{m}$  and fed directly to the cyanide system, after which the residues were accumulated in a dedicated concentrate tailings impoundment (Fig. 1a,b). However, after 1993 the sulphide-rich residue was remixed with silicate tailings and discharged into a nearby larger impoundment, leaving the concentrate impoundment unused from that time. Low gold recoveries from some ore types caused the introduction in 1999 of a pressure oxidation autoclave to decompose the sulphides in the concentrate at 225°C before passing the oxidised material to cyanidation. The success of this change in process prompted reprocessing of the sulphides stored in the dedicated concentrate tailings impoundment (Fig. 1a,b).

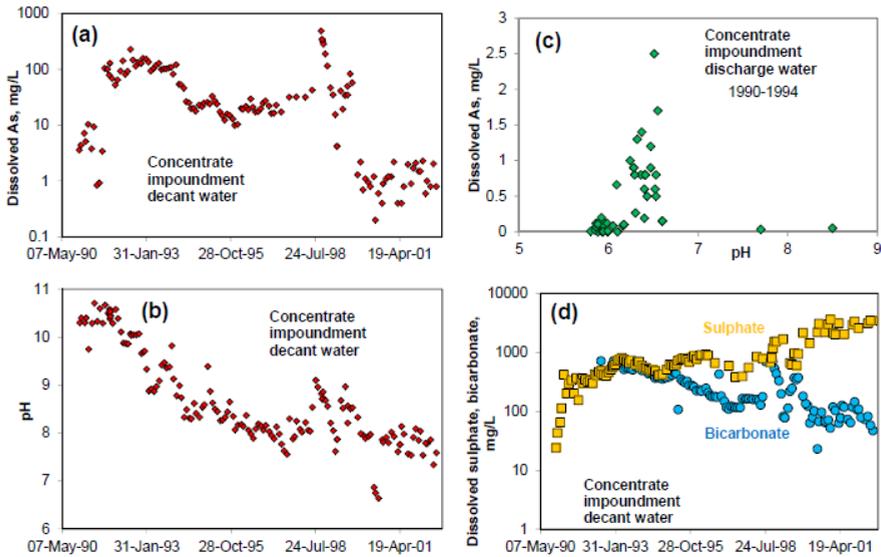
Monitoring of the full 13-year life of the As-rich concentrate tailings impoundment at the Macraes mine provides an example of the geochemical and mineralogical changes that occurred in arsenopyrite-rich tailings during storage. Low permeability of the tailings ensured that most tailings remained water-saturated and arsenopyrite was essentially unaltered (Fig. 1b).

Tailings waters accumulated on the surface of the impoundment in a decant pond (Fig. 1a). Dissolved As concentrations in these decant pond were high and variable over time as processing activities occasionally provided new water inputs, and were commonly tens to hundreds of mg/L (Fig. 2a). The pH was initially high (Fig. 2b) because the waters were derived directly from the cyanidation plant that operates at pH 10-5-11. However, the pH dropped over time (Fig. 2b) as the impoundment was mostly inactive, and waters interacted with rock calcite in the tailings. Tailings waters percolated through the tailings and the retaining dam (constructed of waste rock), and were collected at a sump at the toe of the dam (Fig. 1a). These waters remained below 1 mg/L dissolved As, and the pH was consistently circumneutral, between 6 and 7 (Fig. 2c).

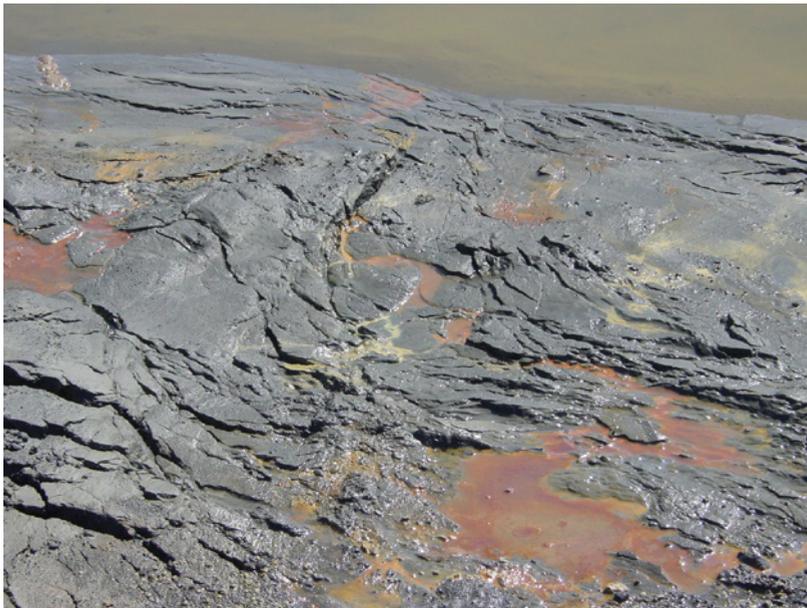
Only minor oxidation of sulphides occurred in the upper metre of the tailings during the 13 years of storage. This caused localised acidification on the centimetre scale (down to pH 3-4), and minor formation of arsenate mineral encrustations (Craw et al. 2002). The resultant acid reacted with abundant calcite in the tailings, resulting in moderate to high levels of dissolved sulphate and bicarbonate in the decant pond (Fig. 2d). The tailings were excavated (Fig. 3) and successfully and economically reprocessed for residual gold when the pressure-oxidation system was added to the processing plant.



**Figure 1** (a). Map of the concentrate tailings impoundment at Macraes mine, with contours on basement and dams to show the volume of tailings. (b) Photograph of tailings after storage for 10 years, observed during excavation for reprocessing. Grey colour and preservation of initial depositional bedding confirms the lack of oxidation.



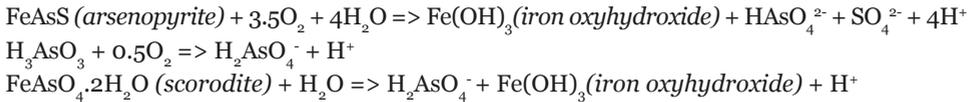
**Figure 2** Geochemistry of waters in the Macraes concentrate tailings impoundment. (a) Time series for dissolved As in the decant pond. (b) Time series for pH in the decant pond. (c) Dissolved As and pH in discharge waters collected at the sump at dam toe. (d) Time series for dissolved sulphate and alkalinity in decant pond waters.



**Figure 3** Photograph (view is 2 metres across) of Macraes mine concentrate tailings during reprocessing. Localised oxidation and acidification of tailings waters (to pH 4-5) occurred, with associated neutralisation by rock calcite in tailings to yield precipitates of gypsum (white) and iron oxyhydroxide (brown). Some jarosite formation (yellow) occurred as well.

### Oxidation mineralogy

Oxidation of iron in pyrite and arsenopyrite in the surficial environment form iron oxyhydroxide under most conditions (Fig. 4a). Arsenic oxidation initially yields dissolved  $\text{H}_3\text{AsO}_3$ , and this can precipitate arsenolite under evaporative conditions (Fig. 4a). Further oxidation produces dissolved  $\text{H}_2\text{AsO}_4^-$  and/or  $\text{HAsO}_4^{2-}$ , which can precipitate as amorphous or crystalline scorodite with iron oxyhydroxide, or jarosite under acid oxidised conditions (Fig. 4a). Oxidation and dissolution of arsenic during these processes can cause some acidification of associated waters at mine sites (e.g., Haffert and Craw 2008):

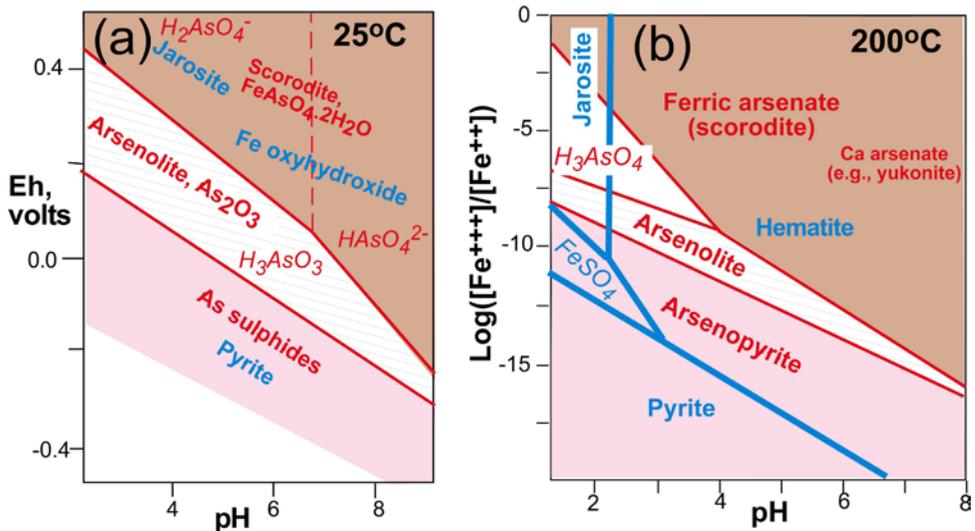


During the reprocessing activity at Macraes, minor oxidation and localised acidification of tailings waters occurred, but this was almost immediately neutralised by calcite, with precipitation of iron oxyhydroxides (Fig. 3). The iron oxyhydroxide precipitates formed from the Macraes mine tailings waters, especially in the vicinity of discharge waters in and near collection sumps, have high surface area, and this readily adsorbs abundant dissolved As (Roddick-Lanzilotta et al. 2002). This adsorption is at least partially responsible for the lowered dissolved As in waters that emanated from the toe of the concentrate tailings dam (Fig. 1a, 2c).

Oxidation of the sulphides at elevated temperatures involves similar mineralogy and reactions, at accelerated rates (Fig. 4b). The principal iron minerals produced in this process are hematite or amorphous iron oxyhydroxide. Arsenolite is an intermediate oxidation product of arsenate, and the ultimate product is iron arsenate (variably hydrated at high temperatures). Jarosite is also a common product of this oxidation process if the system becomes acidified (Fig. 4b), where potassium is typically derived from muscovite in the ore feed. The pressure oxidation process at the modern Macraes mine yields an acidified product consisting mainly of hematite, As-poor jarosite and iron arsenate, with a range of minor compounds (Craw 2006; Kerr et al. 2015).

### Historic mine tailings

The tailings from the pressure oxidation system at Macraes mine are recombined and severely diluted with the silicate rich flotation tailings, so observations on their evolution over time are more difficult than for the older concentrate tailings described above. In order to examine the long-term stability of this type of material, we have focussed on historic tailings at sites in southern New Zealand in which sulphide concentrates were made and roasted, and the resultant tailings were left abandoned for up to 100 years (McLachlan et al. 2016; Malloch et al. 2017). These tailings still contain minor amounts of gold, but the dispersed nature of their current sites and the small volumes involved mean that they are unlikely to be economic for gold extraction in the foreseeable future. However, they provide a useful window into mineralogical and geochemical processes that have occurred on a time scale of decades.



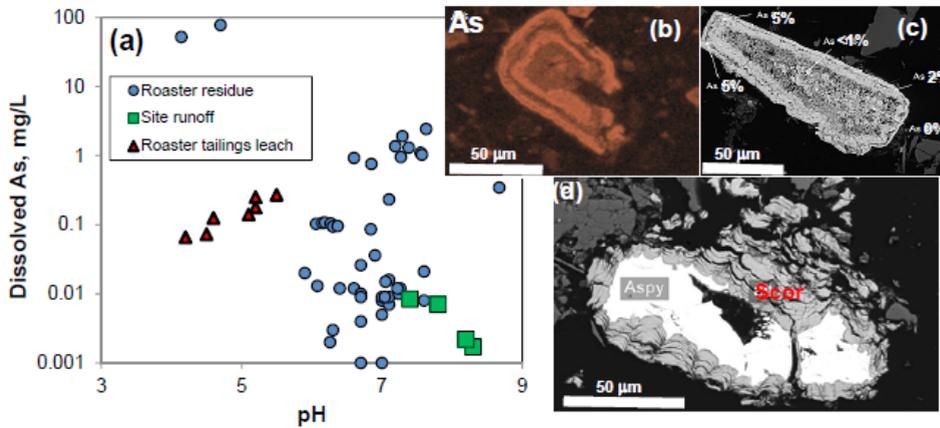
**Figure 4** Mineral stability diagrams for oxidation of pyrite and arsenopyrite (summarised from Craw 2006; Haffert and Craw 2008). (a) Surficial environment. (b) Roasting of sulphide concentrate.

More primitive oxidation processes than pressure oxidation were used at these sites, dominated by Edwards roasters. Waters within these tailings typically have low to moderate dissolved As at circumneutral pH (Fig. 5a). Some scorodite and minor yukonite (Ca-Fe<sup>3+</sup> arsenate; Fig. 5b) were formed in the roaster and discharged to tailings. However, ferric iron compounds such as hematite (±maghemite) were the principal products of the roasting process at the historic sites, and these formed distinctly red tailings deposits. The iron minerals are largely pseudomorphous after the original sulphide grains, and are variably porous as a result of expulsion of sulphur from their structures. The iron compounds contain variable amounts of arsenic, either encapsulated or as solid solution, up to 5 wt% (Fig. 5c). Despite the long periods of subsequent storage, these As-bearing iron compounds are relatively inert in the environment and have provided effective long-term As sequestration. Although dissolved As can be as high as 1 mg/L in tailings waters, waters leaving these sites are more dilute, with dissolved As <0.01 mg/L (Fig. 5a). Laboratory leaching experiments on this material over up to 6 months show that only low levels of dissolved As (~0.1 mg/L) can be extracted from the tailings (Fig. 5a).

Arsenolite was an intermediate oxidation product during the historic roasting process, and this was saved as a separate byproduct at times (Haffert and Craw 2008). Arsenolite locally formed a minor component of the hematite-rich tailings as well. Arsenolite is highly soluble and is the most environmentally undesirable residual mineral, resulting from locally extremely elevated levels (~100 mg/L) of dissolved As (Fig. 5a).

Some residues of unroasted sulphide concentrates occur at the studied historic mine sites. These sulphides have been largely oxidised to iron oxyhydroxides and scorodite (Druzicka

and Craw 2015; Malloch et al. 2017), but some relict sulphide grains have been preserved (Fig. 5d). These sulphides are inevitably armoured and encapsulated in the secondary mineral products, which limits their rates of further decomposition. Further, the abundant iron oxyhydroxide material present in these tailings has adsorbed at least some of the As mobilised from the sulphides. Consequently, the waters leaving these sites have low dissolved As.



**Figure 5** Arsenic mobility in 70-100 year old tailings. (a) Dissolved As vs pH for waters emanating from tailings residues from two historic mine sites. (b) SEM map showing zoned As distribution in a yukonite (Ca-Fe arsenate) bearing particle in roasted sulphide ore tailings. (c) SEM backscatter image of zoned hematite particle showing As compositions. (d) SEM backscatter image of a relict arsenopyrite particle (white) armoured by Fe-As-rich alteration layers (Scor), in unroasted sulphide concentrate tailings.

## Conclusions

Gold mine tailings are potential resources for the future, and they should be managed as such. This management should involve prediction and monitoring of the mobility of accompanying arsenic in the tailings waters. The levels of dissolved As can be predicted from the mineralogy of the tailings and the nature of the water flow pathways around a tailings repository. Short-term (13 years) storage of arsenopyrite-bearing tailings at the Macraes mine allowed subsequent successful reprocessing of those tailings for the remaining gold when processing technology was improved. There were some locally elevated dissolved As concentrations and minor acidification within the tailings repository, but discharging waters remained with circumneutral pH and low dissolved As. Historic mine tailings that had involved roasting of sulphides to release encapsulated gold contain As-bearing hematite. This material has remained largely inert for up to 100 years, and discharging waters from these sites have very low dissolved As contents. However, arsenolite is an intermediate oxidation product of arsenopyrite during roasting, and this mineral has higher solubility and can yield extremely high dissolved As concentrations. Dissolved As is strongly attenuated by adsorption to high surface area iron oxyhydroxides that form during roasting and under surficial conditions. Hence despite the abundance of As-bearing minerals in gold mine tailings, most associated waters have low dissolved As.

### Acknowledgements

This research was funded by NZ Ministry for Business, Innovation and Employment via CRL Energy Ltd. Additional funding was provided by University of Otago. SEM images were obtained at the Otago Centre for Electron Microscopy. Logistical support was kindly provided by OceanaGold Ltd and NZ Department of Conservation, and we particularly appreciate help from Debbie Clarke, Barry Mathieson, and Jim Staton. Discussions with James Pope and Dave Trumm were helpful in formulating ideas for this paper.

### References

- Craw D (2006) Pressure-oxidation autoclave as an analogue for acid-sulphate alteration in epithermal systems. *Mineralium Deposita* 41: 357-368.
- Craw D, MacKenzie D (2016) Macraes gold deposit, New Zealand. SpringerBriefs in World Mineral Deposits. ISBN 978-3-319-35158-2, Berlin, 130 pp.
- Craw D, Koons PO, Chappell DA (2002) Arsenic distribution during formation and capping of an oxidized sulphidic minesoil, Macraes mine, New Zealand. *Journal of Geochemical Exploration* 76: 13-29.
- Druzicka J, Craw D (2015) Metalloid attenuation from runoff waters at an historic orogenic gold mine, New Zealand. *Mine Water and Environment* 34: 417-429.
- Haffert L, Craw D (2008) Mineralogical controls on environmental mobility of arsenic from historic mine processing residues, New Zealand. *Applied Geochemistry* 23: 1467-1483.
- Kerr G, Druzicka J, Lilly K, Craw D (2015) Jarosite solid solution associated with arsenic-rich mine waters, Macraes mine, New Zealand. *Mine Water and Environment* 34: 363-374.
- McLachlan C, Craw D (2016) Characterisation of tailings at Prohibition Mine Site, Waiuta, Westland. Proceedings of the 49th Australasian Institute of Mining and Metallurgy (AusIMM) New Zealand Branch Annual Conference, pp. 259-268.
- Malloch K, Craw D, Trumm D (2017). Arsenic mineralogy and distribution at the historic Alexander gold mine, Reefton Goldfield, New Zealand. *New Zealand Journal of Geology and Geophysics* 60 (in press).
- Roddick-Lanzilotta AJ, McQuillan AJ, Craw D (2002) Infrared spectroscopic characterisation of arsenate(V) ion adsorption from mine waters, Macraes Mine, New Zealand. *Applied Geochemistry* 17: 445-454.