



Stabilisation of extremely As-rich mine processing waste at historic gold mines, New Zealand

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The Prohibition Mill site, a historic gold mining sites in the South Islands, processed arsenopyrite-rich ore from 1938 – 1951. Roasting of the ore, which was part of the processing technique, produced arsenolite (As_2O_3) rich waste with up to 40 wt% As. This waste was discarded into the nearby wetland (up to 10 wt% As) and some arsenolite is also still exposed around the roaster system. The presence of arsenolite has several implications: (1) Arsenolite is soluble in the surficial environment and surface run-off can acquire up to 30 mg/L dissolved As within minutes. In wetland sediment, where reducing conditions and long residence time allow for equilibration of arsenolite and pore water, dissolved As concentrations can be up to 330 mg/L. (2) In the surficial environment, oxidation of AsIII derived from arsenolite dissolution causes acidification, lowering site pH to 3 – 4. High dissolved As concentrations and acidity in oxidising surface waters promote the precipitation of the secondary As mineral scorodite ($\text{FeAsO}_4 \cdot \text{H}_2\text{O}$) and a large volume of As (100 m³ at 10 – 30 wt% As) is currently immobilised as scorodite cement in the site substrate. Downstream dissolved As concentrations are directly dependent on the stability of the As minerals present. While exposure is the only substantial limitation on arsenolite dissolution, scorodite stability is sensitive to redox conditions, dissolved As concentrations and especially pH. In acidic conditions dissolved As in equilibrium with scorodite can theoretically be as low as 0.1 mg/L (e.g. pH 3), whereas in circum-neutral waters, maximum scorodite solubility can exceed 10 mg/L. Environmental changes, such as (a) external site neutralisation, (b) removal of exposed arsenolite resulting in lower dissolved As concentrations, or (c) promoting reducing conditions by capping the material with an impermeable layer, can destabilise scorodite. In order to maximise As stabilisation, the As-rich substrate should be maintained with low pH (near 4), aerated, and porous, allowing for immediate or at least evaporative precipitation of scorodite from run-off. Despite abundant scorodite precipitation, site discharge from the Prohibition mill site is still several orders of magnitude above accepted guidelines. Scorodite precipitation does, however, mitigate the scale of contamination that can be expected from the presence of the highly soluble arsenolite. At older historic gold mining sites in the South Island of New Zealand, where available arsenolite has already been dissolved or was not produced as part of the ore processing, scorodite can dissolve. Scorodite dissolution is accompanied by site acidification to a pH of around 3, at which point scorodite solubility is at its minimum (0.01 – 0.1 mg/L). Thus, scorodite precipitation is a suitable stabilisation process of As under moderately acid conditions. If external control of pH occurs, such as with carbonate buffering, scorodite is 1000 times more soluble, and is unsuitable for arsenic stabilisation.