

Development of a single stage High Density Sludge (HDS) process for the reopening of South Crofty Tin Mine, Cornwall, UK

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Abstract

This paper provides an overview of the pilot plant trials undertaken at South Crofty Tin Mine, Cornwall, UK. The results lead to the design and installation of a full-scale Water Treatment Plant at South Crofty allowing the mine to be reopened by Cornish Metals. These trials led to the development of a single stage high density sludge plant using hydrogen peroxide to oxidise and precipitate an arsenic rich iron sludge. By concurrently air stripping dissolved carbon dioxide and utilising the carbon buffer in the mine water iron/arsenic oxidation and precipitation was found to take place at a near constant pH. Thereby avoiding the addition of alkali (i.e. sodium or calcium hydroxide). After removing the iron/arsenic sludge, the pH was raised to circa pH 10 using a second single stage high density sludge plant to remove manganese. The paper concludes by providing an overview of the full-scale plant and a comparison of the pilot and actual plant performance.

Keywords: South crofty tin Mine, cornwall arsenic, single stage high density sludge, hydrogen peroxide

Introduction

When South Crofty Mine closed in 1998 it ended 600 years of mining in Cornwall. The dewatering pumps were switched off and the workings allowed to flood with an estimated 8,000,000 m³ of water. Once flooded, excess mine water started draining into the nearby surface water course (the Red River) via an ancient adit. The tin reserves were never in doubt, merely the cost of extraction. 25 years later prices have recovered and Cornish Metals Ltd are looking to reopen the mine. The first stage being the installation of submersible pumps and construction of a treatment plant to dewater the mine over an 18 month to 2-year period at a rate of $25,000 \text{ m}^3/\text{d}.$

During the past 25 years a number of pilot trials have been undertaken to assess the treatability of the mine water and agree treated water quality standards with the regulator (Environment Agency). These trials culminated in the development of the UK's (and possibly the world's) first single stage high density sludge (HDS) mine water treatment plant using hydrogen peroxide rather than air (oxygen) as an oxidant.

This paper provides a summary of the trials undertaken leading up to the design, installation and commissioning of the Mine Water Treatment Plant in October 2023. It concludes by presenting a summary of the treated water quality achieved during the first 2 months of operation of the full-scale plant.

Mine Water Quality

On closure of the mine the rising main previously used to pump water from the mine was left intact within the abandoned shaft. This allowed mine water to be taken from depth for the various pilot trials. Thereby avoiding the risk of using near surface water which was likely to comprise a mixture of water from deep within the mine and relatively clean rainwater infiltration. As a result, there was less uncertainty regarding the composition of the mine water once pumping commenced (Table 1).

	рН	TSS mg/L	lron (dis) mg/L	Copper (dis) µg/L	Arsenic (dis) μg/L	Manganese (dis) µg/L
Raw Mine Water						
(Pilot trial	6.1	5	44	10	2010	5140
average)						

Table 1 Typical Composition of South Crofty Mine Water

Pilot testing first commenced using the same high density sludge process as employed at the nearby abandoned Wheal Jane Tin mine (Fig. 1) where the process has successfully been in operation for 5 years removing iron, zinc, manganese, arsenic and copper (Coulton et al. 2003). At that stage it was assumed that the Regulator would impose a similar consent and that the iron concentration at South Crofty was sufficiently high to co-precipitate the arsenic (Iron: Arsenic ratio 22:1 at South Crofty compared to 68:1 at Wheal Jane).

Subsequent discussions revealed the Regulator intended to impose a much stricter consent at South Crofty due to the lower flow rate in the Red River and its better quality. As a result, a further pilot trial was undertaken in 2016/17 culminating in the addition of a hydrogen peroxide dosing stage up front of the HDS reactors (Fig. 2) to ensure all the arsenic was oxidised from the As³⁺ to the less soluble As5+ form and precipitated as ferric arsenate. Data derived from this trial was shared with Regulator who issued a treated water discharge permit prescribing 3 levels of compliance (Table 2), namely:

• Consent/statuary limits imposed by the EU Water Framework Directive.

- Trigger levels which if exceeded require the Mine to implement process improvements.
- Warning levels, which if exceed require the mine to advise the Regulator and implement immediate process improvements.

Whilst the 2016/17 process produced acceptable water quality, it resulted in high sludge generation and high lime consumption rates (475 mg/L and 320 mg/L respectively). In addition, the use of hydrogen peroxide in the first reactor resulted in the formation of a low density, arsenic rich iron sludge. At the proposed operating flow rate, the plant was predicted to make 12.5 t/d of dry solids which at 8%w/w underflow density achieved by the pilot plant would have resulted in 150 m^{3}/d of slurry. As the nearest sludge storage facility was located some 11 miles away, the 2017 design incorporated 2 filter presses to dewater the sludge to around 16 m3/d and thereby reduce transport costs.

Analysis of the sludge generated by the 2017 process revealed it comprised predominantly of calcium carbonate (55%) and only 13% iron. Further investigation revealed the mine water contained some



Figure 1 Wheal Jane HDS Plant



Figure 2 2016/17 Pilot Plant Configuration

70 mg/L of carbonate alkalinity and approximately 90 mg/L of dissolved carbon dioxide resulting in the precipitation of calcium carbonate on increasing the pH to around 10 to precipitate the manganese.

Laboratory scale pilot studies undertaken by the Authors in 2018 (Evans, Morgan & Coulton, 2019) revealed it was possible to form HDS in a single reactor using hydrogen peroxide as the oxidant rather than oxygen/air. In addition, as the rate of iron oxidation is not pH dependent the process offered the benefit of utilising the carbonate buffer to maintain a near constant pH. Thereby avoiding the need to add alkali (in the form of either sodium or calcium hydroxide) to counter the acidity generated by iron precipitation.

A further series of pilot trials were undertaken in 2021/22 (using a 1.3 m3/h containerised pilot plant) with the objective of reducing both the lime consumption and sludge generation by pre-stripping the dissolved carbon dioxide with air. These led to the conclusions that:

- Air stripping the carbon dioxide beneficially reduced both the lime consumption and sludge generation rates by minimising the amount of carbonate precipitated.
- As a result of degassing and the reduced carbonate precipitation, it was not

possible to achieve consent compliance using the process trialled in 2017 (Fig. 2). The inference being that during that trial the sludge chemistry was dominated/ swamped by carbonate precipitation which both diluted the arsenic concentration in the sludge and prevented the arsenic redissolving when the pH was increased to precipitate the manganese.

- The only way to achieve both reduced operating cost and consent compliance was to introduce a 2-phase process with the iron/ arsenic and manganese removed separately from the mine water (Fig. 3), in which:
 - Phase I precipitate an arsenic rich high density iron sludge at circa pH
 6 in a single reactor by recirculating sludge whilst concurrently airstripping the carbon dioxide. (Fig. 4 – left sample)
 - Phase II precipitate a high-density manganese sludge (Coulton et al, 2004) by increasing the pH within the reactor by the addition of lime and recirculating sludge into a single reactor (Fig. 4 – right sample)
- As a result of the above, the final pilot trials demonstrated an 82.8% reduction in lime consumption and 67.4% reduction in sludge generation in comparison to the 2017 trial.

Table 2 South Crofty Mine water Discharge Consent Parameters

	рН	TSS mg/L	lron (dis) mg/L	Copper (dis) µg/L	Arsenic (dis) µg/L	Manganese (dis) µg/L
Consent Level	6–9	-	-			
Trigger Level	6.5-8.5	20	0.040	5	40	60
Warning Level	-	-	-	-	20	20

• The reduced sludge generation and the formation of HDS, allowed the sludge to be thickened to circa 30% w/w reducing the daily sludge generation rate to 22 m³/ day thereby avoiding the need to install filter presses.

Full Scale Plant

Construction of the full-scale plant commenced in September 2022 and was commissioned in October 2023. The plant comprises 3 identical treatment streams each with a rated capacity of 350 m³/h (Fig. 5). Each stream comprising the following stages:

- Stage I precipitation of both the iron and arsenic as HDS in a 180m3 stirred reactor, at pH 6.3 without the addition of lime, together with concurrently air stripping dissolved carbon dioxide at a ratio of 3:1 (Stripping air: Mine water)
- Stage II addition of flocculant followed be separation of iron/arsenic sludge using a lamella clarifier with an effective settlement area of 400 m2.
- Stage III raising the pH to circa pH 10 by the addition of lime to precipitate the dissolved manganese as a HDS in a 160 m3 capacity stirred reactor.
- Stage IV addition of flocculant followed by separation of manganese precipitant (along with precipitated calcium carbonate) using a lamella clarifier with an effective settlement area of 400 m².
- Stage V reduction in the treated water pH to less than pH 8.5 using carbon dioxide in a 120 m3 reactor to comply with the consent.

Excess sludge from each set of clarifiers is withdrawn at around 10-12%w/w by a peristaltic pump controlled via a mass flowmeter configured to maintain the underflow density within a user specified The sludge is then thickened to range. circa 30% w/w using a deep cone thickener before being transported off site in a slurry tanker. Underflow solids concentrations of up to 45%w/w have been achieved from the deep cone thickener, but operating at this concentration offers little advantage in terms of transport cost and the need to discharge the sludge as low viscosity slurry into the receiving tailings disposal facility.

Conclusions

The recently commissioned South Crofty mine water treatment plant is the result of nearly 20 years pilot testing and process development. It is the first deployment in the UK of a single stage HDS reactor using peroxide for iron precipitation. A second single stage HDS reactor is also used for manganese precipitation. Since commissioning in October 2023, the plant has processed over 1.5 million m³ of water and has reliably achieved the required treated water characteristics (Table 3).

Average lime consumption is 59 mg/L and the sludge generation rate is 162 mg/L. Both are very much in line with the 55 mg/L lime consumption and 151 mg/L sludge produced measured in the pilot trials. The iron rich sludge generated by the stage I reactor, contains 43%w/w iron and 3%w/w arsenic.



Figure 3 Adopted 2 phase Single Stage HDS Plant



Figure 4 Sludge produced during pilot trails, Iron / Arsenic Stage II sludge on the left and Manganese Stage IV sludge on the right.

Precipitation is being achieved without lime addition and without substantial carbonate precipitation, suggesting single stage peroxide HDS formation may offer a cost-effective alternative to a conventional air/lime based HDS process for iron removal from circum neutral mine waters. Depending on the application, this has the potential to offer savings in both the capital and operating costs.

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Table 3 - South Crofty Mine water pilot trial and full-scale plant results

	рН	TSS mg/L	lron (dis) mg/L	Copper (dis) µg/L	Arsenic (dis) μg/L	Manganese (dis) µg/L
Pilot Plant 2022	9	1	0.2	6	17	20
MWTP December 2023	7.5-8.5	<0.4 (LOD)	0.2	2	22	10

LOD - Limit of Detection



Figure 5 South Crofty MWTP - 26th October 2023 Stage I in the Background