

# The Effects of Using Hydrogen Peroxide to Provide an Improved HDS Process

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## Abstract

HDS treatment plants are effective active AMD remediation processes, comprising of two-stage systems using aeration as the oxidant. In this paper, the practicality of using  $H_2O_2$  as an alternative oxidant to reduce to a single-stage HDS plant was assessed. Comparative trials were conducted (two-stage (conventional HDS) and single-stage processes) on a bench-scale HDS rig, treating a continuous flow of 150 mg/L Fe net alkaline synthetic mine water. Results demonstrate that HDS treatment plants can be modified to a single stage when using  $H_2O_2$  without compromising water quality or dewatering capabilities (42% dewatered solid content) of the HDS process.

**Keywords:** AMD, HDS, Aeration,  $H_2O_2$

## Introduction

Whilst the mining industry is one of the leading markets of the global economy (Rudko 2020), the consequences of mining cause substantial long-term environmental and ecological threats (Ojonimi et al. 2019). Acid Mine Drainage (AMD) is considered a global environmental issue (Balci and Demirel 2017) with strict surface and ground water quality targets driving the development of AMD remediation strategies. Although passive treatment processes are more favourable remedial options for AMD, if the contaminant load is too high, or there are constraints with land availability, then active treatment is necessary (Coulton et al. 2007).

One of the most well-established forms of active AMD remediation involves chemical treatment to oxidise Fe (II) to Fe (III), manipulate pH and subsequently precipitate Fe(III) as oxyhydroxides ( $Fe(OH)_3$ ) (Fan et al. 2019). Fe oxidation and precipitation can also aid in the removal of other dissolved metallic species by co-precipitation. Removing metals in this way chemically entraps large amounts of water, generating a gelatinous Low-Density Sludge (LDS) with a solids content of 2-5% (Coulton et al. 2004). Resulting in poor settling velocities and a voluminous sludge

for disposal. Continuous recirculation of LDS back into the process provides sites for crystal nucleation, increasing the solids content to 20-50% (Coulton et al. 2004; Murdock, Fox and Bensley 1993) converting from LDS to High Density Sludge (HDS). Examples of UK based HDS treatment plants include, Wheal Jane (Coulton et al. 2003a), Dawdon Colliery (Bailey et al. 2013), Horden Colliery and Blenkinsopp (Wyatt et al. 2018).

Conventionally the HDS process is undertaken in two stages using air for oxidation. Consequently, the process has high capital costs requiring at least 2 reaction vessels; the sizing of main vessel being determined by the pH and the rate of Fe oxidation. In addition, operating costs are high due to the amount of energy required to break up the air into small bubbles and the consumption of alkali required to maximise the oxygen transfer rate. Theoretically, the HDS process can be reduced to a single-stage system. In this paper the practical feasibility of using a strong chemical oxidant, hydrogen peroxide ( $H_2O_2$ ) as an alternative to air, with the aim of reducing the HDS process to a single stage is assessed.  $H_2O_2$  is considered favourable as the Fe oxidation reaction rate is almost

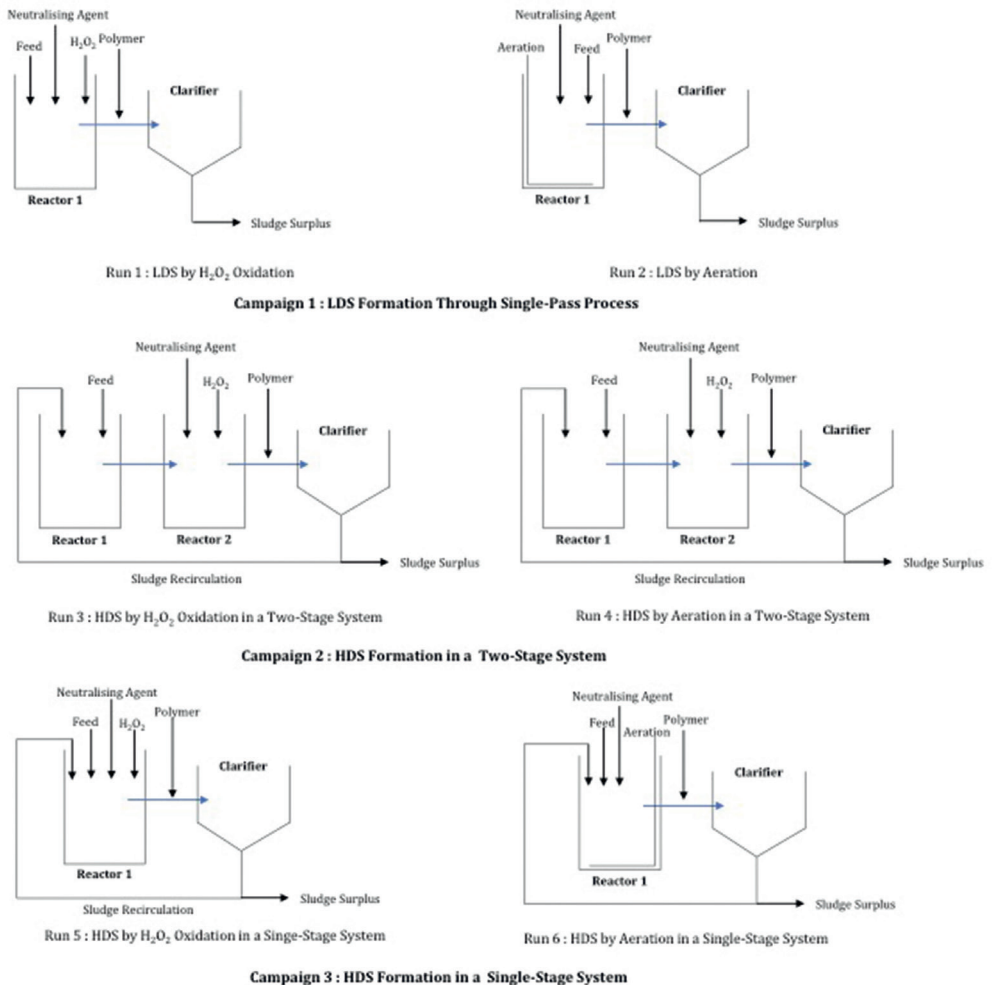
instantaneous (Leavitt 2010) requires little mixing energy and is less dependent on pH than aeration.

A purpose-built bench scale HDS rig was used to treat a continuous flow (10 L/h) of 150 mg/L Fe circa pH 6 (net alkaline) synthetic mine water for each 10-day run (fig. 1). A fresh supply of mine water was prepared

daily and kept under a CO<sub>2</sub> atmosphere to prevent atmospheric oxidation, ensuring a representative feed. 1% sodium hydroxide (NaOH) was used as the alkali solution and an anionic polymer (AD985) was prepared at a 0.01% working strength. NaOH addition was managed through a pH-controlled dosing pump.

**Table 1** Parameters of each run and associated campaign.

Campaign	Run	No. Reaction Stages	Oxidising Reagent	Sludge Recirc	Volumetric Recirc Ratio
1	1	1	H <sub>2</sub> O <sub>2</sub>	No	0%
	2	1	Air	No	0%
2	3	2	H <sub>2</sub> O <sub>2</sub>	Yes	25–30%
	4	2	Air	Yes	25–30%
3	5	1	H <sub>2</sub> O <sub>2</sub>	Yes	25–30%
	6	1	Air	Yes	25–30%



**Figure 1** Structure of Runs 1-6 for the bench scale comparative study

Reactors used for homogenisation and oxidation hold a volume of ~ 5 L, providing a retention time of 30 minutes. Each reactor was paired with a mechanical mixer to provide sufficient mixing as required to ensure homogenisation of feed water, sludge and dispersal of oxidant and alkali. Following the precipitation reaction AD985 was added to promote floc formation and aid settlement within the clarifier.

As the rate of oxidation through the aeration process is predominantly pH dependent, every unit drop in pH promotes a decrease in the rate of oxidation by a factor of 100 (Coulton et al. 2003b). Thus, to ensure an optimum oxidation rate of Fe (II) to Fe (III) in the aerated trials, a pH of >8.4 was required and achieved through addition of NaOH. As H<sub>2</sub>O<sub>2</sub> is an extremely powerful oxidant, the pH required relates to the solubility of Fe(OH)<sub>3</sub>. Therefore, for the runs using H<sub>2</sub>O<sub>2</sub> (1% active ingredient), NaOH was added to maintain a pH >5.5 to achieve a discharge Fe limit of <1 mg/L.

For each run, 100ml samples were collected daily from the clarifier inlet and a 1-hour settlement test conducted, providing an initial settling velocity (m/h) and settled solid content (w/v) by mudline analysis. Total suspended solids (TSS) was analysed post settlement test. To establish the mechanical dewatering capabilities, a 50 mL sludge sample was drawn from the bottom of the clarifier daily and dewatered under 1 bar of pressure, providing the dewatered solid content (w/w). Monitoring of reactor pH and reagent consumption was conducted throughout.

## Results

### Average TSS

For campaign 1, the average TSS concentration of sludge produced was 267 – 289 mg/L (tab. 2). Results compared well to the theoretical value of 286.6 mg/L (equation 1), suggesting that all the Fe (II) was oxidised and precipitated through the system.

$$TSS = \frac{(\text{Fe}^{2+} \text{ concentration in feed water} \times \text{atomic mass of Fe(OH)}_3)}{\text{atomic mass of Fe}^{3+}} \quad (1)$$

Once conditions stabilised, Fe<sub>(total)</sub> concentration in the clarifier supernatant was <1 mg/L consistently.

TSS values for the H<sub>2</sub>O<sub>2</sub> process (Campaign 2 and 3) were over 6000 mg/L greater than the conventional two-stage aeration process and over 7000 mg/L greater than the single-stage aeration LDS processes (fig. 2).

### Initial Settling Velocities

Initial settling velocities in Campaign 1 were 1–1.1 m/h, as expected for LDS. A conversion from LDS to HDS was observed in Campaign 2, where initial settling velocities were more than ten times that of Campaign 1 (tab. 2). In Campaign 3, the H<sub>2</sub>O<sub>2</sub> run had an initial settling velocity of 9.4 m/h compared to the aerated run which only achieved 4.8 m/h.

For Campaign 2 and 3, mudline analysis showed that the H<sub>2</sub>O<sub>2</sub> runs followed a similar pattern to the conventional two-stage aeration run (fig. 3). However, the Campaign 3 aeration run did not, suggesting that this process does not form true HDS.

### NaOH Consumption

H<sub>2</sub>O<sub>2</sub> runs were operated at pH 5.5 and consumed between 115–125 mg/L NaOH (tab. 2). Aerated runs were operated at pH 8.4 and consumed 298–370 mg/L.

### Settled and Dewatered Solid Content

Settled solid content for Campaign 1 was <5% in both runs. Dewatered solid content within the sludge was 30% when using H<sub>2</sub>O<sub>2</sub> compared to 16.5% with aeration. For both Campaign 2 and 3, the aerated runs had a higher settled solid content, but a lower dewatered solid content than the H<sub>2</sub>O<sub>2</sub> runs. For the Campaign 3 aerated run, the dewatered solid content was much lower than any other HDS process, indicating once more that true HDS did not form during this run.

### Time to form HDS

The conversion of LDS to HDS in the H<sub>2</sub>O<sub>2</sub> runs took 4–5 days compared to 9 days for the conventional two-stage aerated runs (tab. 2). HDS had not formed in the Campaign 3 aerated run after 10 days.

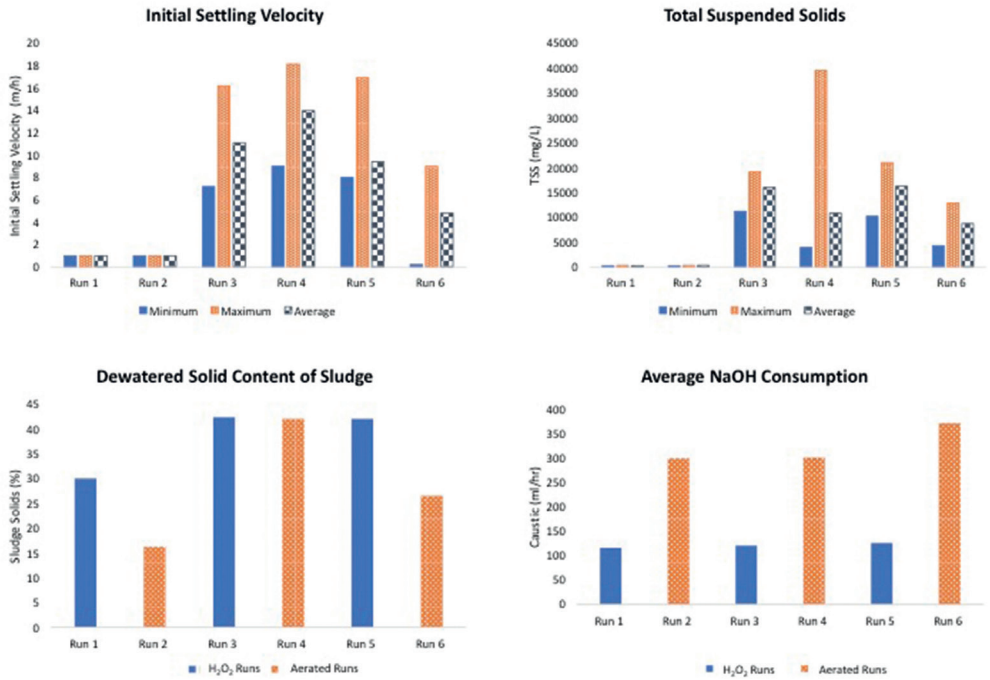


Figure 2 Results from the bench scale comparative study.

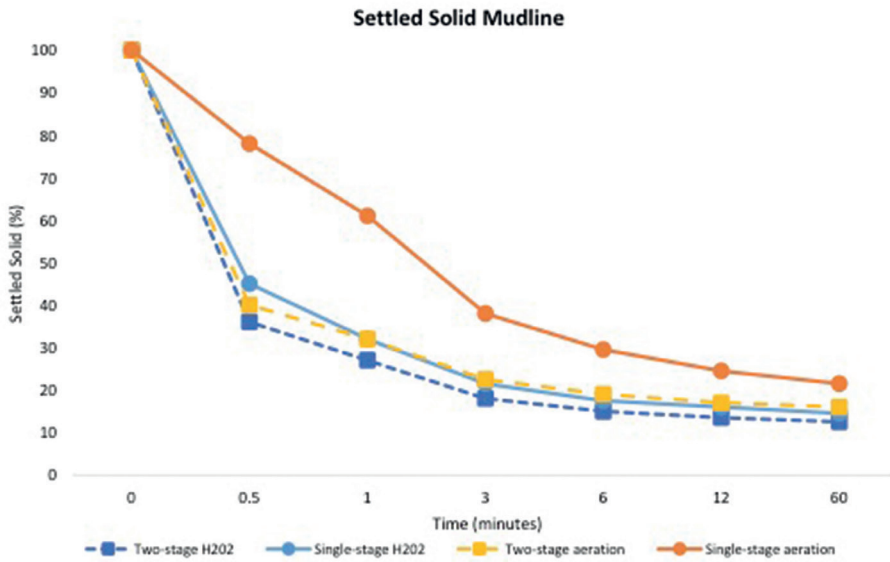


Figure 3 Settled solid mudline for Campaign 2 & 3 (Run 3-6).

Table 2 Summary of bench scale results.

Cam- paign	Run	Operating pH	Average NaOH Dose	Average Clarifier TSS <sup>1</sup>	Mass Recirc Ratio <sup>2</sup>	Initial Settling Velocity	Settled Solid Content (weight/ volume)	Dewatered Solid Content (weight/ volume)	Time to Form HDS	Sludge Type
1	1	5.5	115 ml	267 mg/L	N/A	1.1 m/h	<5%	30%	N/A	LDS
	2	8.4	298 ml	289 mg/L	N/A	1 m/h	<5%	16%	N/A	LDS
2	3	5.5	120 ml	16021 mg/L	1:56	11.1 m/h	12.5%	42.3%	4 days	HDS
	4	8.4	300 ml	10830 mg/L	1:38	14 m/h	16%	42%	9 days	HDS
3	5	5.5	125 ml	16228 mg/L	1:56	9.4 m/h	14.5%	42%	5 days	HDS
	6	8.4	370 ml	8738 mg/L	1:30	4.8 m/h	26.5%	26.5%	N/A	MDS <sup>3</sup>

Note:

<sup>1</sup>Refers to the Clarifier inlet TSS

<sup>2</sup>Refers to the ration between Fe(OH)<sub>3</sub> generated by oxidation/precipitation to Fe(OH)<sub>3</sub> within the recirculated sludge.

<sup>3</sup>Medium Density Sludge (MDS)

## Discussion

Reduction of the HDS process to a single stage could not be achieved using aeration. This was demonstrated when comparing the Campaign 3 aerated run with the Campaign 2 aerated run, where settling velocities were 4.8 m/h and 14 m/h, respectively. Sludge produced in Campaign 3 aerated run did not comply to the descriptions of LDS or HDS and in this instance was referred to as medium density sludge (MDS).

However, Campaign 2 and 3 H<sub>2</sub>O<sub>2</sub> runs produced HDS with a low formation time and with improved sludge characteristics, including lower settled solid content. For example, 12.5% versus 14.5% in Campaign 2, showing less voluminous sludge was generated using H<sub>2</sub>O<sub>2</sub>. Furthermore, the dewatered solid content of H<sub>2</sub>O<sub>2</sub> HDS in Campaign 2 and 3 was comparable to that of the conventional process. An improvement in dewatered solid content was also seen in Campaign 1, where the H<sub>2</sub>O<sub>2</sub> sludge dewatered to 30% (w/w) compared to 15% (w/w) in the aerated sludge.

Alkali consumption in the H<sub>2</sub>O<sub>2</sub> runs was less than in the aerated runs. Theoretically, 215 mg/L of NaOH was required to completely neutralise Fe oxidation and precipitation, with only an additional 0.23 mg/L required to raise the pH from 5.5 to 8.4.

Increases over theoretical NaOH consumption within the aerated runs were due to the alkalinity buffering change in pH, resulting in a reduction in alkali efficiency. H<sub>2</sub>O<sub>2</sub> runs consumed less than the theoretical

value due to the consumption of alkalinity and low reaction pH.

## Conclusions

Results from this study demonstrate that the design of the conventional HDS plant can be modified to a single stage system by using H<sub>2</sub>O<sub>2</sub> as the oxidant, without compromising water quality or sacrificing the dewatering capabilities of the conventional HDS process. The benefits associated with this include reduction in capital, maintenance, and operational costs due to the simplicity of a single reactor system. Furthermore, the reduced plant footprint and faster HDS establishment time allows the single stage system to become a more widely applicable solution to temporary and permanent treatment of net alkaline AMD.

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