Inference of Green Rust Formation and Fe^{2+}/Fe^{3+} Redox Cycling in Treatment of Acid Metalliferous Drainage

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Abstract

This paper presents field and laboratory investigations into aeration and alkaline treatment of a high-load, low-pH acid metalliferous drainage (AMD). Trials showed hydrated lime addition promoted the formation of a precipitate believed to be sulfate green rust (GR), resulting in reductive recycling of Fe^{3+} to Fe^{2+} and therefor reduced iron removal efficiency. NaOH buffering, and pre-oxidation with H_2O_2, limited GR formation but introduced operational and cost limitations. Treatment of a lower-load AMD sample exhibited no GR formation, allowing efficient lime treatment and ferric oxyhydroxide sludge generation. These findings emphasise the need to control Fe^{2+} loading and redox conditions to prevent GR-related treatment inefficiencies.

Keywords: AMD, aeration, oxidation, lime buffering, green rust

Introduction

Acid metalliferous drainage (AMD) is near-ubiquitous issue within sulfidic mining environments. If left untreated, AMD can have serious deleterious effects on local and regional receptors such as surface and groundwater quality. This in turn poses potential hazard to ecosystems and human health. To mitigate against these environmental liabilities, governing and regulatory bodies set prescriptive limits on the maximum concentrations / loads of given geochemical parameters for any waters released into local water courses from areas of mining operations. As global mining output increases to accommodate consumer demand, effective and economically sustainable AMD treatment solutions are essential to mitigate these effects and ensure regulatory compliance.

A range of active and passive treatment technologies have been developed to treat AMD, with chemical neutralisation using alkaline reagents such as hydrated lime remaining one of the most widely applied methods. However, active treatment via chemical addition can be costly, energy intensive, and generate large volumes of metalliferous sludge requiring safe disposal. Consequently, there is increasing emphasis on treatment optimisation techniques that reduce reagent consumption and lower operational costs. Aeration is one such optimisation strategy that plays a critical supporting role in many mine water treatment systems. Aeration aims to increase the concentration of dissolved oxygen (DO) within AMD whilst simultaneously degassing dissolved CO_2. By increasing the DO within the system, the oxidation of highly soluble ferrous iron (Fe^{2+}) to lower solubility ferric iron (Fe^{3+}) is accelerated. This allows the precipitation of iron at lower pH (approximately pH 4-5) and in turn reduces lime requirements.

This paper presents a case study into the use of active aeration and alkaline chemical treatment to treat a high load, low pH AMD. Due to the high manganese content of the AMD requiring treatment at the case study site, pH buffering to ≈pH 10 was required to facilitate its precipitation and removal from the aqueous phase. In an effort to avoid a high volume hazardous sludge, comprising iron oxyhydroxides, gypsum and metal hydroxides, a treatment system was developed that would generated two distinct waste sludges; 1) a high volume iron-rich relatively “clean” sludge with potential re-use applications as a sorption media elsewhere on site and 2) a low volume gypsum and metal hydroxide (e.g. Mn) sludge for disposal as hazardous waste.

This paper will discuss observations of the formation of suspected green rust minerals during treatment and the resultant effect on system efficacy. Green rusts (GR) are a group of mixed-valence iron oxyhydroxide minerals, with a layered double hydroxide structure, that are typically meta-stable with limited stability in acidic conditions. GR typically occurs under reducing, circumneutral pH conditions where both Fe^{2+} and Fe^{3+} are present (Génin *et al.* 1998). There are numerous variants of GR but "Green Rust 2" is of particular interest in AMD settings. Within this variant, sulfate is intercalated between the positively charged iron-hydroxide sheets providing greater stability. It has also been shown to exchange and/or reduce some groundwater contaminants such as U (Latta *et al.* 2015), Se (Refait *et al.* 2000) and Cr^{6+} (Thomas *et al.* 2018) leading to their use to aid AMD remediation (Bearcock *et al.* 2011).

Methods and Materials

Testing comprised field trials of a prospective aeration-lime dosing AMD treatment system and associated laboratory scale tests. In both cases testing was performed on a low pH, high load AMD referred to henceforth as "Sample 1". A summary of the key geochemical properties of "Sample 1" is displayed in Table 1. "Sample 1" was collected after the target AMD had been passed through the venturi pump used to provide aeration within the field trial system. As such the estimation of Chemical Oxygen Demand (COD) should be conservative as oxidation provided by the venturi will have resulted in some Fe^{2+} oxidising to Fe^{3+}. A subsequent sample was acquired in the same manner 4 days after "Sample 1". Termed "Sample 1b", this represents the same source AMD after dilution by rainfall to loads more reflective of levels typically encountered at the case study site.

The field trials for AMD treatment consisted of initial runs of a bespoke designed in-line treatment system. This treatment system consists of a venturi pump to provide aeration (and oxidation) of the AMD, a dosing pump providing 20% (w/w) hydrated lime slurry prior to an in-line mixer all in series. This then outputted into a settling pond. The flow rate of AMD through the system and rate of hydrated lime dosing rates were continuously monitored with in-situ flowmeters. Measurement of pH and ORP was performed on "grab samples" acquired from the output of the in-line mixer. Samples for laboratory testing were collected in 10 L HDPE buckets with sealed lids. When collecting samples, headspace was kept to a minimum within the buckets to mitigated against potential further oxidation of samples. Prior to sealing the sample in buckets, pH and ORP was recorded. These were then verified when received at the laboratory for testing.

Laboratory bench scale testing was performed within laboratory facilities on the mine site to mitigate against sample oxidation / degradation due to excessive transportation times and the lack of suitable preservation techniques for met-stable minerals such as the suspected GR. Lab testing consisted of beaker trials performed within borosilicate glassware placed on a magnetic stirrer plate with PTFE stirrer beads to facilitate effective mixing. Sample volumes were measured gravimetrically on a balance accurate to ±0.1 g. Volumes used during titrations varied from 200 mL to 50 mL due to equipment limitations at the on-site field laboratory and due to sequential nature of testing requiring

Table 1 Basic characterisation of "Sample 1" and "Sample 1b" AMD.

ID	pH	ORP	Electrical Conductivity	Al	Cu	Fe	Mn	Acidity	Chemical Oxygen Demand*
		mV	mS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Sample 1	2.30	878	8.31	198	67.4	1550	10.2	1790	225
Sample 1b	2.40	957	3.98	90.7	25.3	461	7.00	399	68.1

*Chemical Oxygen Demand calculated assuming all Fe and Mn are present in respective reduced forms aliquots to be taken for analysis. Titrations were performed with both hydrated lime and sodium hydroxide (also referred to as "caustic"). In both cases LR grade reagents (Merck) were used to produce titrants. The hydrated lime was utilised as a 20% (w/v) slurry mixed with 18.2 MΩ deionised water. The mass of lime required was measured to 4 d.p. with a calibrated balance accurate to ±0.0001 g. When titrating with hydrated lime, the slurry was kept well mixed via the use of a magnetic stirrer and PTFE bead. The slurry was added incrementally through the use of calibrated digital pipettors. In an effort to ensure all lime was removed from the pipettor tip, small volumes of the sample were taken into the pipettor tip to rinse lime slurry out. Pipettor tips were then discarded to prevent contamination of the lime slurry reservoir.

NaOH was utilised at a concentration of 0.5 M. This was also produced with 18.2 MΩ deionised water, with the required volume of NaOH measured volumetrically using calibrated digital pipettors. NaOH was introduced to the sample via titration from a Grade A glassware burette. Where hydrogen peroxide (H_2O_2) was used to enhance oxidation of Fe^{2+}, 30% LR grade H_2O_2 was used. Volumes required are reported as 60% H_2O_2 equivalent to be reflective of industrial grades likely to be used in potential site trials.

After the pH was adjusted to the required pH, the sample was left to stir to ensure a stable pH (consistent pH reading ±0.2 pH units over 5 minute period). The resulting precipitate was removed via vacuum filtration through 0.45 µm mixed cellulose filters before being dried at 105 °C for 24 hours. An aliquot of filtrate was taken for subsequent elemental analysis by Atomic Absorption Spectroscopy at on-site Intertek® laboratory. The remnant filtrate was then, if necessary for further investigation, subjected to further pH adjustment as described above.

Results & Discussion

The initial run of the aeration treatment system field trial aimed to assess the efficacy of aeration (via venturi) with lime addition at removing metal load when the pH was raised to approximately 4.5. The system was run at 30 PSI, equating to a flow of ≈8.4 m3/h with 20% (w/v) hydrated lime at a rate of 1.18 m^3/h to raise the pH to 4.5. A distinct colour change was observed in the AMD. Rather than

Figure 1 *Green-blue colouration within treated "Sample 1" AMD, dosed with hydrated lime to pH 4.5.*

the anticipated orange brown colouration typical of iron oxyhydroxides, the AMD was observed to turn a dark blue-green colour as seen in Figure 1. Subsequent testing within the laboratory showed that when oxidised / dried the green colour changed to an orange colour typical of ferric oxyhydroxides. This was interpreted as indicative that the green colouration was due to the presence of meta-stable green rust type minerals.

The Oxidation Reduction Potential (ORP) of the AMD was observed to decrease sharply with the addition of hydrated lime. Dropping from ≈900 mV post venturi pump to ≈100 mV post lime addition. This is a result of the increased pH and subsequent shift in redox equilibria causing precipitation of ferric iron from solution, thereby removing an oxidant and contributing to lowering the ORP. Given the use of a Ag/AgCl ORP probe this equates to an Eh of ≈300 mV. The pH of the treated AMD was checked after 30 minutes and observed to have decreased to pH 3.98 from pH 4.5 suggesting either further oxidation of ferrous iron or, potentially, the reduction of ferric iron. Analysis of the AMD showed dissolved Fe concentrations had decreased from 1550 mg/L to 661 mg/L, orders of magnitude in excess of release limits (5 mg/L), and suggesting that there is still an abundance of Fe^{2+} which is contributing to the formation of suspected GR in the treated AMD. When these conditions are plotted on a Pourbaix diagram for green rust 2 and iron oxyhydroxides (Figure 2) where Fe^{2+} activity is approximately -2 we observe that whilst Fe^{2+} is stable in solution the presence of GR is not predicted as a stable phase. Despite this, observations imply that a GR-like phase may form reflecting kinetic limitations not fully captured by the diagram.

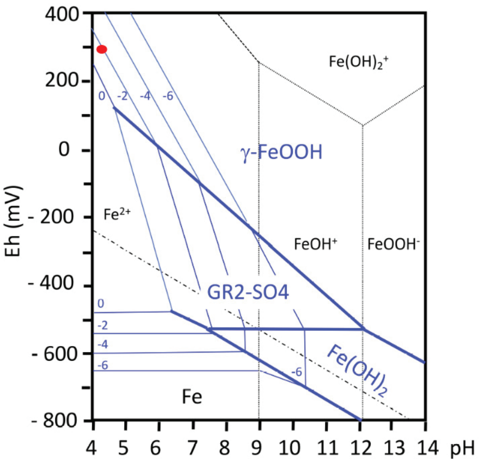

***Figure 2** Pourbaix diagram for synthetic sulfate green rust (GR2-SO4) calcualted with sulfate activity of 0.1. thin lines labelled "-n" denote Fe^{2+} activity of 10-n. Red dot represents post lime "Sample 1". Amended from Trolard* et al. *(2022).*

Beaker tests on "Sample 1" with lime addition to simulate the field trial yielded similar results to the field trial with >700 mg/L Fe remaining in solution at pH 4.3. Green colouration (interpreted as GR) was observed as in the field trials. ORP across these tests was observed to decrease as pH increased from an initial ≈460 mV to ≈170 mV after buffering, again similar to the field trial results. Addition of 30% H_2O_2 to oxidise the suspected GR and raise the ORP of the solution proved ineffective with no substantive change in dissolved Fe observed. As shown in Figure 3, the addition of H_2O_2 resulted in a rapid change in colour from blue-green to brown. However, subsequent mixing resulted in the sample returning to blue-green within a matter of seconds. This trend continued even with H_2O_2 being added in excess of 40 times calculated COD requirements. It is known that GR have the capability to reduce ferric iron back to ferrous iron (Usman *et al.* 2012). Observations of hydrated lime armoured by suspected green rust (Figure 3) lead the authors to believe that the localised high pH around the lime, in conjunction with ORP decreases from Fe^{3+} precipitation and the presence of nucleation sites for mineral formation, is resulting in higher stability for GR which are subsequently reducing Fe^{3+}. Given the high sulfate environment, the formation of gypsum within these localised high pH zones could theoretically also promote sulfate GR formation by providing further nucleation sites and a dynamic sulfate reservoir that buffers local sulfate activity, sustaining supply required for sulfate green rust formation. Testing with H_2O_2 addition prior to lime also yielded negligible improvement in Fe removal (Figure 4).

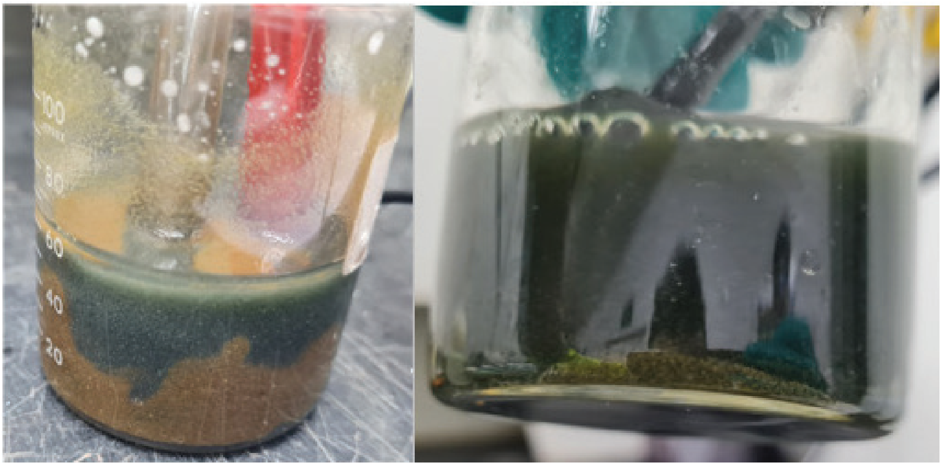

***Figure 3** "Sample 1" buffered to pH 4.3 with hydrated lime and subsequent addition of 30% H2O2 (left) and hydrated lime coated with green rust (right).*

To assess this hypothesis, hydrated lime was replaced with NaOH to buffer "Sample 1" to the desired pH. The addition of NaOH to the AMD resulted in no observable GR, supporting the hypothesis that lime addition caused the formation of suspected GR in the sample. A resulting dissolved Fe concentration of 630 mg/L demonstrates that high concentrations of soluble Fe (likely Fe^{2+}) still exist within the AMD. This again supports the assertion that the addition of lime is the causal factor to suspected GR formation rather than the presence of Fe^{2+} alone. When NaOH was utilised to buffer an aliquot of "Sample 1" that had undergone pre-treatment with the equivalent of 1 L/m^3 60% H_2O_2, a substantially lower dissolved Fe concentration was achieved (16 mg/L). This demonstrates that initial addition of H_2O_2 does result in lower Fe^{2+} concentration and that the elevated Fe observed when hydrated lime is later added is the result of suspected GR generating Fe^{2+} from the reduction of Fe^{3+} in solution. This is indicative that the formation of the suspected GR minerals introduces notable inefficiency for lime use and effectively renders H_2O_2 use as redundant.

Whilst the use of NaOH in place of hydrated lime, or the addition of high volumes of H_2O_2 have been shown to be effective, they are relatively high-cost solutions. Other methods to mitigate effects of suspected GR generation including buffering to higher pH and reducing the initial Fe^{2+} concentration to levels were also explored. Whilst buffering to pH 5 with hydrated lime yielded substantial reductions in dissolved Fe (<1 mg/L) it required a ≈30% increase in lime dosing. The resultant GR sludge is also then unstable. As the GR breaks down to form ferric oxyhydroxides, latent acidity is released potentially resulting in acid generation from the GR sludge (Legrand *et al.* 2004). This makes all forms of GR sludge unfavourable from a long-term storage viewpoint.

Given that "Sample 1" was known to represent an extreme "worst case" scenario, testing was re-run on a newer sample from the same source, post rainfall. As shown in Table 1, this "Sample 1b" had far lower Fe load and therefor COD requirements. As such when this was passed through the field trial treatment system a greater proportion of the Fe^{2+} was seemingly oxidised as no green rust was observed after the introduction of hydrated lime. In contrast to previous treatments with hydrated lime, in the absence of GR buffering to ≈pH 4.3 resulted in dissolved Fe concentrations of ≈60 mg/L. This represents an 87% reduction in with no additional oxidation via H_2O_2 required. This was comparable to the Fe removal efficiency resulting from buffering with NaOH (data

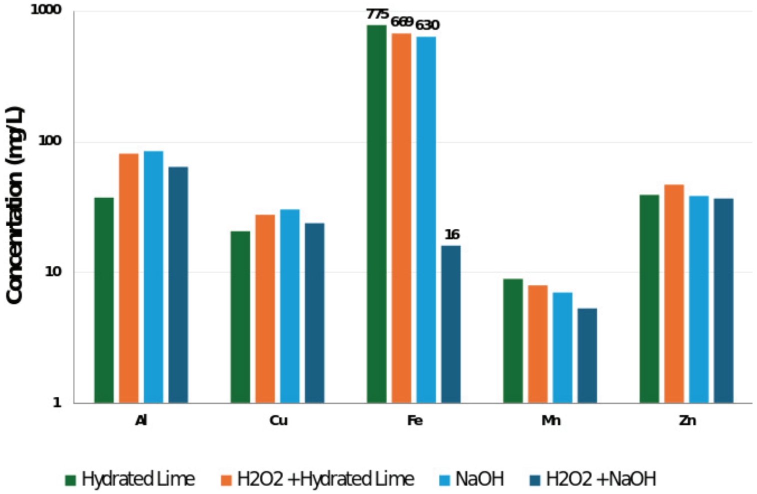

Figure 4 *Concentrations of selected analytes in "Sample 1" AMD buffered to pH 4.3 with hydrated lime and NaOH both with and without pre-treatment with 1 L/m³ 60%* H_2O_2 *(equiv.) and. Note: logarithmic Y axis.*

not shown) and, crucially, generated a ferric oxyhydroxide sludge which is considered less reactive from a waste disposal viewpoint. When additional oxidation was provided via the equivalent of 0.1 L/m³ 60% H_2O_2, dissolved Fe concentrations were seen to decrease to 6.6 mg/L and 0.7 mg/L with hydrated lime and NaOH respectively (data not shown). These represent Fe reductions of 99.6% and 99.8% respectively. Whilst these are impressive values, cost benefit analysis would have to be performed to assess whether it is necessary to reduce Fe to this level in the first stage or whether to accept relatively minor Fe being included in the planned secondary lower volume, gypsum & Mn oxide sludge.

Conclusions

The findings from both field trials and laboratory testing demonstrate that the formation of a suspected GR type mineral during hydrated lime treatment of high-load, low-pH AMD can hinder iron removal efficiency. It is suggested that the introduction of hydrated lime promotes localised conditions conducive to sulfate GR formation, which subsequently reduces ferric iron back to ferrous iron, counteracting oxidation efforts and limiting treatment performance. The resulting GR sludge is known to have potential for acid generation making disposal more problematic.

Alternative approaches – such as substituting lime with NaOH or implementing pre-oxidation with H_2O_2 – proved effective but come with economic and/or operational consideration. Crucially, tests on the lower load "Sample 1b" showed that when initial ferrous iron loads were consumed efficiently via the venturi pump, GR formation was avoided and hydrated lime treatment performed far more efficiently, producing a more stable ferric oxyhydroxide sludge precluding the requirements for more costly reagents like NaOH and H_2O_2.

These outcomes highlight the importance of monitoring and understanding the changing AMD characteristics on site, particularly Fe^{2+} loading and oxidation state, to optimise aeration–alkaline treatment systems and minimise the risk of undesirable GR generation. It is noted that the GR mineral phase has not been directly confirmed (e.g. by XRD, and its identification as GR is therefore based on indirect evidence. Future work intends to address this uncertainty.

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