THE USE OF GREEN RUST TO ACCELERATE PRECIPITATION OF OCHRE FOR MINE WATER REMEDIATION

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Abstract

Metal-rich mine drainage is a worldwide environmental problem, its treatment can be passive or active. This paper presents examples from a series of laboratory scale experiments which investigated the accelerated precipitation of ochre for the treatment of metal-rich mine waters.

This paper discusses the effects that the addition of the $Fe^{II,III}$ hydroxy salt green rust (GR), found in an unusual deposit in the South Wales Coalfield, has on 2 polluted discharges. The Parys Mountain discharge contains 79 and 8 mg L^{-1} Fe and Cu respectively. The addition of GR was able to acclerate precipitation of ochre and reduce the concentration to ~10 and 0 mg L^{-1} for Fe and Cu respectively. The Bwlch effluent releases high levels of Zn (~20 mg L^{-1}), the addition of GR aided its complete removal within 5 minutes.

This effect is attributed to a combination of the neutralisation effect of the GR, the additional sites available for sorption and the potential for the GR to aid surface catalysed oxidation of ferrous iron. The accelerated precipitation of Fe has the potential to enhance passive and/ or active treatment of mine waters. The ochre produced can be recycled back into the system to encourage precipitation of Fe oxy-hydroxides from these toxic mine waters. The rapid nature of the precipitation causes co-precipitated elements to be adsorbed, which generates a more stable solid waste

Introduction

Mine drainage is a problem which affects thousands of kilometres of streams worldwide (Herlihy et al., 1990). Although acid mine drainage (AMD) is well documented and commonly reported (e.g. Nordstrom et al., 2000; Courtin-Nomade et al., 2005) it is not a term which can be applied to all mine drainage. AMD is caused by the oxidation of FeS_2 when it is exposed to oxygen and water. Pyrite is common in most coal and metal mine deposits, and is responsible for the majority of AMD produced. AMD presents itself as an Fe, SO_4^{2-}, and H^+ rich discharge. Where there are other acid soluble metals present this discharge may emerge as a toxic metal-laden effluent (Jage et al., 2001). In areas where there is a buffering capacity, (e.g. carbonate bedrock) the effluent can be neutralized and this can emerge as a neutral discharge. Hence AMD can be a misleading term, and refers to the point of pyrite dissolution rather than to the discharge itself (White, 2000).

Where sulphide minerals occur without the presence of pyrite a metal-rich drainage can be produced without the influence of acidity. Sulphide minerals weather rapidly and ore deposits rich in metal sulphides (such as those of Cu, Zn, Mo, Ag, Hg, Pb) can give rise to high concentrations of dissolved trace elements in local drainage (Drever, 1997). In spoil tips and tailings, where many surfaces of reactive sulphide minerals are exposed, a neutral metal-rich discharge may form.

One of the main problems of mine drainage, caused by pyrite dissolution, is the high Fe concentration. In certain Eh/pH conditions this precipitates as an Fe oxide or oxyhydroxide, commonly referred to as ochre (White, 2000). This Fe either occurs naturally, for instance when the contaminated effluent mixes with an unpolluted stream, or as a result of forced precipitation through remediation. This ochre has been shown to co-precipitate other harmful elements at a pH where they would normally remain in solution. (Coulton et al., 2003). Coulton et al. (2003) state that ochre has a low solid content (usually 2-5% w/w), and this presents a problem with regards to its removal and disposal (Hancock, 2005).

In this work a novel remediation approach is suggested for the removal of potentially harmful elements from a variety of mine water types. Ochre is used to encourage the precipitation of iron and co-precipitation of other harmful elements from the contaminated waters. The data presented describes a selection of the results.

Sample sites in this study

A small selection of the data collected is presented here from sites in North Wales (Parys Mountain), Mid Wales (Bwlch) and South Wales (Ynysarwed). Parys Mountain (SH 443 903) is situated on Anglesey. The main sulphide minerals present at Parys Mountain are chalcopyrite, sphalerite, galena, arsenopyrite, and predominantly pyrite. The site was mainly exploited for high-grade Cu ore, but Zn and Pb ores were also mined (Fuge et al., 1994). The site discharges an effluent with a pH value of 2.7 and contains many toxic elements.

Bwlch (SN 703 825) is a Pb-Zn mine near Aberystwyth, mid Wales. It is typical of the mines in the area in that there is low pyrite in the ores. The discharge which issues from the site is consequently neutral pH and low in Fe (<0.5 mg L^{-1}). One of the main problems of this mine is that it contributes significant amounts of Zn (~1 kg day^{-1}) to the River Clarach. Zinc is considered difficult to remove from neutral effluents (e.g. Nuttall and Younger, 2000).

The Ynysarwed mine site (SN 806 015) in the South Wales Coalfield has an Fe-rich (~45 mg L^{-1}) discharge. The ochre from this site is presented here as it an interesting deposit. Below the red (Munsell 10R 4/8) oxidised surface the deposit abruptly becomes dark green-black (Munsell Gley1 2.5/2 – very dark greyish green) for ~4.5-6 cm. Below this layer the deposit returns to an oxidised red (Munsell 2.5YR 5/8). The unusual green layer at this site has previously been identified by the authors as a mixture of green rust (GR) with aragonite (Bearcock et al., 2006). GR is an $Fe^{II,III}$ hydroxy salt (Schwertmann and Cornell, 2000), which can be represented by the general formula $[Fe_4^{2+}\ Fe_2^{3+}\ (OH)_{12}\ ]^{2+}\ [\ A \cdot 2H_2O]$ where A represents an anion which is either SO_3^{2-}, SO_4^{2-}, $2Cl^-$ or CO_3^{2-}. GRs have a pyroaurite-like layered structure (Brindley and Bish, 1976). The ratio of Fe(II) to Fe(III) in GR is known to vary between a maximum of 4:1 and a minimum of 2:1 (Schwertmann and Cornell, 2000). When exposed to air GRs oxidise rapidly; in this study the Ynysarwed deposit shows a colour change from green-black to orange within minutes of exposure.

Methods

1. Sample collection

Mine waters with differing physico chemical parameters and contaminant problems were collected in bulk (10-25 L in pre-contaminated polyethylene containers). Physico chemical parameters were tested in the field. The ochres were selected according to the physico chemical parameters of the water from which they precipitated. They were selected from a range of Eh/pH conditions in order that different types of ochre could be expected to form (Bigham et al., 1996). The ochres were scooped into a plastic box with a plastic ladle. They were characterised by SEM and XRD.

2. Laboratory Preparation

The GR sample was prepared in two ways. The first is referred to as "DGR" (dry GR). A sub sample of the bulk material was dried at 60° in an oven overnight. Dried samples of GR, referred to as ferric GR in previous work, have been shown to retain their internal structure (Ruby et al., 2006). The dried sample was carefully disaggregated and sieved through an 180 μm nylon mesh. The second preparation method was referred to as "WGR" (wet GR) and the Fe II/III ratio was maintained. The GR was removed from beneath the oxidised surface and weighed out as a dry weight equivalent. It was used as soon as possible to prevent oxidation. The Bwlch water contained very little Fe (<0.5 mg L^{-1}), so $FeSO_4$ was added to a concentration of ~ 40 mg L^{-1}, enabling ochre to form

3. Batch experiments

The GR was mixed with each of the mine waters in batch experiments. These involved a series of different dry weight (GR) to volume (mine water) ratios. A control was used which had no added GR. Three ratios were used: 0.1 g L^{-1}, 1 g L^{-1} and 5 g L^{-1}. These are described here as "low", "medium" and "high". The waters were sampled regularly throughout the duration of the experiment. The first sample of mine water was taken just before the ochre was added and samples were taken after 1, 2, 3, 5, 10, 30, and 60 minutes. The samples were extracted using a syringe and were filtered to < 0.1 μm. The filtrate was acidified with 50% (v/v) HNO_3.

Results

Figure 1 shows how the addition of DGR affected the Parys Mountain water over the hour of the experiment. The concentration of Fe in the control and low addition of DGR experiments shows no real change. They remain constant at ~80 mg L^{-1}. However, the medium addition of DGR had a rapid effect on Fe concentration in the <0.1 μm filtrate, reducing it from 79 mg L^{-1} to 11 mg L^{-1} in 30 minutes. The high addition had an even more dramatic effect rapidly reducing the concentration of Fe in the filtrate to 10 mg L^{-1} within the first minute of the addition of DGR.

The concentration of Cu in the control remains constant, like the Fe concentration. The low addition has a negligible effect on the Cu concentration in the <0.1 μm filtrate. The concentration remains at around 8 mg L^{-1}. The addition of a medium concentration of DGR had less effect on Cu than it did on Fe. After 30 minutes the concentration of Cu in the filtrate had only been reduced to ~6 mg L^{-1}, and after an hour it was ~5 mg L^{-1}. The high addition of DGR was effective at removing Cu from the filtrate. This was reduced to around 4 mg L^{-1} after 1 minute of contact time with the DGR, and was negligible after 10 minutes.

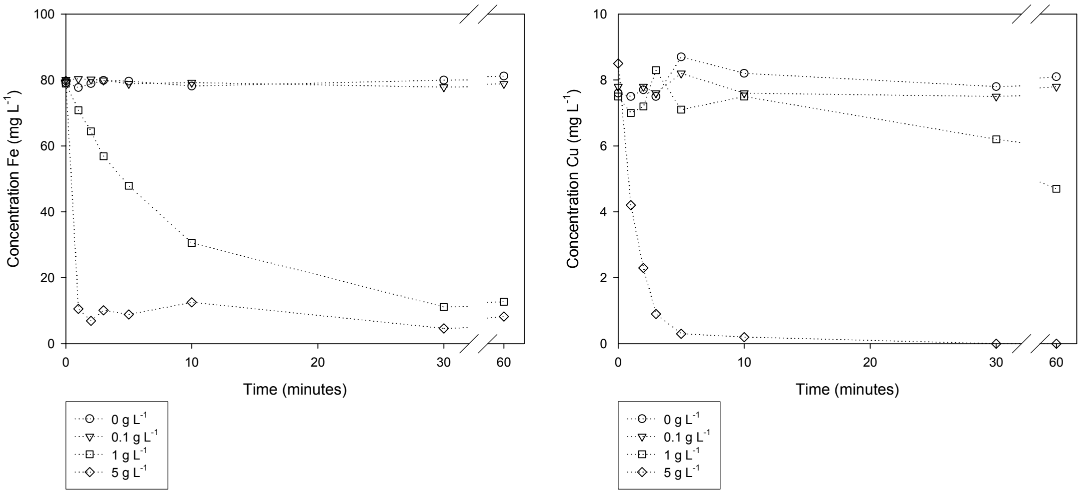

Figure 1. The effects of the DGR addition on the <0.1 µm filtrate in Parys Mountain water for Fe and Cu.

Figure 2 shows the effects of the experiment using Parys Mountain water and WGR on the Fe and Cu concentration in the <0.1 µm filtrate. Like the DGR the control has no effect, remaining stable throughout the experiment at around 77 mg L^{-1} for the Fe and ~8 mg L^{-1} for the Cu. The low addition of GR has a different effect on Fe in the filtrate than the previous example. The concentration of Fe in the >0.1 µm filtrate initially increases to >90 mg L^{-1}, before declining to around 60 mg L^{-1} after an hour had elapsed. The medium addition and the high addition both had a similar effect on the Fe concentration in the <0.1 µm filtrate. They reduced the concentration of Fe to ~40 mg L^{-1} after 10 minutes, and ~ 30 mg L^{-1} after 30 minutes.

The figure for Cu shows that the low addition of GR also remains stable throughout the 60 minutes at ~ 7-8 mg L^{-1}; in contrast to the effect on Fe in this experiment. There is a reduction in Cu for the medium and high additions. This effect is both more rapid than the Fe decrease in this experiment and the effect on Cu using DGR. The medium addition of WGR reduces the concentration of Cu in the <0.1 µm filtrate to ~1 mg L^{-1} after 10 minutes and < 0.5 mg L^{-1} after the hour had passed. The high addition of WGR reduces the concentration of Cu in the filtrate to <0.5 mg L^{-1} within 2 minutes of the addition of the particles.

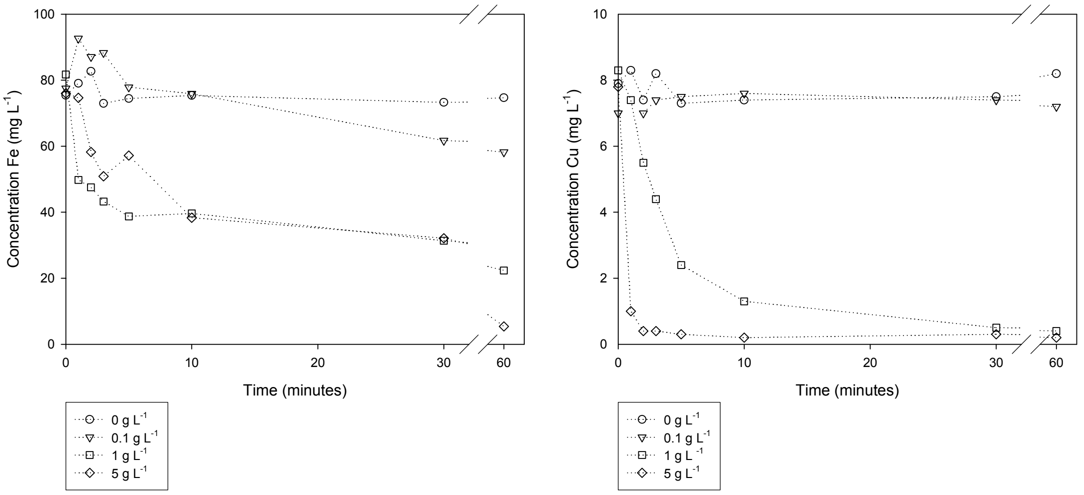

Figure 2. The effects of the WGR addition on the <0.1 µm filtrate in Parys Mountain water for Fe and Cu.

Only the results for WGR will be shown for Bwlch, because there was negligible difference between the effects of DGR and WGR on the filtrate. The Bwlch mine water has low Fe and in order to encourage the precipitation of ochre $FeSO_4$ was added to increase the concentration of Fe to ~ 40 mg L^{-1}.

Figure 3 shows the effects of the addition of WGR to Fe-seeded Bwlch water. The control remains stable at around 40 mg L^{-1}. Although over a longer timeframe (~ 2-3 hours), the concentration of Fe in control water decreased, because the Fe^{2+} was not stable in solution. With successive additions of WGR the removal of Fe from the water was more rapid and more effective. The high addition of WGR decreased Fe in the filtrate to 5 mg L^{-1} after 5 minutes and ~ 2 mg L^{-1} after 60 minutes. It took an hour for the high addition to decrease the Fe back to acceptable levels in the water.

The effect that the experiment had on the zinc, which is very difficult to remove from neutral waters, was quite distinct. The zinc had an initial concentration of around 20 mg L^{-1}. This was constant in the control. Each successive addition of WGR increased the removal rate of Zn. The medium addition of WGR caused the concentration of Zn in the filtrate to drop to negligible levels after 30 minutes. The high addition of WGR caused concentration in the filtrate to be reduced to <0.5 mg L^{-1} after only 5 minutes.

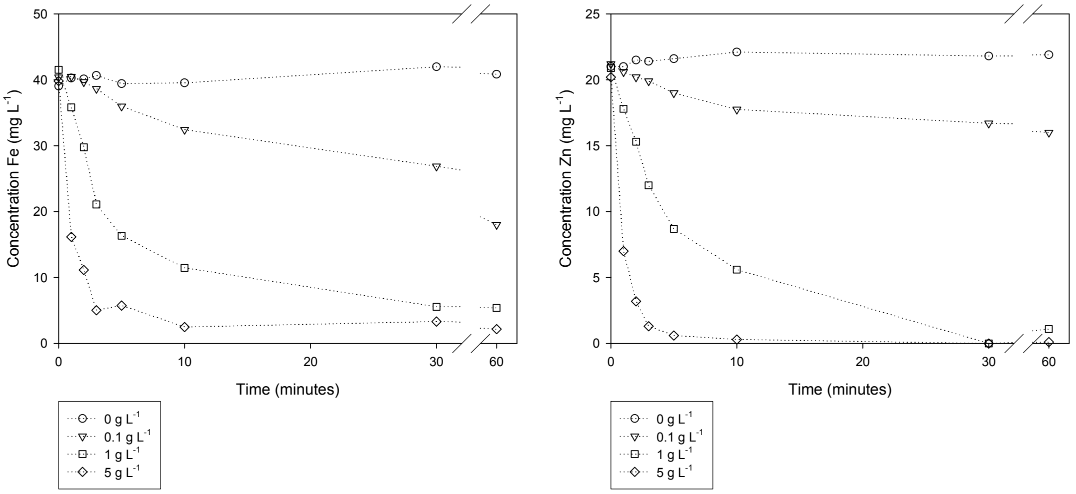

Figure 3. The effects of the WGR addition on the <0.1 µm filtrate in Bwlch water for Fe and Zn.

Discussion

The addition of GR to contaminated mine waters causes an improvement in the water quality. The precipitation of ochre, and co-precipitation of sorbed contaminants is accelerated by the addition of GR when compared to the control experiments. The control samples in this study remain relatively constant throughout the experiment. They will eventually precipitate naturally, removing other contaminants, but this would take weeks, rather than minutes as shown by the experiments presented here.

The addition of GRs to these waters aids the water quality improvement in 3 ways. Firstly, the GR sample was very rich in $CaCO_3$ (60-80%). This neutralises the Parys Mountain waters, meaning Fe is no longer stable in solution and thus encourages precipitation. It could also have the desirable effect that a marginal pH increase in Zn-rich circum-neutral waters could cause the formation of the stable zinc carbonate mineral smithsonite ($ZnCO_3$). This could be why the addition of GR is effective at removing Zn from the Bwlch water. This method of introducing a neutralising agent is also beneficial because it negates the need for harsh, expensive chemicals and puts a waste product to good use.

The second reason that the addition of GR has aided the improvement in water quality is due to the presence of extra sites for sorption of Fe and other elements. This theory is confirmed by the fact that higher concentrations of GR added to the waters had a great effect, both in terms of increased rate and concentration removed.

The third method of water quality improvement is by the process of surface-catalysed oxidation of ferrous iron (SCOOFI) as proposed by Younger (2000). The added ochre would serve as a catalyst for the increased oxidation of Fe^{2+} in solution. Younger (2000) presented SCOOFI as a 2 stage process. Firstly Fe^{2+} is adsorbed from the water to the surface of the ochre. Once the irons are attached they are oxidised *in situ* by dissolved O_2. The ferric Fe of the ochre acts as a catalyst, and a further layer is accreted on the surface of the ochre. Oxidation of Fe^{2+} by SCOOFI is more rapid than by oxidation by dissolved O_2 alone (Younger, 2000).

SCOOFI would explain why the DGR was more effective at removing Fe than WGR, which was only 40% ferric Fe. In many cases the WGR became oxidised during the duration of the experiment, especially for the lower concentrations of added WGR. The dissolved oxygen from the waters caused this oxidation, and once the GR was ferric SCOOFI could commence. The high additions of WGR were not affected by oxidation from the water, yet were more effective at removing Fe and other contaminants. This could be because neutralisation and providing sites for sorption were a more important processes than SCOOFI.

Despite WGR being less effective at removing Fe from the <0.1 µm filtrate, it was more effective at aiding the co-precipitation of other elements, especially in high concentrations of added WGR. This could be because providing extra sites for sorption is more important for co-precipitation than the SCOOFI process. The reduced nature of the GR could also cause the contaminants to take on a more insoluble form.

The re-cycling of ochre back into remediation works was discovered in the 1970s. It was developed to encourage a higher density ochreous sludge, which would be easier for waste disposal (Coulton et al., 2003). The increased settling rates of added ochre experiments over control experiments evident in the current study confirm that a denser waste product is produced. The added advantage of the current study is that by using GR there is no need to use additional chemicals to encourage the ochreous precipitation to commence in the first place.

Conclusions

Unpublished data by the authors shows that mine water samples can be stabilised effectively in the short term by removing suspended particles. Such particles provide sites for sorption and SCOOFI. This prompted a series of experiments to find out whether the addition of ochreous particles to mine water could aid an improvement in water quality. The most effective ochre used in these experiments, GR, has been presented in this work as an example of how a waste product from disused mines can be recycled back to increase efficiency of remediation treatment works.

With a more complete knowledge of GR and its formation the concept outlined in this study can be taken further. The formation of GR could potentially be encouraged with the right Eh/pH conditions and microbial influence. This could be done in a settling pond at the final polishing stage in a treatment works, and the GR produced could then be recycled back into the treatment system. This would negate the need for neutralising and flocculating chemicals. This could have the potential to improve the efficiency and cost of active treatment.

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