



# Laboratory studies using naturally occurring “green rust” to aid metal mine water remediation

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## ABSTRACT

Green rust, an Fe (II) and (III) oxyhydroxy salt, can alter the aqueous oxidation state, mobility and toxicity, of inorganic contaminants and thus could have applications in water treatment. This paper discusses a series of stirred, open batch experiments designed to evaluate green rust, and its oxidised equivalent in this context comparing it to a ferrihydrite/goethite ‘ochre’. Natural green rust was added to different mine waters as either a wet, reduced material or a dry, partially oxidised material. Experiments showed that the addition of either form accelerated the removal of potentially harmful elements from solution. Within one hour Fe, Al and Cu were completely removed from mine waters with initial concentrations of 80, 70 and 8.5 mg/L, respectively, and Zn was reduced from 60 to <5 mg/L. These experiments show the potential of green rust in mine water treatment, especially as it is able to remove problematic elements such as Al and Zn. The material is effective even after being dried and mostly oxidised. Changes to the pH and ORP of the mine waters and surface catalysis are the suggested mechanisms of accelerated removal of contaminants.

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## 1. Introduction

Contaminated mine drainage is a global problem that affects thousands of kilometres of rivers and streams [1]. Whilst ferruginous discharges are not the only type of mine waters, these are often the most studied because the Fe (III) oxyhydroxide precipitates (“ochres”) are obvious clues to the pollution problems of the site and have the greatest aesthetic impact. Freshly precipitated ochres have the largest sorption capacity of any environmental material [2], and if this can be harnessed, then this toxic waste material could have useful applications in mine water remediation.

Green rust (GR) is the generic term for the partially reduced Fe (II) and Fe (III) oxyhydroxy salt. It is commonly simulated in the laboratory [3], although it can be found in natural environments where it occurs as a corrosion product [4,5]. It has recently been described in soils [6] and within ochreous mine drainage precipitates [7]. In recent years there has been increasing interest in GR because it can alter the oxidation state, and hence mobility and toxicity, of inorganic contaminants in aqueous environment [3,8–10].

The potential for GR as a reactive material in mine water remediation [11,12] and to decrease toxicity [3] has been alluded to in the literature. Provisional results from the laboratory studies, reported here, were presented in Bearcock and Perkins [13]. There are, however, no comprehensive reports of experiments carried out to examine GR as a remediation material. To evaluate this potential a series of stirred, open batch experiments was undertaken using a variety of contaminated mine waters. A selection of the data is addressed in this paper and the full data set can be found in the [supplementary data](#).

The batch experiments used a naturally occurring Fe (II) and Fe (III) GR sample as a remediation product. The GR was from Ynysarwed, an abandoned coal mine site in south Wales, UK [7] (see [Fig. 1](#)). Here the GR occurs as a discrete layer, 4–6 cm thick, with an Fe (II) and Fe (total) ratio of around 0.6, closely associated with aragonite (present at ~60% w/w CaCO<sub>3</sub>), within a ferrihydrite/goethite (FG) precipitate [7]. The GR has a measured specific surface area of 0.81 m<sup>2</sup> g<sup>-1</sup> (calculated from laser granulometry measurements). Typical electron micrographs of the constituents of this material are presented in the [supplementary material](#). The experiments described here compare the effectiveness of GR with ochre from a FG deposit, the more typical mineralogy of mine drainage precipitates where the discharge is greater than pH 4.5 [14].

## 2. Experimental methods

A series of open vessel, stirred, batch experiments was conducted to establish the effectiveness of GR for removing con-

Abbreviations: GR, green rust; FG, ferrihydrite/goethite; DGR, dried green rust; WGR, wet green rust; PHE, potentially harmful elements.

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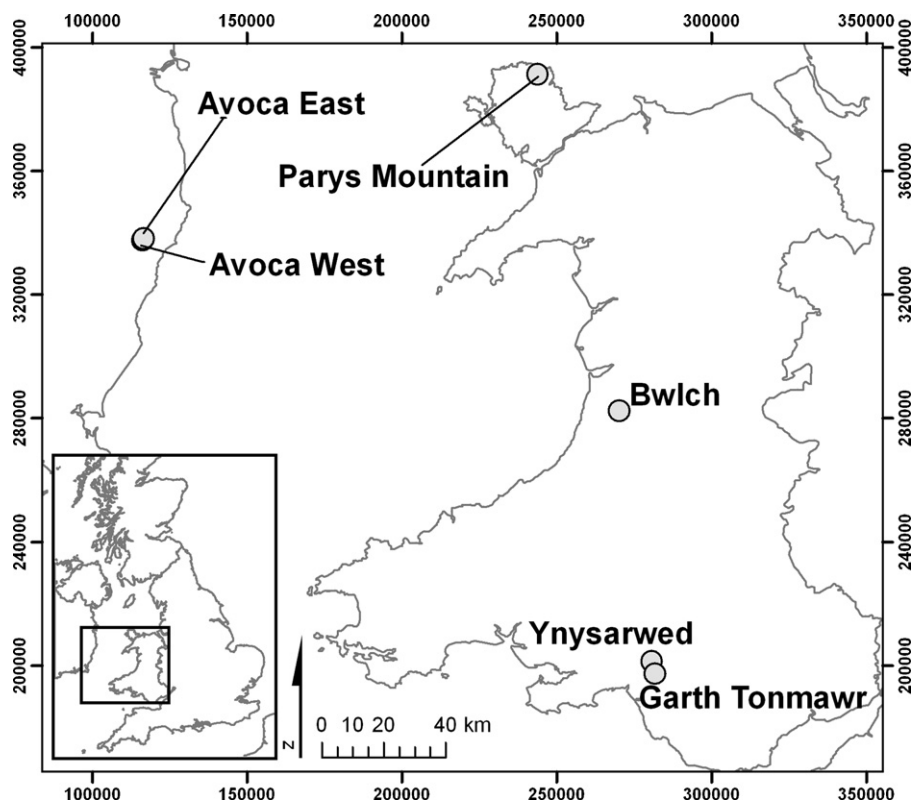


Fig. 1. Location of sites in this study presented on the British National Grid. OS topography ©Crown Copyright. All rights reserved. BGS 100017897/2011.

taminants from mine waters. Naturally occurring GR, FG ochre, and mine waters were used in each experiment.

### 2.1. Sample sites and field methods

Samples of mine water were collected in 25 L acid-washed high density polyethylene containers from four sites in the British Isles. Three are ochreous acid mine drainage sites: Parys Mountain on Anglesey, north Wales; Avoca East; and Avoca West, in Ireland. One site, Bwlch, located in mid-Wales, is a circum-neutral drainage site (see Fig. 1).

The Parys Mountain site is an abandoned Cu mine. The discharge has a typical pH value of  $\sim 2$  and contains up to 80 mg/L Fe, 24 mg/L Zn and 8 mg/L Cu. The Avoca sites are abandoned Cu–Zn–Pb mines. The Avoca East discharge, pH 3.5, contains 35 mg/L Fe, 60 mg/L Zn, 3 mg/L Cu and 70 mg/L Al. The Avoca West discharge, pH 4, contains 75 mg/L Fe, 20 mg/L Zn and 13 mg/L Al. The Bwlch site is an abandoned Pb–Zn mine where the discharge is  $\sim$ pH 6 and contains 20 mg/L Zn.

The GR and FG ochre were previously identified by the authors [7,15]. The GR was sealed in 5 cm diameter ABS (acrylonitrile–butadiene–styrene) pipes. The most important anion in the Ynysarwed discharge is sulphate which would tend to favour the formation of sulphate green rust. The sample of FG ochre, used as a comparison with the GR, was taken from the Garth Tonmawr coal mine site in south Wales (see Fig. 1).

### 2.2. Laboratory preparation

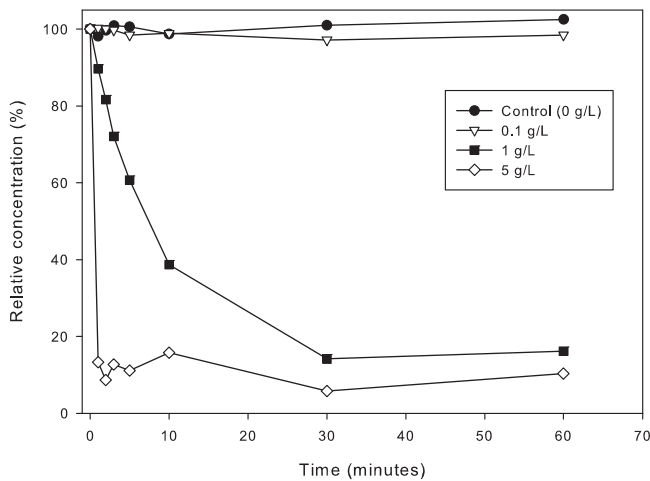
The FG and a sub-sample of the GR were dried overnight at 60 °C. During this process the GR was exposed to air and rapidly oxidised [16] although it retained around 3% Fe(II) by mass. These dried substances were then ground using an agate mortar and pestle and sieved to  $<180 \mu\text{m}$  through a nylon mesh. All the remain-

ing GR was kept sealed to minimize any oxidation. The separate GR materials were termed dried green rust (DGR), for the oven-dried material, and wet green rust (WGR) for the stored/sealed material.

The Bwlch water, a  $\text{ZnSO}_4$  water with Fe  $<0.5$  mg/L, was spiked with  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Fisher, UK Certified analytical reagent) to raise the Fe concentration to  $\sim 40$  mg/L: sufficient Fe for the forced precipitation of Fe(III) oxyhydroxides by addition of GR or FG ochre. In this form Fe is unstable in the circum-neutral and oxidised Bwlch water, so the  $\text{FeSO}_4$  was added in solution immediately before the experiments commenced.

### 2.3. Batch experiments

The FG, DGR and WGR were each mixed with the various mine waters in a series of open batch experiments conducted at laboratory temperature ( $\sim 18$  °C). For each experiment 200 mL of mine water was transferred to a 600 mL Pyrex® beaker using a glass measuring cylinder. The pH of these waters was measured immediately. 1, 0.2 or 0.02 g of DGR or dried FG were weighed out and added. For the WGR the same dry weight equivalents were measured ( $\sim 3.2$  g wet = 1 g dry) and added. This gave three different dry weights of solid to mine water concentrations: 5 g/L, 1 g/L, and 0.1 g/L. In addition a control experiment was included for each water, which had no GR or FG ochre added. The waters were sampled just before the addition of GR or FG ochre. Once the solid had been added the samples were mixed on a magnetic stirrer at sufficient speed to maintain a homogeneous mixture throughout the experiment, and 15 mL samples removed from the beaker after 1, 2, 3, 5, 10, 30, and 60 min. Each sample was extracted using a polyethylene syringe and was immediately filtered to  $<0.1 \mu\text{m}$  through a Whatman Anotop 25 disposable filter cartridge to remove the suspended solid material. During the experiment the solid:water ratio was not changed. The filtrate was acidified to  $<\text{pH } 2$  with 50% (v/v)  $\text{HNO}_3$



**Fig. 2.** Effect of the addition of dried green rust on the Fe concentration in Parys Mountain water. Each ratio of solid: mine water is shown, demonstrating an increase in effectiveness of removal from the solution with each increase of solid material. Samples were mixed in an open vessel at  $\sim 18^\circ\text{C}$ .

(Fisher, Certified Analytical Reagent grade) and stored in sealed LDPE test tubes prior to analysis.

#### 2.4. Analyses

Once the samples had been collected they were analysed for a variety of potentially harmful elements (PHEs) (Fe, Al, Zn, Cu, Co Ni, Cd, REEs, Pb, Th, U) by ICP-MS and AAS. Iron, and where appropriate, Zn, Cu and Al were determined using either a Pye-Unicam SP

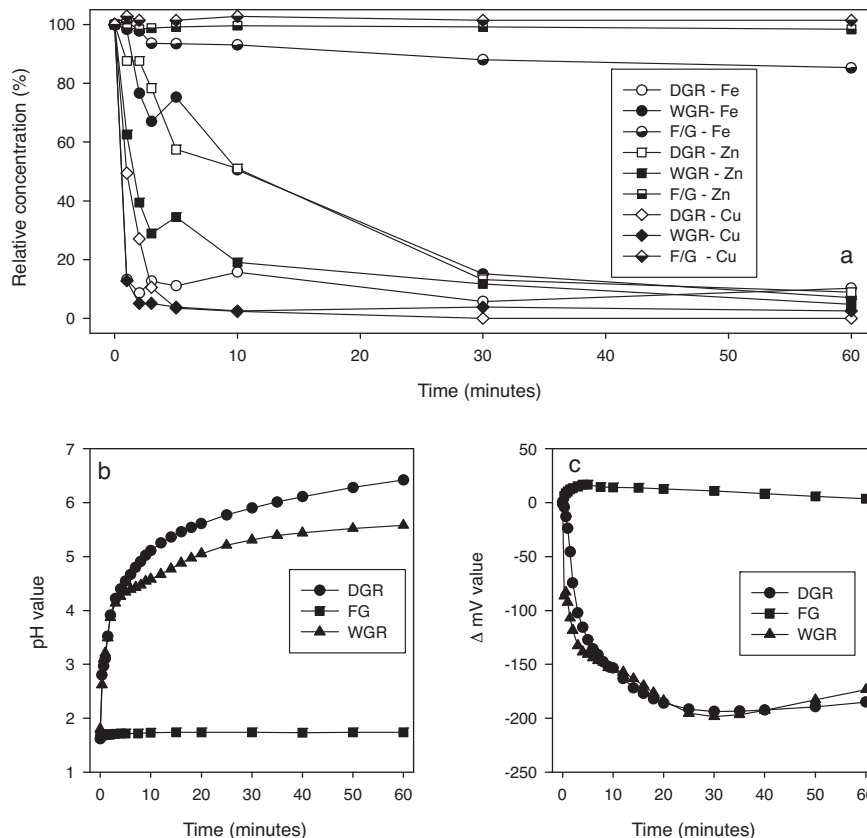
9 or a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer (AAS) calibrated with a series of at least three synthetic, multi-element standards. The ICP-MS was a Fisons PlasmaQuad PQ II+ (STE) ICP-MS, calibrated using synthetic multi-element solutions. Measurements of pH and Eh were made using two Hanna HI 9025 microcomputer meters equipped with either a VWR 662-1761 pH electrode or a Hanna HI 3230 ORP electrode.

#### 2.5. Quality control

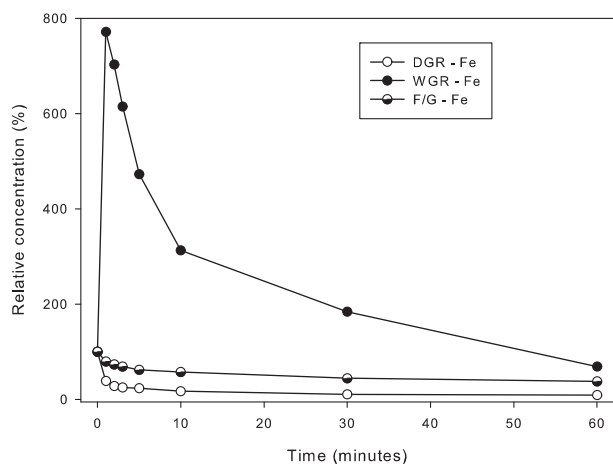
Instrumental precision was estimated using sample duplicates. Precision is quoted as coefficient of variation, using an estimate of the standard deviation presented as a percentage of the mean [17]. Precision of AAS data was typically  $<1\%$ , with the exception of samples with low ( $<10\text{ mg/L}$ ) concentrations and the Al analyses which had a precision of  $\sim 2.5\%$ . ICP-MS data generally had a precision of  $<1\%$ . Experimental precision was estimated by repeating an entire experiment. For the elements considered in this study the experimental precision was  $\sim 5\%$ .

The accuracy of the analyses was established with an absolute method using a series of synthetic mine waters. These solutions were produced from single element 1000 mg/L standards (Aldrich). The accuracy of the AAS data was generally 2–3%, and the ICP-MS data was accurate to  $<5\%$ .

Lower limits of detection (LLD) were calculated as three times the standard deviation of a laboratory blank solution. All the elements analysed by ICP-MS were calculated to have a LLD of  $<0.5\ \mu\text{g/L}$ . The AAS LLDs were obtained from the literature [18], as these are well established. For most elements the detection limits are  $<0.1\text{ mg/L}$ , the Al detection limits are  $<1\text{ mg/L}$ .



**Fig. 3.** Effect of the addition of solids on dissolved Fe, Zn and Cu in the Parys Mountain water. (a) DGR is represented by open symbols, WGR by closed symbols, and FG by half filled symbols. (b) changes in pH throughout the experiment. (c)  $\Delta\text{ mV}$ —the difference between calculated mV change, resulting from pH changes, and measured mV. Experimental conditions: open vessel at  $\sim 18^\circ\text{C}$ ; sub-samples removed from the same vessel.

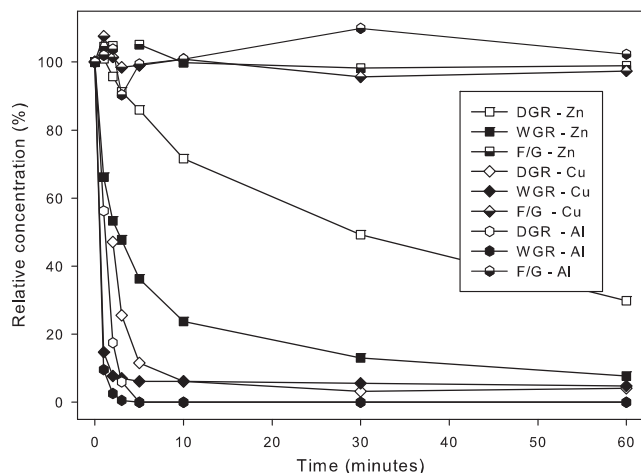


**Fig. 4.** Effect of the addition of reactive solids on dissolved Fe in the Avoca East water. Experimental conditions: open vessel at  $\sim 18^\circ\text{C}$ ; sub-samples removed from the same vessel.

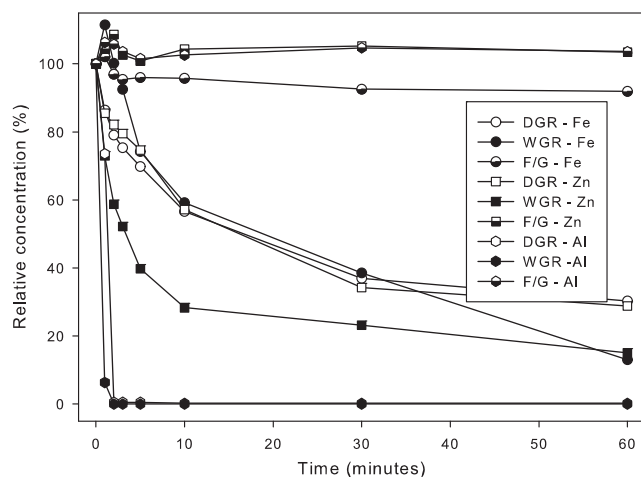
### 3. Results

In all experiments the control solution (i.e. subjected to the same stirring but with no addition of solid) produced no detectable change in the concentration of the analytes (i.e. within the precision of the measurements) through the 60 min experiments. As the solid to mine water ratio increased an accelerated rate of removal of contaminants from solution was clearly observed. This is illustrated in Fig. 2 which shows that low solid concentrations only have a minor effect on the water chemistry, but once the concentration reaches 1 g/L the effect is clearly demonstrated. A similar effect was observed in most other experiments. To simplify the rest of the data presentation of the batch experiments, Figs. 3–7 show only the 5 g/L solid experimental data. The full data set can be found in the supplementary data.

Each of Figs. 3–7 present relative concentration over time; i.e. the concentration is presented as the percentage of the initial concentration, which allows easy comparison of individual elements. Figs. 3–7 show a selection of analytes, which reflect the contamination issues of each site. Table 1 shows the pH changes which occurred during the experiments. The pH changes are critical to the elemental concentration changes in these waters, and are discussed in Section 4.1.



**Fig. 5.** Effect of the addition of reactive solids on dissolved Zn, Cu, and Al in the Avoca East water. Experimental conditions: open vessel at  $\sim 18^\circ\text{C}$ ; sub-samples removed from the same vessel.



**Fig. 6.** Effect of the addition of reactive solids on dissolved Fe, Zn, and Al in the Avoca West water. Experimental conditions: open vessel at  $\sim 18^\circ\text{C}$ ; sub-samples removed from the same vessel.

#### 3.1. Parys Mountain

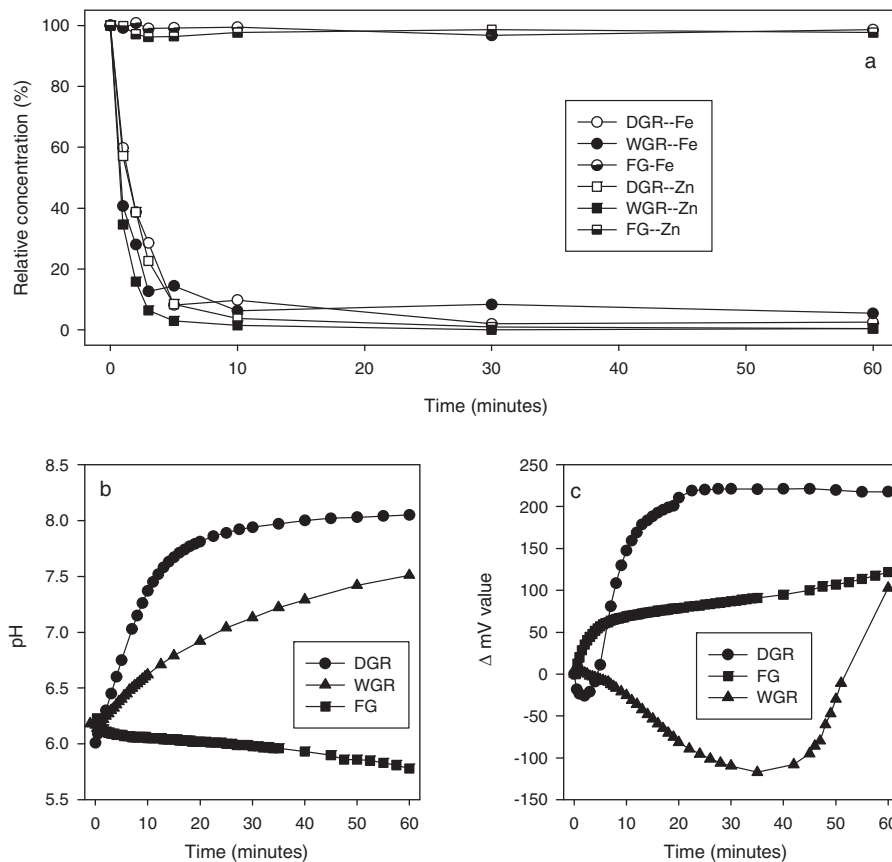
Fig. 3 shows the response of the Parys Mountain water ( $<0.1 \mu\text{m}$  filtrate) to the addition of 5 g/L of each solid material. The FG has little effect on the removal of Fe, Zn or Cu; after 60 min only 15, 2 and 0%, respectively, were removed from solution. The use of DGR and WGR gave a decrease of over 80% for each element after the 60 min experiment. Copper was most effectively removed with 100 and 97.5% removal using DGR and WGR, respectively. Fig. 3 also shows the corresponding changes in pH and  $\Delta \text{mV}$  (calculated mV, from pH change, minus the measured mV). The  $\Delta \text{mV}$  plot shows that the changes in the Eh measured in the experiments are different from that predicted from the pH change alone. In the FG experiment the difference is small and positive (more oxidising) whilst the differences in the GR experiments are both strongly negative (more reducing). This indicates that the GR exerts a strong reducing effect and further that the drying process does not remove all of the reducing 'potential' of the GR.

There are interesting differences in the rates of the removal of Fe and Zn using wet and dried GR. Iron is removed much more rapidly using DGR than WGR. In the first 5 min of the experiment the addition of DGR removed 89% of the Fe whilst the WGR removed only 25% of the Fe. In contrast Zn shows the opposite trend, as the WGR removed Zn more rapidly than the DGR.

#### 3.2. Avoca East

The Avoca East drainage contains appreciable quantities of Fe, Zn, Cu and Al. The effect of the solids on the Fe in the solution ( $<0.1 \mu\text{m}$  filtrate) is presented in Fig. 4. The FG removes 62% of the initial concentration and DGR removes 91% of initial concentration in 1 h. However here the WGR demonstrates some very different effects to those previously described; in the first minute of the experiment the addition of WGR increases the Fe concentration to almost 8 times higher than the initial concentration. The Fe concentration then decreases throughout the experiment, finally removing only 38% of the initial concentration.

The behaviour of Fe has an interesting effect on the other contaminants in this solution, especially when compared to the Parys Mountain water, which has similar pH and contaminant concentrations. The effect of the solids on Zn, Cu and Al is presented in



**Fig. 7.** (a) Effect of the addition of reactive solids on dissolved Fe and Zn in Bwlch water. (b) changes in pH throughout the experiment. (c)  $\Delta$  mV—the difference between calculated mV change, resulting from pH changes, and measured mV. Experimental conditions: open vessel at  $\sim 18^\circ\text{C}$ ; sub-samples removed from the same vessel.

**Fig. 5.** The FG is ineffectual and over the hour of the experiment Zn, Cu and Al were removed by no more than 2.5%. It is worthy of note that whilst both the DGR and WGR remove Zn, Cu, and Al from solution, it is WGR that acts most quickly, even after causing such a dramatic increase in Fe concentration in the first minute of the experiment. In the experiment using DGR, Al decreased by 44% after one minute. In the same time period WGR removed 33% of Zn, 85% of Cu and 90% of Al. After five minutes both the DGR and WGR had removed 100% Al from solution, and after 60 min the addition of DGR had caused Zn and Cu concentrations to reduce by 70 and 96%, respectively, and the WGR caused a decrease of 92 and 95%, respectively.

### 3.3. Avoca West

The FG ochre does not remove any Zn or Al, and only removes 8% of the Fe from the Avoca West water ( $<1\ \mu\text{m}$  filtrate). Both forms of GR are effective at removing Fe, Zn and Al, the DGR removing 70, 71, and 100%, respectively and the WGR removing 87, 85, and 100%, respectively (see Fig. 6).

### 3.4. Bwlch

The main contaminant issue at the Bwlch site is Zn, which is present at  $\sim 20\ \text{mg/L}$ . As discussed in Section 2.2  $\text{FeSO}_4$  was added to the water to give an initial Fe concentration of  $40\ \text{mg/L}$  to enable formation and precipitation of Fe(III) oxyhydroxides. Fig. 7 presents the percentage changes in Fe and Zn concentration in the Bwlch water ( $<0.1\ \mu\text{m}$  filtrate) as a consequence of adding each solid material. The FG produces no change in either Fe or Zn concentration. Both forms of GR produces an immediate ( $<1\ \text{min}$ ) decrease in Fe and Zn concentration. By the end of the experiment 97 and 91% of the Fe has been removed using DGR and WGR, respectively, reducing the Fe concentration to  $\sim 1.5\ \text{mg/L}$ . Fig. 7 also shows the corresponding changes in pH and  $\Delta$  mV through the experiments. There is an initial reduction step in all tests as a result of the addition of  $\text{FeSO}_4$ . The  $\Delta$  mV plots reflect changes after the addition of the GR or FG and do not show the initial reduction step. Thus any changes in the  $\Delta$  mV reflect the solid additions and not the  $\text{FeSO}_4$ . The FG causes a slight lowering of the pH and a slow increase in the Eh during the experiment. The GR additions both produce rela-

**Table 1**  
Initial and final pH values of each water type after 60 min reaction time with  $5\ \text{g L}^{-1}$  of each solid type. Column headers indicate the initial pH value of natural mine waters. Row headers indicate the measured pH of GR and FG ochre when mixed with Mili-Q<sup>®</sup> water.

	Parys Mountain (initial pH = 1.8)	Avoca East (initial pH = 2.6)	Avoca West (initial pH = 2.6)	Bwlch (initial pH = 6.2)
DGR				
GR + MiliQ $\text{H}_2\text{O}$ = pH 9.2	6.4	6.6	6.6	8.1
WGR				
GR + MiliQ $\text{H}_2\text{O}$ = pH 9.2	5	6.6	6.7	7.5
FG				
Ochre + MiliQ $\text{H}_2\text{O}$ = pH 3.4	1.9	2.7	2.7	5.8

tively steady increase in the pH but have different effects on the Eh. The DGR causes an initial reduction followed, after 5 min, by oxidation whilst the WGR causes a reduction for most of the experiment. The slow pH increase is caused by the dissolution of the aragonite whilst the Eh changes reflect the oxidation kinetics of the GR.

Whilst the added Fe was not completely removed, the addition of either form of GR was very effective at removing Zn from solution. Zinc is notoriously difficult to remove from aqueous solutions, and, after 60 min, was reduced by >99% in the Bwlch water by addition of each form of GR.

### 3.5. Rates of reaction

Data can be modelled to provide rate constants that describe the effects of the addition of solids to the contaminant concentrations in the mine waters. The experiments in this study present complex systems comprising natural waters and natural solids. Thus the rates of reaction do not describe a simple process, but instead may be a combination of processes of varying and unknown degrees. Indeed Kirby and Elder Brady [19] identified the complexity of natural systems as a problem when attempting to calculate rate laws. They stated that no single rate law could be developed using  $\text{Fe}^{2+}$ ,  $\text{O}_2$  and pH data alone to predict field rates of oxidation and precipitation, given the variety of processes acting in a natural system. Rate laws are most commonly used for describing simple, closed, well mixed systems [20].

Here, rate constants were calculated for each 5 g/L experiment, as a zero, first or second order rate constant ( $k$  value). One rate law alone cannot describe the changes observed during these experiments, and this compares with the conclusions of Kirby and Elder Brady [19]. Indeed, in many cases the rate law fitting the data changed over time. The best fitting rate law was therefore selected individually from the data from each experiment. The  $k$  value of the rate law which best represents the data for each experiment (zero, first or second order) are presented in Table 2.

Without a more detailed knowledge of the individual component reactions within these complex systems it is impossible to present a more detailed mathematical description. However, these rates are representative of a natural system requiring remediation. Second order rate constants for the oxidation of Fe(II) species by  $\text{O}_2$  were calculated by Wherli [21] (see Table 3). The data produced in this study indicate that the addition of green rust can increase the rate of Fe oxidation and precipitation by up to 7 orders of magnitude, compared to the data from Wherli [21].

## 4. Discussion

The concentrations in the control samples remain relatively constant throughout the experiments. These untreated waters may eventually precipitate Fe naturally, removing other contaminants, but this could take days to weeks. In the case of Parys Mountain water, which has a pH value of 1.8, it is unlikely that any significant precipitation will take place. In contrast to the rapid removal rates shown by GR in the batch experiments completed here. The coal mine drainage ochre, a ferrihydrite/goethite (FG) mixture, is generally ineffective as an aid to removing contaminants from the mine waters used in this study and it exhibited limited ability to remove Fe from solution. The addition of GR to mine waters causes a rapid removal of contaminants and a dramatic improvement in the water quality.

The WGR and DGR are both capable of aiding the removal of Fe, Zn, Cu and Al from solution. Analysis of the GR and FG shows that levels of PHEs are generally less than 5 mg/kg and thus the dissolution of the solids would not contaminate the waters. In general the DGR is most effective at removing Fe from solution and the WGR is

most effective at removing the other contaminants. Since both GR materials contain the same amount of aragonite this effect cannot be attributed to changes in pH alone. Data presented here shows that the Eh of the solutions is affected by the addition of GR to the mine waters.

### 4.1. Mechanisms

The addition of GRs to waters aids the removal of metallic contaminants in at least three ways. Firstly, the GR sample used here contains ~60% (w/w) aragonite. Dissolution of this aragonite increases the pH of acidic mine drainage, exceeding the pH of hydrolysis of Fe at higher concentrations of added solid. The Parys Mountain (PM) water was initially pH 1.8, but after addition of DGR or WGR (5 g/L) the pH was raised to 5.5–6, encouraging some Fe oxyhydroxide precipitation which counteracts the pH increase by the release of protons. In one set of experiments the effect of calcium carbonate addition alone was investigated by adding the equivalent mass of  $\text{CaCO}_3$  to the PM water. The results show an increase in pH comparable to the GR but the Eh value is consistently higher than the GR. These data are reported in the [supplementary material](#). In addition a marginal pH increase (up to pH 7.5–8) in Zn-rich circum-neutral waters could cause the formation of the stable zinc carbonate mineral smithsonite ( $\text{ZnCO}_3$ ) [22] or possibly  $\text{Zn}(\text{OH})_2$ . This could be why the addition of DGR and WGR are equally as effective at removing Zn from the Bwlch water. However it should be pointed out that the pH increase for the WGR experiment is relatively slow compared to the rapid removal of zinc (c.f. Fig. 7). It is noteworthy that the Eh of the experiments showed rapid changes following the addition of the  $\text{FeSO}_4$  solution at the start of the experiment. The Eh value was lowered even further by the addition of either the DGR or WGR on a timescale which is comparable to the removal of Zn and thus it seems reasonable to assign this removal to an Eh as well as a pH change.

Secondly, the GR provides extra sites for sorption of Fe and other elements. It has been shown that sequential removal of suspended particles from contaminated mine water can slow the precipitation of Fe and thus an increase of particulate matter will increase Fe precipitation [15]. This is confirmed in this study by the observation that higher concentrations of GR added to the waters had a greater effect, both in terms of increased rate and concentration removed (see [supplementary data](#)).

The third method of water quality improvement is by the process of surface-catalysed oxidation of ferrous iron (SCOOFI) [23]. The added solid material serves as a catalyst for the increased oxidation of  $\text{Fe}^{2+}$  in solution. Oxidation of  $\text{Fe}^{2+}$  by SCOOFI is more rapid than oxidation by dissolved  $\text{O}_2$  alone [23].

SCOOFI explains why the DGR was more effective at removing Fe than WGR, in which only 40% of the Fe was Fe (III). In many cases the WGR became oxidised during the experiment, especially at the lower concentrations. Dissolved oxygen from the waters caused the oxidation of WGR and once the Fe was Fe III, SCOOFI could commence. The high additions of WGR (5 g/L) to the acidic Parys Mountain water 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 dominant over SCOOFI. The change in Eh observed for the F/G addition to the Bwlch water (Fig. 3) also indicate that some SCOOFI reactions are occurring in this experiment.

Despite WGR being less effective at removing Fe from the <0.1  $\mu\text{m}$  filtrate, it was more effective at aiding the removal of other elements, especially in high concentrations of added solid. Providing extra sites for sorption is more important for co-precipitation than the SCOOFI process. The reduced nature of the GR could also cause speciation changes in the contaminants leading to more insoluble forms [3,24,25].

**Table 2**  
Summary of rate constant (*k*) values for data presented in this paper. The *k* value is presented for the rate law which best represents the data. Where a zero order rate constant is presented it describes the immediate, rapid decrease in concentration. Values in bold represent data with  $r^2 > 0.95$ . "no fit" indicates that no rate law fits because the concentration does not decrease. PM = Parys Mountain, B = Bwlch, AW = Avoca West, AE = Avoca East. DGR = dried green rust, WGR = wet green rust, FG = ferrihydrite/goethite.

	Zero order k values			First order k values			Second order k values		
	DGR	WGR	FG	DGR	WGR	FG	DGR	WGR	FG
PM									
Fe	$2.06 \times 10^{-5}$	Second	Second	Zero	Second	Second	zero	<b>2.6779</b>	0.046
Zn	Second	First	No fit	Second	<b>0.007</b>	No fit	<b>7.8433</b>	First	No fit
Cu	First	Second	No fit	0.0113	Second	No fit	First	501.1	No fit
B									
Fe	Second	Second	No fit	Second	Second	No fit	<b>37.993</b>	34.036	No fit
Zn	Second	Second	No fit	Second	Second	No fit	<b>185.22</b>	<b>379.08</b>	No fit
AW									
Fe	Second	First	Second	Second	<b><math>5.67 \times 10^{-4}</math></b>	Second	<b>0.488</b>	First	0.0167
Zn	Second	Second	No fit	Second	Second	No fit	<b>4.318</b>	<b>18.724</b>	No fit
Cu	$6.07 \times 10^{-5}$	$1.12 \times 10^{-4}$	No fit	Zero	Zero	No fit	Zero	Zero	No fit
Al	$3.22 \times 10^{-6}$	$2.65 \times 10^{-6}$	No fit	Zero	Zero	No fit	Zero	Zero	No fit
AE									
Fe	$6.35 \times 10^{-6}$	First	Second	Zero	<b>1.67</b>	Second	Zero	First	6.12
Zn	Second	Second	No fit	Second	Second	No fit	<b>0.666</b>	<b>3.44</b>	No fit
Cu	Second	$6.73 \times 10^{-4}$	No fit	Second	Zero	No fit	<b>0.434</b>	Zero	No fit
Al	First	First	No fit	<b>0.016</b>	<b>0.0287</b>	No fit	First	First	No fit

**Table 3**  
Second order rate constants (*k*) for Fe(II) species [21].

Fe (II) species	pH range at which rate dominated by species	2nd order rate constant L Mol <sup>-1</sup> s <sup>-1</sup>
Fe <sup>2+</sup>	<3.5	$7.9 \times 10^{-6}$
FeOH <sup>+</sup>	3.5–5	25.1
Fe(OH) <sub>2</sub>	>5	$7.94 \times 10^6$

The advantages of re-cycling ochre in remediation works was discovered in the 1970s. It was developed to encourage a higher density ochreous sludge [26]. The increased settling rates of added solid material over control experiments are evident in the current study and 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 ochre precipitation to commence.

It is known that mine water samples can be stabilised effectively in the short term by removing suspended particles [15]. Such particles provide sites for sorption and SCOOFI. The experiments reported here were designed to find out whether the addition of ochreous particles to mine water could produce an improvement in water quality. The most effective solid material used in these experiments, GR is an example of a waste product which can be recycled to increase efficiency of remediation treatment. 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 be encouraged with the right Eh/pH conditions, microbial influence, and water and ochre chemistry. This could be done in a settling pond at the treatment works, and the GR produced could then be used in the treatment system. This would negate or reduce the need for neutralising and flocculating chemicals. This has the potential to improve the efficiency and cost of active treatment. Furthermore the evidence presented here shows that GR can be dried and stabilised yet retain its effectiveness allowing the material to be easily transported to other mine treatment sites.

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Tabulated data of all experiments, including all the concentrations of added solid material not discussed in the paper can be found in the [supplementary data](#).

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jhazmat.2011.03.074](https://doi.org/10.1016/j.jhazmat.2011.03.074).

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