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C–S–Fe geochemistry of a wetland constructed to treat acidic mine waters

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Abstract

The intertwined redox geochemistry of carbon, sulphur and iron is at the heart of remediation of acidic waters within passive, anaerobic wetland sediments. Here, we present some preliminary data from a sediment core taken from the Quaking Houses constructed wetland in County Durham, England. The data indicate rapid reduction of both sulphate and iron oxide, with precipitation of iron sulphides and buildup of dissolved iron in sediment porewaters. Successful remediation requires concomitant reduction of sulphate and iron and should guide the future design of treatment systems. Future work must determine the specific reactions occurring within the C–S–Fe system and also the critical rate-limiting step.

Key words: artificial wetlands, cycling, geochemistry, iron, sulphur

INTRODUCTION

Since the mine closures programme of the mid-1980s, the problem of how to treat mine water discharges emanating from abandoned pit workings and colliery spoil heaps in the UK has become increasingly significant (NRA 1994). Although both active and passive treatments are possible, active chemical treatment strategies incur large costs both in initial investment and in subsequent maintenance. In contrast, passive treatment technologies offer a cheaper and more benign approach to remediation. Once the initial investment has been made, the running costs of a passive system are minimal, and can often be carried out by the local community.

Passive treatment systems exploit the linked biogeochemical redox cycles of carbon, sulphur and iron, with the dual aims of raising pH and alkalinity, and removing metal pollutants such as iron, aluminium, lead and zinc. Both aerobic and anaerobic passive treatment systems have been deployed. At least for net acidic waters, aerobic systems are of limited use. Certainly iron can be successfully removed by oxidation and hydrolysis:

$$4Fe^{2+} + O_2 + 6H_2O \rightarrow 4FeOOH + 8H^+$$

Trace metals can be subsequently removed from solution by scavenging onto the surface of the oxihydroxides (Johnson and Thornton 1987). However, the oxidation and hydrolysis of both Fe and Al generates significant acidity. For this reason anaerobic systems provide a much higher potential for successful remediation. Successful remediation using anaerobic systems depends on the balance of the interwoven cycles of both microbially catalysed and abiotic reactions involving carbon, iron and sulphur. An immense literature on the C–S–Fe geochemistry of marine and freshwater sediments (e.g. Berner 1985; Lin and Morse 1991; Kostka and Luther 1994; Thamdrup *et al.* 2000; Holmer and Storkholm 2001) reveals a diverse suite of potential reactions. Some of the key reactions include the microbially mediated, dissimilatory reduction of sulphate and iron oxide; the formation of iron sulphides; and the reoxidation of sulphide by either iron oxides or oxygen. For example:

$$CH_2O + 4FeOOH + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 6H_2O$$

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$$

$$6CH_2O + 3SO_4^{2-} + 2FeOOH \rightarrow 6HCO_3^- + FeS + FeS_2 + 4H_2O$$

$$2FeOOH + H_2S \rightarrow 2Fe^{2+} + S^0 + 4OH^-$$

$$3H_2S + 2FeOOH \rightarrow S^0 + 2FeS + 4H_2O$$

$$FeS_2 + 14FeOOH + 6H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 26OH^-$$

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$$

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Since most of these reactions involve the generation or consumption of protons and/or the generation of bicarbonate, it is clear that it is the overall balance of the C–S–Fe cycle which dictates the remediation potential of an anaerobic treatment system. Our general aim is thus to quantify the rates and mechanisms of the various parts of the C–S–Fe cycle within a passive treatment system. This paper shows the early results of a study of the Quaking Houses constructed wetland in County Durham, England.

Quaking Houses constructed wetland

The artificial wetland was commissioned in November 1997 outside the village of Quaking Houses ('Quakies'), Co. Durham to treat acidic colliery spoil leachate which was draining into the Stanley Burn. Prior to treatment the leachate waters were characterised by high loadings of iron and aluminium, and low pH (~4). In 1998 the spoil heap responsible for the discharge was capped, resulting in raised pH, although still net-acidic. Hydrology and geochemical factors strongly influenced the design of the wetland, which comprises a surface-flow, dual-celled, composted system. Fresh horse and cow manure plus composted municipal waste, in the ratio of 30:40:30, were used as substrate for both cells (Jarvis 2000). Water from the influent pipe is distributed across the width of the first cell, then decants over a weir into the second cell where it is dispersed by vegetation and baffles. This is primarily a surface-flow system with nominal average water retention time of ~24 hours (Younger *et al.* 2002).

Influent and effluent data gathered since 1997 (Table 1) give a very general impression of the performance of the wetland (Jarvis 2000). It appears that a few milligrams of iron, manganese, aluminium and sulphate have been removed from each litre of water passing through the wetland, and that the mean pH has risen from around 6.1 to 6.6. However, influent and effluent data say nothing about *how* the wetland removes iron, or generates alkalinity. Effluent data do not distinguish between species which have merely passed through the system, or those for which contaminants can be calculated (Jarvis 2000), but we cannot say that these values represent optimal removal rates without: (a) describing the key reactions in the system; (b) quantifying the rates of reaction; and (c) determining the limiting factors for these reactions.

SAMPLING PROTOCOL AND GEOCHEMICAL ANALYSES

Table 1. Mean concentrations and values of influent and effluent waters for Quaking Houses wetland. Samples were collected over a period of 27 months from 14.11.97 (Jarvis 2000)

Determinand	Influent	Effluent	n
Flow (L/min)	99	128	80,61
pH	6.06	6.60	84,83
Alkalinity (mg/L as $CaCO_3$)	49	66	71,70
Fe (total) (mg/L)	5.4	2.4	106,104
Al (mg/L)	5.3	2.1	102,101
Mn (mg/L)	3.8	2.7	106,104
SO_4^{2-} (mg/l)	801	768	99,97

The overall aim of this work is to define the C–S–Fe cycle of the wetland over an annual cycle. Here, we focus on the initial results on surface waters and a sediment core sampled in May 2001. Surface water samples were collected in duplicate for the analysis of major anions and cations, also pH and alkalinity. Cation samples were preserved using 2 mL of 36% HCl (AnalaR grade), and all water samples were filtered on-site through 0.45 μm membrane filters (Whatman, 47 mm diameter). The sediment core was taken from the centre of the wetland using a section of plastic piping, 600 mm × 50 mm. Once in position the core was sealed at both ends, preventing ingress of oxygen and leakage of pore-waters. All samples were stored at 4^{o}C, or frozen prior to analysis.

Analyses of the surface waters established concentrations of major anions and cations using ion chromatography and flame atomic absorption spectroscopy, respectively. The pH and alkalinity were determined by titration.

The sediment core was extruded and the pore-waters extracted under anoxic conditions. Pore-waters were analysed for SO_4^{2-}, Fe (II/III), alkalinity and pH, sulphide and manganese. As for the surface waters, the same techniques applied. Sulphide was determined by iodometric back-titration with thiosulphate.

Analyses performed on sediment samples included sulphur speciation as HCl-extractable sulphide (FeS or AVS), and chromium-reducible sulphur (FeS_2 and S^o); amorphous-$Fe(OH)_3$ phases were extracted using a dithionite or ascorbate leaching technique (Kostka and Luther 1994); total organic carbon, inorganic carbon and sulphur were extracted using a Leco-244 C-S Analyser.

Iron and sulphur geochemistry

Pore-water and solid phase data for iron and sulphur species are shown in Figures 1 and 2 respectively. Superficially, the pore-water data resemble trends which have been reported previously in natural, marine sediments (e.g. Canfield *et al.* 1993; Thamdrup *et al.* 2000). Reduction of iron oxides in the top few centimetres of the wetland sediments results in increasing abundances of dissolved iron, below which concentrations of dissolved Fe decline steadily. Directly from the surface sediments, microbial sulphate reduction results in steadily declining concentrations with increasing

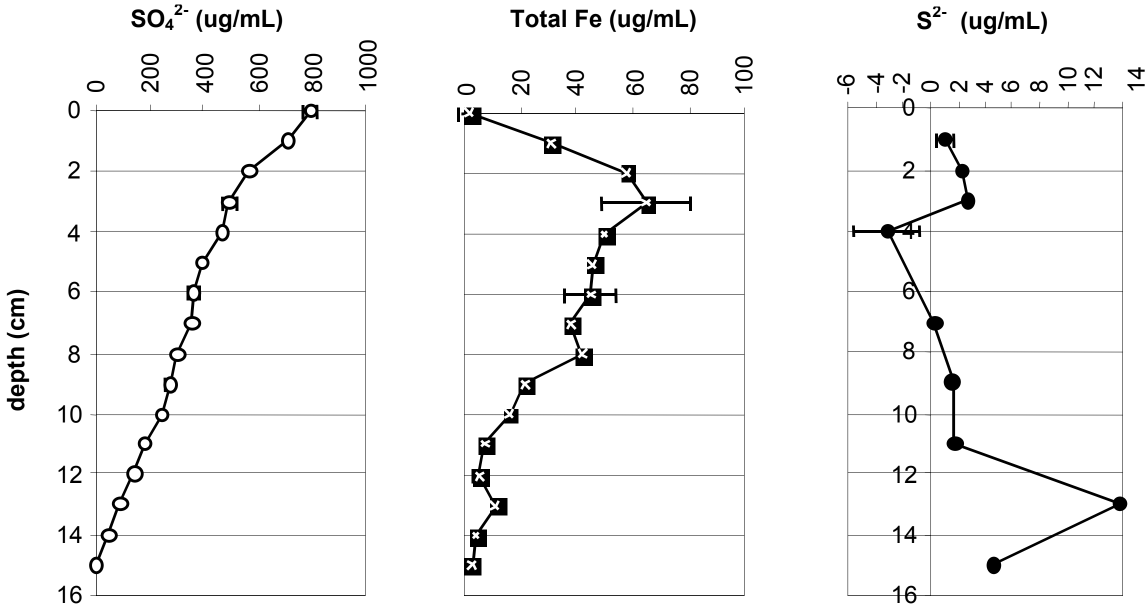

Figure 1. Pore-water profiles from a sediment core collected on 11.5.01. Sulphate has been completely removed from the aqueous phase at the bottom of the core, but sulphide has appeared. Fe^{2+} is intensively generated in the top 3 cm of sediment, and then removed over the next 8 cm. As concentrations of Fe^{2+} decrease, sulphide appears.

depth, and dissolved sulphide (the product of sulphate reduction) appears at depth, as concentrations of iron decrease.

Careful appraisal of the pore-water profiles reveals that in fact they differ from those reported in natural sediments in several important ways. Most obviously, pore-water Fe increases to the very high concentration of 65 µg/mL, despite the rapid generation of sulphide via sulphate reduction. In the top few centimetres of the sediment, rapid reduction of iron occurs concomitantly with rapid reduction of sulphate, with net production of reduced iron being greater than net production of reduced sulphur. We have not yet quantified the rates of sulphate and iron reduction, but anticipate that they will be substantially higher than those measured in natural sediments, reflecting the fact that we have, by design, created a highly reactive system comprising high loadings not only of organic carbon, but also of sulphate (25% of seawater abundance) and colloidal iron oxyhydroxides. Solid phase sulphide data (Figure 2) shows that the reduced iron and sulphur precipitates as pyrite (FeS_2) and acid volatile sulphide (FeS and similar compounds). Pathways of iron sulphide formation in these sediments are not yet defined but could include direct precipitation from pore-water iron and sulphide and the reaction of dissolved sulphide with solid phase iron oxides. Consistent with the partial reoxidation of sulphide by iron oxides, Heasman (1996) showed the occurrence of large amounts of elemental sulphur in the pilot Quaking Houses wetland.

There are exceptionally high concentrations of (operationally defined) iron oxides in the sediments (Figure 2). The apparent abundance of solid phase iron oxide, as measured by citrate dithionite leaching, decreases from 7% by weight in surface sediments to around 1% at 16 cm. The occurrence of iron oxide in surface sediments clearly reflects deposition from surface waters, and also that the rate of addition of oxidised iron must be greater than the rate at which it can be reduced either by dissimilatory microbial reduction (Lovley and Phillips 1988; Nealson and Saffarani 1994) or by abiotic reaction with dissolved sulphide. The importance of surficial iron oxide is that it ensures that microbially produced H_2S does not escape to surface waters, where it would reoxidise to give sulphuric acid. More puzzling is the apparent occurrence of iron oxide deep in the sediment. There is uncertainty as to the significance of this observation, which might be real or might relate to the dissolution of iron sulphides by the citrate dithionite leach.

IMPLICATIONS AND FURTHER WORK

Much previous work on anaerobic constructed wetlands has focused on microbial sulphate reduction as

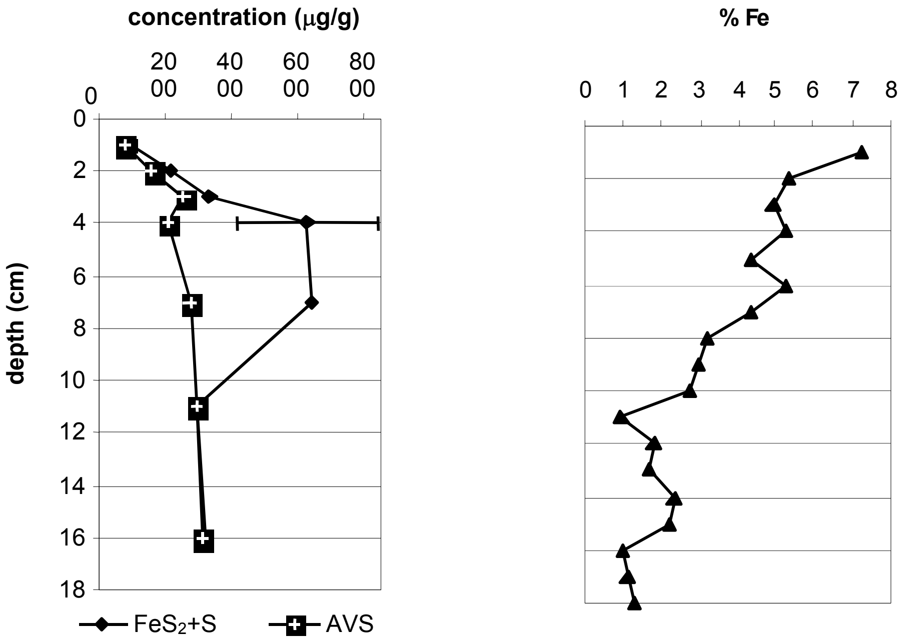

Figure 2. Solid-phase sediment profiles for the core sampled on 11.5.01. Sulphide was produced throughout the core depth, but especially between 3–11 cm as pyrite and elemental sulphur. The accumulation of reduced sulphur species as precipitates of iron over this depth is in conjunction with the decrease in Fe^{2+} from the pore-waters. Dithionite/ascorbate iron appears to be present down the entire depth of the core. There was no evidence of bioturbation in the sediments, and the core was extracted from an area free of vegetation.

the key process in carbon mineralisation and alkalinity production (e.g. Hedin *et al.* 1989; McIntyre *et al.* 1990; Fortin *et al.* 2000; Younger *et al.* 2002). Our data show that the iron cycle is equally important and is, of course, inextricably linked with the sulphur cycle. Without iron, sulphide generated from sulphate reduction would diffuse from the wetland sediment and be reoxidised to sulphuric acid; without sulphate reduction, reduced iron would diffuse from the wetland sediment and be reoxidised to iron oxide, with the concomitant generation of protons. Effective remediation of acidic waters in anaerobic passive treatment systems thus requires the appropriate balance within the Fe–S cycle and, by direct implication, within the C–S–Fe cycle. This is equally true for both surface water and flow-through treatment systems.

Further work is needed to quantify the annual C–S–Fe cycle in constructed wetlands, focusing in particular on defining not only the key reactions within the sediments, but also their rates. From a practical perspective, the rate of a reaction defines the amount of water that can be treated per unit time. From a scientific perspective, our future work will focus on defining not only the rates of key processes, but also the ultimate rate-limiting step.

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