Reactive barrier treatment of groundwater contaminated by acid mine drainage: sulphur accumulation and sulphide formation

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Abstract A permeable reactive barrier was installed in August 1995 at the Nickel Rim Mine near Sudbury, Ontario, Canada, for the passive remediation of groundwater contaminated with acid mine drainage. The reactive component of the barrier consists of a mixture of municipal and leaf compost and wood chips; the organic material promotes bacterially-mediated sulphate reduction. Hydrogen sulphide, a product of sulphate reduction, may then complex with aqueous ferrous iron and precipitate as iron sulphide. This study presents the solid phase sulphur chemistry of the reactive wall after two years of operation, and discusses the formation and accumulation of iron sulphide minerals in the reactive material. The results from the solid-phase chemical analysis of core samples indicate that there is an accumulation of reduced inorganic sulphur in the reactive wall, with levels reaching 190 μmol g⁻¹ (dry weight) by July 1997.

INTRODUCTION

At the inactive Nickel Rim Mine site near Sudbury, Ontario, Canada, the atmospheric oxidation of pyrrhotite (Fe₇₈S) in the tailings impoundment has lead to the generation of an acidic leachate plume in the groundwater downgradient from the deposit (Johnson, 1993; Bain et al., 1995; Bain, 1996). At the base of the impoundment, the groundwater is characterized by near-neutral pH and relatively high concentrations of sulphate (<7000 mg l⁻¹) and ferrous iron (<2200 mg l⁻¹) (Bain, 1996). The discharge of the contaminated groundwater to the oxic sediments of Moose Lake, 130 m downgradient from the tailings deposit, results in the oxidation of Fe(II) to Fe(III) and subsequently in the hydrolysis and precipitation of ferric iron. The precipitation of iron oxides is evident on the sediment surfaces at the lake bottom. Iron hydrolysis reactions release H⁺ and are partially responsible for the acidification of Moose Lake (pH ≈ 3; Bain, 1996).

In August 1995, a permeable reactive barrier (Blowes & Ptacek, 1994) was installed at the Nickel Rim site to intercept the groundwater contaminant plume and prevent the discharge of the contaminated water to Moose Lake (Benner et al., 1997). The barrier was installed in the glaciofluvial aquifer, approximately 60 m downgradient from the toe of the impoundment wall, where the groundwater pH is 4–6 and sulphate and iron concentrations are 2400–4800 mg l⁻¹ and 250–1300 mg l⁻¹, respectively. A mixture of leaf and municipal compost and wood chips was chosen as
the reactive material (Waybrant, 1995). To ensure that groundwater flowed through the barrier, the reactive material was mixed with approximately 50% (by volume) pea gravel so as to enhance the porosity and hydraulic conductivity of the material (Waybrant, 1995; Benner et al., 1997). Limestone was added to the mixture to ensure that near-neutral pH conditions were maintained in the wall. A description of the construction of the reactive wall and choice of reactive mixtures is presented in Benner et al. (1997) and Waybrant (1995), respectively.

The decomposition of the organic matter in the reactive barrier creates a zone of low redox potential in the wall. These conditions promote the growth of sulphate-reducing bacteria, which obtain energy and nutrients by oxidizing low molecular weight organic carbon compounds (e.g. lactate, acetate), using sulphate as an external electron acceptor:

\[
2\text{CH}_3\text{CHOHCOO}^- + \text{SO}_4^{2-} \rightarrow 2\text{CH}_3\text{COO}^- + 2\text{HCO}_3^- + \text{H}_2\text{S}
\]

Bicarbonate (\(\text{HCO}_3^-\)) and hydrogen sulphide (\(\text{H}_2\text{S}\)) are reaction products. Aqueous hydrogen sulphide (or bisulphide) and aqueous ferrous iron species may then react and precipitate as iron sulphides:

\[
\text{Fe}^{2+} + \text{H}_2\text{S} \rightleftharpoons \text{FeS}(s) + 2\text{H}^+
\]

Thus, sulphate reduction in the reactive wall generates alkalinity and may lead to the formation of iron sulphides; ferrous iron is therefore removed from the flow system, minimizing the potential for acid generation during groundwater discharge to oxic lake sediments. This paper presents the solid-phase sulphur chemistry of the reactive wall two years after installation, and discusses the formation and accumulation of iron sulphide minerals in the reactive material.

METHODOLOGY

Sampling and sample preparation

Cores of the reactive wall material were taken by driving 170 cm lengths of 5-cm (2-inch) aluminium tubing, encased in a steel core barrel, using a pneumatic hammer. The reactive wall was covered by a clay layer of about 30 cm depth to prevent the infiltration of surface water; the cores were driven from below the clay cover to bedrock (approximately 4 m depth); two sequential cores were collected from below the clay cover at most locations. However, core recovery averaged approximately 70% because of the non-cohesive nature of the barrier material. After sampling, the aluminum core casings were immediately cut into approximately 30 cm sections, capped, and stored on ice during transport to the laboratory, where they were frozen. Three cores are discussed in this report, collected in November 1995 (core 9511), October 1996 (core 9610), and July 1997 (core 9707); all cores were collected within 1 m of the up-gradient edge of the reactive wall, and within 1 m of piezometer nest RW29 (cf. Benner et al., 1997). In addition to the samples from the barrier, samples of the original, unreacted barrier material were analysed.
Prior to analysis, a 4–8 cm sample was cut from a frozen 30 cm core section and the sediment was extracted into a plastic vial. The frozen sample was thawed under N₂ gas, whereupon the sample was homogenized and then analysed for acid volatile sulphides (see below). The portion of the sample not used for AVS analysis was placed in a vacuum desiccator for the determination of the gravimetric water content and further analysis.

**Sulphur speciation**

Within the reactive wall, the major S pools may include aqueous sulphate and sulphide species, gaseous hydrogen sulhide, and solid phase sulphide and sulphate minerals, elemental sulphur, and organically-bound S. Aqueous phase sampling and results are discussed elsewhere (Benner et al., 1997; Blowes, 1998), and gaseous H₂S (and other volatile S gases) are expected to contribute little to the total S pool (Giblin & Wieder, 1992; Machemer et al., 1993). For the determination of solid phase S speciation in the reactive wall material, a non-sequential extraction scheme was implemented, using methodologies presented in Canfield et al. (1986), Lyons & Berner (1992) and Machemer et al. (1993). Most samples were analysed in three replicates, and results are given in dry weight.

Sulphide minerals in the wall material are divided into two operationally-defined groups: acid volatile sulphides (AVS), including the monosulphides amorphous Fe sulphide (“FeS”), mackinawite (Fe₁₊xS), and greigite (Fe₃S₄), and total reduced (inorganic) sulphur (TRS), including the AVS fraction plus disulphides such as pyrite and also elemental sulphur (S₈). The AVS and TRS fractions were extracted in a digestion apparatus described by Canfield et al. (1986). The extraction schemes for these two fractions have been tested in many investigations (Canfield et al., 1986; Morse & Cornwell, 1987; Lyons & Berner, 1992), and yield reliable and reproducible results.

For the extraction of AVS, two to three grams of wet, homogenized, freshly-thawed sediment is reacted, at room temperature for 90 min, with 60 ml 6 N HCl containing 15% (w/v) SnCl₂ (Morse & Cornwell, 1987; Lyons & Berner, 1992). In the digestion apparatus discussed by Canfield et al. (1986), the evolved H₂S is trapped as ZnS and analysed by iodimetric titration using a 1% starch indicator solution. Following the analysis of a sample for AVS, the 6M HCl digestion solution was filtered through a 0.45 μm cellulose nitrate membrane filter. This solution was then analysed for S by ICP-AES. The concentration of S in this solution (HCl-S) gives an upper limit to sulphate present in the porewater and/or present in HCl-soluble sulphate minerals (e.g. gypsum, CaSO₄·2H₂O) and surface complexes; some low molecular weight organic S compounds (e.g. thiols, sulphate esters) are also soluble in HCl, but these are expected to be only a minor component of this fraction.

The analysis of TRS involves the hot extraction of a one to two grams vacuum-dried sample with 1M CrCl₃ in 0.5N HCl, using the digestion apparatus from Canfield et al. (1986), where the chromous solution is produced by passing CrCl₃ through a Jones reductor. This method is described in detail by Canfield et al. (1986). The dried residue from the TRS analysis was then reweighed and analysed for total sulphur; this fraction represents organically-bound S that is not accessible by
the AVS and TRS extractions. Total S is determined by sample combustion in a LECO model 532 induction furnace, where S is released as SO$_2$, converted to sulphuric acid, and analysed iodimetrically.

RESULTS AND DISCUSSION

Sulphur accumulation in the reactive barrier

The depth profiles for the TRS fraction from the three cores are illustrated in Fig. 1, where the TRS fraction represents the total accumulation of S in reduced inorganic S species. As the unreacted barrier material contains only 8 µmol g$^{-1}$ TRS, Fig. 1 indicates that there is an accumulation of S in the TRS fraction in the reactive barrier. According to the analytical results (data not shown), the AVS concentrations are generally greater than 75% of the TRS values, indicating that the accumulation of reduced inorganic sulphur in the reactive wall consists of primarily acid volatile sulphides, with disulphides and/or elemental S accounting for $<$25% of TRS. The TRS fraction accumulates to levels in excess of 190 µmol g$^{-1}$ reactive material (dry weight) by July 1997. The rate of sulphide accumulation at the up-gradient edge of the barrier was greatest during the first year after installation, and decreased thereafter (see Fig. 1).

As shown in Fig. 2, the levels of organically-bound S in cores 9511 and 9707 are, in all cases, less than the levels determined in the unreacted material (70 µmol g$^{-1}$). Although these values represent the lower limits for organically-bound S, as some low molecular weight organic compounds may have been leached from

![Sulfur Concentration (µmol g$^{-1}$)](image)

**Fig. 1** Total reduced (inorganic) sulphur in three cores from the reactive barrier.
the samples during the acidic TRS extraction procedure, the data suggest that there is little S accumulation as organic S compounds. For the HCl-S fraction, S concentrations are observed in excess of 100 μmol g⁻¹ (Fig. 3). The majority of this sulphate, however, is probably porewater sulphate that has been incorporated into the
sample during drying; porewater containing 3000 mg l\(^{-1}\) SO\(_4\) in a 2 g sample with 60% water content would contribute \(-50 \mu\text{mol g}^{-1} \text{ S}\) to the total S concentration in the sample.

Iron sulphide formation

The analytical results indicate that acid volatile sulphides are the primary sulphide phases precipitating in the reactive barrier. Attempts to determine the mineralogy of particular solid phases by X-ray diffractometry and scanning electron microscopy have been unsuccessful, possibly because AVS phases such as amorphous FeS and mackinawite are often characterized by small crystallite size and poor crystallinity (e.g. Morse & Cornwell, 1987).

The low levels of pyrite and/or elemental sulphur in the core samples, relative to the AVS fraction, suggest that the geochemical conditions in the reactive wall have not been favourable for their formation. Recent studies (Schoonen & Barnes, 1991; Wilkin & Barnes, 1996) have demonstrated that mackinawite is a precursor phase to pyrite (FeS\(_2\)) formation. Pyrite does not nucleate significantly at temperatures typical of sedimentary environments, but may instead form by the sulphidation of an iron monosulphide precursor phase by intermediate sulphur species, such as polysulphides (S\(_{x}^{2-}\)):

\[
\text{FeS}(s) + S_{x}^{2-} \rightarrow \text{FeS}_{2}(s) + S_{(x-1)}^{2-}
\]

(3)

The formation of polysulphides from H\(_2\)S requires the presence of electron acceptors. Field measurements indicate (Benner et al., 1997) that appropriate electron acceptors (e.g. oxygen, nitrate, iron oxides) are not present in the reactive barrier, so equation (3) may not be significant in this environment. Alternatively, with strictly anoxic, reduced conditions, hydrogen sulphide reacts with FeS to yield pyrite (Rickard, 1997):

\[
\text{FeS}(s) + H_{2}S \rightarrow \text{FeS}_{2}(s) + H_{2}(g)
\]

(4)

where hydrogen gas is produced in the reduction of H\(^{+}\). Although equation (4) may be proceeding at sulphide surfaces in the reactive barrier, the reaction of hydrogen sulphide with ferrous iron (equation (2)) is probably kinetically favoured in the presence of excess Fe\(^{2+}\), and equation (4) is favoured only when the availability of Fe\(^{3+}\) is limiting.

In conclusion, the solid-phase analytical results indicate that S has accumulated in the Nickel Rim reactive barrier during the two year period following installation. Sulphur is predominantly accumulating as poorly crystalline iron monosulphides; there is currently no evidence to support the \textit{in situ} formation of complexes containing carbon-bonded S or the precipitation of sulphate minerals (e.g. gypsum) in the reactive barrier.

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REFERENCES


