Bench Scale Reactor to Test In-situ Remediation of Mining Influenced Groundwaters by Autotrophic Sulphate Reduction and Sulphide Stripping

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Abstract

Removal of iron, sulphate and acidity from mining influenced waters is performed by autotrophic sulphate reduction (SR) in a set of 3 bench scale reactors (60L each) preparing future in-situ field application. In reactor 1 complete precipitation of iron (3.8 mmol/L) is achieved by recirculating sulphide rich water from reactor 2. In reactor 2 and 3 the initial sulphate concentration (17 mmol/L) is lowered to about 2 mmol/L by microbial SR using hydrogen as substrate. pH of the groundwater is controlled by adjusting the p(CO_2). Biomass carriers are found to be crucial for performance. No temperature dependence of SR was detected between 10-20°C.

Motivation

Mining affected areas often present sources of sulphate and iron rich waters due to increased sulphide mineral weathering. Water treatment technologies exist to lower acidity and ferrous iron content of the waters. In contrast elevated sulphate contents are irreducible with state of the art techniques. Microbial sulphate reduction (SR), being a promising technology to extract sulphate, acidity and iron from waters is thus being investigated for a long time (Tuttle et al. 1969). Despite this still many difficulties are encountered with this technology. Sulphate reduction rates above 5 mmol/(L*h) have only been achieved in laboratory scale reactors at 30-35°C using biosludges from other anaerobic processes like biogas production (e.g. Van Houten et al. 1994, Muthumbi et al. 2001). This is done because sulphate reducing bacteria (SRB) are considered not to be capable to quickly create sufficient amounts of biosludge by themselves (e.g. De Smul and Verstraete 1999). It is generally assumed that SRB relay on biosludge mainly produced by methanogens to provide habitats for SRB (Visser et al. 1993). Disadvantages of using methanogenic sludge are a) the initial predominance of methanogens which compete for the electron donators and thus hamper the population increase of SRB and b) the deterioration of the sludge which makes periodic replacement necessary (e.g. Dries et al. 1998) Often severe diminishing of reactor performance is observed due to too high hydraulic velocities and subsequent biomass washout (Dries et al. 1998). Use of organic carbon instead of H_2 as substrate might lead to elevated concentrations of organics in the discharge. Inertisation of biomass might be caused by FeS-precipitation (Utgikar et al. 2002).

To treat sulphate rich groundwater a special type of permeable reactive wall is planned to be employed to host a series of technical in-situ SR-reactors [1]. It temporarily separates the contaminated ground water from the sediments to overcome heterogeneities of the subsurface (**fig. 1a**). Full hydraulic and biochemical process control is possible due to good access from the surface. Reagents are continuously dosed from the surface to treat the high mass fluxes typical for mining affected groundwater and products are easily removed in that way.

Using technical in-situ reactors high turnover rates are necessary due to limited reactor volume. To increase rates, optimum conditions for the growth of SRB have to be guaranteed (pH between 6 and 9, Eh below -150 mV, sufficient nutrient supply, low sulphide concentrations, high concentrations of sulphate and substrate). Also the amount of biomass per volume of reactor has to be maximized.

Method

A bench scale reactor system (180 L) was constructed (**fig 1b**) to test future in-situ sulphate reduction in a technical reactor system (**fig 1a**) under ground-water temperature conditions, taking into account the previously mentioned findings. H_2 was used as substrate because it is readily available for SRB (Lens et al. 2002), is easily producible by electrolysis in the field, it does not pollute the treated ground water with organic substances and it is easily and homogeneously supplied to the SRB by a closed gas cycle which prevents gas leakage to the environment. Nutrients N and P (0.9 and 0.3 mmol/l respectively) were added to the feed water. To reduce biomass washout highly porous expanded clay particles are used as biomass carriers. To prevent clogging of the biomass carriers all FeS-sludge is precipitated before SR is performed in the biomass carrier fixed bed.

One limiting factor for the in-situ sulphate reduction was considered to be the groundwater temperature of about 10-12°C. All of the previously cited high rate laboratory tests have been performed at temperatures between 30 and 35°C. Main goal of this investigation was the long term test of the stability of the SR-process in bench scale in preparation of a future full scale field test plant and to find out about the limitation of the rate in such a system. Temperature dependence (10-20°C) of the autotrophic sulphate reduction and the usefulness of biomass carriers was evaluated because there still is inconsistent information about it in literature.

The reactor was inoculated with autochtonuous SRB from mine dumps (LMBV 2007) to avoid later competition when charging the reactor with natural groundwater (e.g. Lens et al. 2002). It was run at 1.1 to 1.2 bar$_{abs}$ and at 20°C. After 51 bed volumes temperature was reduced to 10°C. The total test time up to now is 450 days.

The reactor system (**fig 1a and b**) consists of five treatment units

1) Microbial autotrophic sulphate reduction with H_2 (eq. 1) in a fixed bed reactor
2) Separate, iron sulphide precipitation (eq. 2) by recirculating sulphide rich water from the subsequent sulphate reducing reactor in an upstream settling tank to remove solids and to avoid clogging of the fixed bed.
3) Discharge of all excess sulphide via aqueous phase
4) Transforming aqueous sulphide to gaseaous sulphide (eq. 3) by increasing $p(CO_2)$ and thus lowering the pH to increase stripping efficiency for gaseous sulphide
5) Partial reoxidation of sulphide to S^0 with oxygen

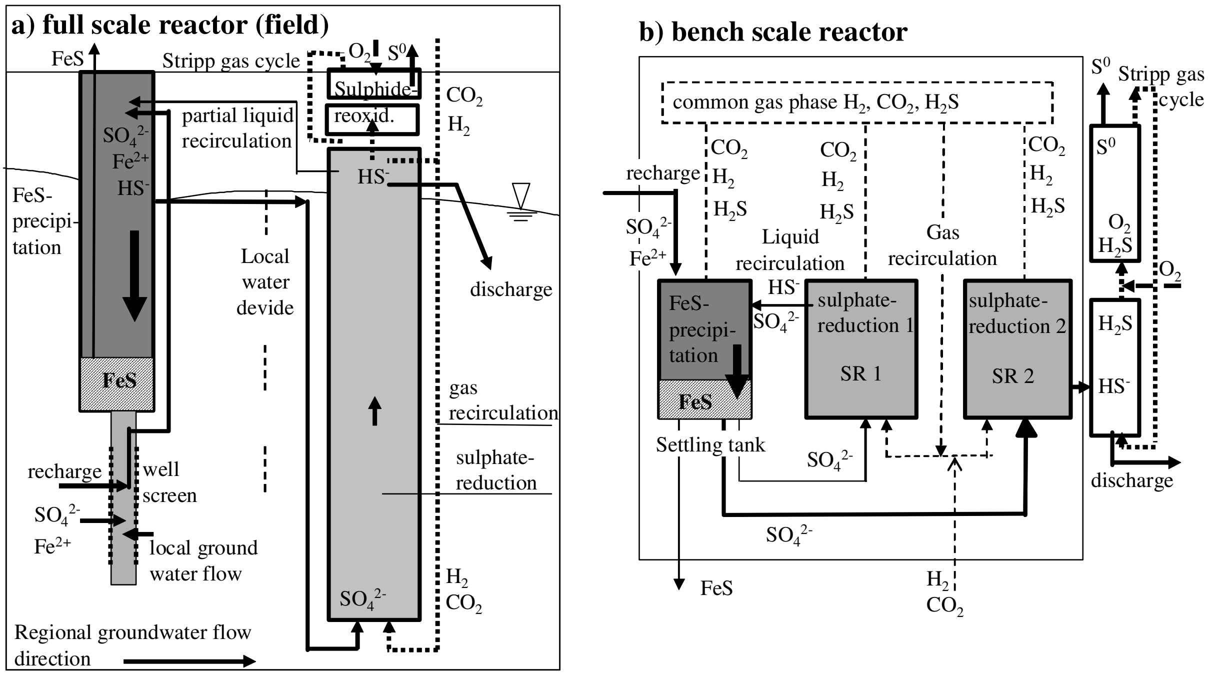
$$SO_4^{2-} + 4H_2 + 2H^+ \quad \Rightarrow H_2S + 8H_2O \qquad (1)$$

$$Fe^{2+} + HS^- \quad \Rightarrow FeS\downarrow + H^+ \qquad (2)$$

$$H_2S_{(g)}\uparrow \Leftrightarrow H_2S_{(aq)} \qquad H_2S_{(aq)} \Leftrightarrow HS^- + H^+ \qquad pK = 7.0 \qquad (3)$$

Microbially used H_2 and dissolving CO_2 lead to a pressure decrease in the reactor and thus trigger gas recharge. In the head of the reactor a H_2S-/CO_2/H_2-gas mixture of constant composition evolves in equilibrium with the fluid. Thus eventually all of the continuously produced $HS^-_{(aq)}$ is discharged and stripped of the fluid.

Figure 1 Fluxes in the full scale and the bench scale reactor


a) full scale reactor (field)

b) bench scale reactor

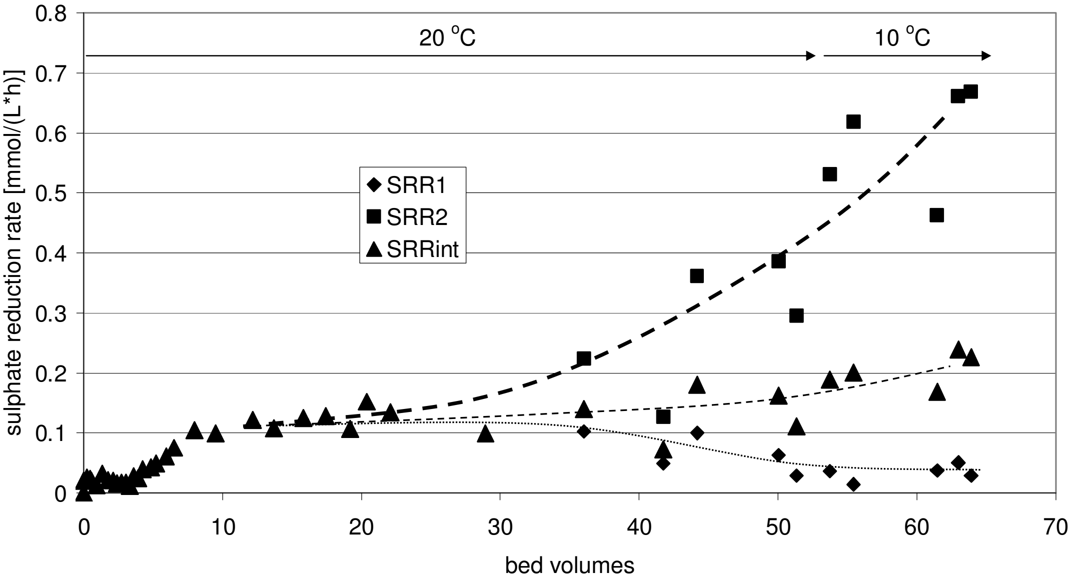
Results

Iron (init. 3.8 mmol/l) was completely removed in the precipitation reactor. Initial sulphate concentrations of 15-17 mmol/L could have been microbially reduced and extracted completely but a discharge concentration of about 2 mmol/l turned out to be necessary to minimize methane production to 3-15% of the total electron uptake which confirms the findings of other workers (e.g. Weijma et al. 2002). Initial pH of about 4.9 was increased and successfully controlled to be between 7.0 and 8.0 by adjusting the $p(CO_2)$ to be between 0.05 and 0.2 bar (Bilek et al. 2007). This was necessary because

1) depending on the iron/sulphate-relationship and the buffer capacity of the water autotrophic microbial sulphate reduction results in a pH-increase (eq. 1 and 2) up to 10.
2) microbial SRB-activity shows an optimum at pH 6 to 9 (Widdel and Bak 1991).
3) many mining influenced waters show high Ca- and high TIC-concentrations. Thus unwanted calcite precipitation (loss of alkalinity, loss of pore space) may occur due to microbially induced pH increase above 8.
4) the produced sulphide has to be kept in aqueous phase as $HS^{-}_{(aq)}$ to be removed from the reactor (eq. 3) and to maximize $p(H_2)$ in the gas phase. This is done by increasing the pH above 7.

A $H_{2(aq)}$-concentration in the reactor of 0.5 up to 0.85 mmol/L was constantly achieved, which is about 60-100% of the concentration which is thermodynamically possible. SR-rates have been increasing up to 0.13 mmol/(L*h) within 150 days (10 bed volumes) and then levelled out. After 20 bed volumes of continuously running the reactor, it was stopped for two weeks and opened for maintenance. The overall performance was not impeded by this procedure. Afterwards different rates were observed in the two reaction chambers. As it turned out, ongoing transport of expanded clay particles into the settling tank slowly reduced the performance in SR1 while the rates increased up to 0.6 mmol/(h*L) in SR2. Rates increased continuously even after reducing the temperature from 20 to 10 °C (**fig. 2**).

Figure 2 Sulphate reduction rates



Discussion

No severe rate decline was observed within the hitherto runtime of 450 days. pH-control by $p(CO_2)$ proved to be a successful technique. A toxic enrichment of H_2S and calcite precipitation in the reactor was thus avoided. Control of methane production was possible by adjusting the sulphate-runoff concentration.

The development of the rates showes that biomass increase is still in progress. No final limitation of the rate is recognizable up to now. Assuming a completely mixed reactor, no substrate limitation and growth rates typical for anaerobes, calculations of biomass increase in the aqueous phase showed that a high percentage of the biomass (<60%) must be attached to the carrier material. This shows that biomass carriers are necessary for the consortium of microorganisms found in the reactor (LMBV, 2007) and under the conditions described above. The importance of carrier material was also underlined by the fact that repeated opening of the reactor for maintenance was not affecting the SRB-population. Also the decline of the rate in SR1 due to the declining amount of carrier material compared with SR2 with a constant amount of carrier material shows the necessity of the carrier material and the suitability of the expanded clay particles to support SRB-dominated biofilms. The development of the rates shows that long time periods have to be faced for the startup period of a SR-reactor.

No decrease of the rates due to temperature reduction was recognized. This is in accordance with findings form other workers which found only slight correlation of SR-Rates and temperature (Preuss et al. 2007) Moosa et al. (2005) found no correlation between growth rate and temperature (20-30°C). SR-Rate however increased as temperature increased. This shows that microbial sulphate reduction is a suitable technology to remediate sulphate rich waters not only at elevated temperatures, which are available in industrial environment, but also in the field. In the field increased partial gas pressures are possible if the technical reactors are positioned below the ground water surface due to increased hydrostatic pressures. It is expected that the increase of $p(H_{2(aq)})$ will lead to additional rate increase.

Acknoledgements

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