

# Biological sulphate removal from acid mine effluent using ethanol as carbon and energy source

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**Abstract** Mining effluents are major contributors to mineralization of receiving waters and can be toxic to man, animals and plants due to unacceptably high concentrations of heavy metals. A biological sulphate removal process has been developed for the treatment of sulphate-rich industrial effluents, where sulphate is converted via sulphide to sulphur in an anaerobic single-stage reactor. Ethanol is used as carbon and energy source. Sulphate was removed from acid mine water over a period of 95 days from 3000 mg/l down to less than 200 mg/l and the formed sulphides to less than 200 mg/l. The VSS value in the reactor varied between 3 and 4 g/l, resulting in a specific sulphate removal rate from 0.47 to 2.47 g SO<sub>4</sub>/(g VSS.d), while the volumetric rate was 2.5 and 8.4 g SO<sub>4</sub>/(2.d) at HRT of 18 to 4.3 h. The experimental COD/sulphate ratio was between 0.55 and 0.84, which is in accordance with the theoretical value of 0.67. The experimental sulphide/sulphate ratio was less than the theoretical value of 0.33 due to the conversion of sulphate to sulphur and due to metal sulphide precipitation. Iron and copper were removed completely and aluminium, manganese and zinc to less than 4 mg/l.

**Keywords** Acid mine water; anaerobic treatment; completely mixed; ethanol; single-stage; sulphate reduction

## Introduction

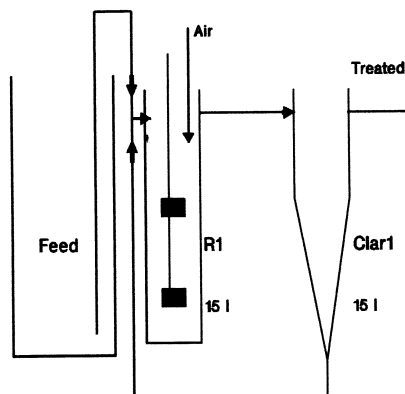
Mining effluents are often acidic, containing high concentrations of sulphate and metals. Traditionally this type of wastewater has been treated by the addition of lime, to increase the pH and to precipitate the heavy metals as metal hydroxides. Increasing attention has been given to biological sulphate removal (e.g. Maree & Strydom, 1985; Maree *et al.*, 1986). Sulphate can be removed biologically as sulphide or sulphur provided that a suitable carbon and energy source is available, such as ethanol. During biological sulphate removal sulphides are produced, which are dissolved in the treated effluent. As they are environmentally unfriendly it is desirable to remove the sulphides from the waste streams, e.g. through chemical precipitation by metals. Metal sulphides have low solubilities and can be discarded with the sludge wasting process. Buisman (1989) showed that H<sub>2</sub>S produced during biological sulphate reduction can be oxidised to elemental sulphur provided that the oxygen level is kept low.

The aims of this investigation were to determine: the process stability, the volumetric and specific sulphate reduction rates, the stoichiometric relationships between various parameters, the efficiency of metal removal from acid mine water and the sludge characteristics.

## Materials and methods

### Reactor configuration (Figure 1)

Two completely mixed reactor systems, comprising of a reactor (R1, volume 15 l) and a clarifier (volume 15 l) were operated concurrently. Initially the reactors received synthetic feed (HRT, 12 h), in which the sulphate as CaSO<sub>4</sub> and the COD concentrations were 1500 mg/l, each. Technical ethanol (Crest Industries, Johannesburg) was used (1 ml per l feed) as



**Figure 1** Completely mixed reactor system

the carbon and energy source. The feed was supplemented with both macro nutrients: (Ammonia- N, 75 mg/l and Phosphate-P 15 mg/l) and micro nutrients: 100 µg/l Fe, 210 µg/l Co, 0.28 µg/l Mn, 0.44 µg/l V, 0.25 µg/l Ni, 0.48 µg/l Zn, 0.40 µg/l Mo, 0.18 µg/l B, 0.37 µg/l Cu. The reactors were initially inoculated with anaerobic sludge obtained from the local municipal sewage treatment plant which with time became conditioned for sulphate removal. Both reactor and clarifier were open to the atmosphere so that air was introduced into the system. After feeding synthetic feed, the first reactor system received part acid mine water (a.m.w.) and part sulphate removal treated synthetic feed (1:1) at HRT of 10, 5.3 and 4.3 h. After adapting to synthetic feed, the second system received undiluted a.m.w. at HRT of 18 and 14 h, respectively.

#### Analytical

Determinations of sulphate, sulphide, COD, alkalinity, and pH were carried out according to standard analytical procedures as described in Methods (APHA, 1985). With the exception of sulphide and feed COD, all analyses were carried out on filtered samples (Whatman #1). The acidity determination of the feed was done by titrating with 0.1 N NaOH to a pH of 9.0. The COD samples were pre-treated to eliminate the sulphide (COD) contribution.

## Results and discussion

#### Process stability

The sulphate concentration of the feed and treated water determined over a continuous period of 65 days is illustrated in Figure 2. Sulphate was removed from 3000 to less than 200 mg/l (as  $\text{SO}_4$ ). From days 1 to 25 the biomass adapted to the feed and feed rate. Thereafter the reactor pattern stabilized, except from days 40-48 when performance declined due to mechanical failure.

#### Sulphate removal and sulphate reduction rates

The results when different feed waters were fed are shown in Table 2

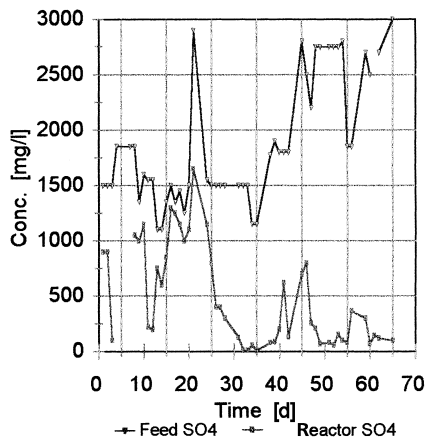
The results in Table 2 showed that the sulphate reduction rate was 2.5 g  $\text{SO}_4$ /(2.d) at a HRT of 12 h, feeding synthetic feed. When feeding the 1:1 mixture it increased from 2.9 to 8.4 g  $\text{SO}_4$ /(2.d) when the HRT decreased from 10 h to 4.3 h. The increased sulphate removal rate is therefore not only a function of the feed rate, but also of the time during which the biomass adapted. The specific sulphate reduction rate increased from 1.29 to 1.67 and to 2.47 g  $\text{SO}_4$ /(g VSS.d) when the HRT decreased from 10 h to 5.3 to 4.3 h. The specific sulphate reduction rate of 2.47 g  $\text{SO}_4$ /(g VSS.d), as determined for the single stage process,

**Table 2** Experimental conditions, chemical composition of feed and treated water, reaction rates and stoichiometric ratios between various parameters when ethanol was used to treat acid water.

Determinand	Unit	Values						
		Synthetic	A.m.w : Treated synthetic feed			Acid mine water		
Dilutions		Undil.	1:1	1:1	1:1	Undil.	Undil.	
Feed rate	(l/d)	30	36	67.6	83	20	25	
HRT (h)*		12	5.3	4.3	18	14.4		
<b>Feed:</b>								
Sulphate	mg/l	1550	1950	1715	1912	2500	3150	
COD	mg/l	1630	1319	1444	1316	1694	1627	
Alkalinity	mg/l	200						
Acidity	mg/l	-	300	300	300	600	600	
pH		7	7.1	7.3	7.3	3.2	3.5	
<b>Treated:</b>								
Sulphate	mg/l	235	755	329	397	628	194	
COD	mg/l	553	569	282	286	535	600	
Alkalinity	mg/l	518	945	1111	781	573	712	
Sulphide (S <sup>2-</sup> )	mg/l	181	201	273	213	170	281	
VSS	µg/l	5.3	2.2	3.7	3.4	3.4	3.6	
pH		7.7	8	7.8	8	8.2	7.9	
<b>Rates:</b>								
SO <sub>4</sub> reduction	g/(l.d)	2.5	2.9	6.2	8.4	2.5	4.9	
Specific SO <sub>4</sub> <sup>2-</sup> reduction	g SO <sub>4</sub> <sup>2-</sup> / (g VSS.d)	0.47	1.29	1.67	2.47	0.74	1.36	<b>Theoretical ratios</b>
<b>Ratios:</b>								
COD/SO <sub>4</sub> <sup>2-</sup>		0.82	0.63	0.84	0.68	0.8	0.55	<b>0.67</b>
S <sup>2-</sup> /SO <sub>4</sub> <sup>2-</sup>		0.16	0.17	0.2	0.15	0.09	0.1	<b>0.33</b>
Alkalinity/ SO <sub>4</sub>		0.44	0.79	0.8	0.55	0.31	0.24	<b>1.04</b>

\* HRT is based on reactor volume only and excludes clarifier volume.

compared favourably with that in other systems (0.2 g SO<sub>4</sub>/ (g VSS.d)(Smith & Middleton, 1980). This can be ascribed to the low sulphide concentration in solution which, at high concentrations, is toxic to sulphate reducing bacteria. The sulphate reduction rate increased from 2.5 to 4.9 g SO<sub>4</sub>/(2.d) when the HRT decreased from 18 h to 14.4 h when feeding undiluted acid mine water. Direct feeding of acid water without pre-neutralisation offers bene-



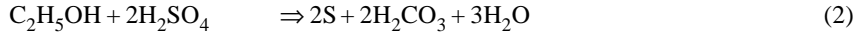
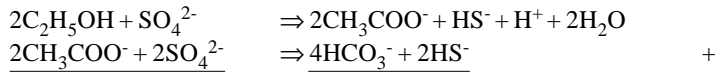
**Figure 2** Feed and reactor sulphate concentration during the first 65d of continuous operation of the sulphate removal reactor

fits for full-scale implementation, as neither lime treatment nor a separate stage for pre-neutralization is required.

The stoichiometric relationships between various parameters as shown in Table 2

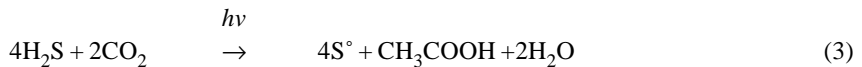
#### *COD/sulphate*

The experimental COD/SO<sub>4</sub><sup>2-</sup>-ratio varied between 0.55 and 0.84. The theoretical values are 0.67 and 0.50 when sulphate is reduced to sulphides (Reaction 1) and to sulphur (Reaction 2), respectively, excluding the COD requirement for cell production. The experimental values as low as 0.55 indicated that a portion of the sulphate was converted, via sulphide, to sulphur. When sulphur is the end product, which can partly be ascribed to photosynthetic bacteria and partly to sulphide oxidizing bacteria, the feed COD requirement amounts to only 75 % of that when sulphide is the end product. COD is also needed for new biomass growth and part of the available COD is used by other bacteria present in the reactor, for their consumption. Ethanol, as carbon source, degrades to acetate, which can be used by sulphate reducing bacteria (SRB), acetogenic bacteria (AB) and methanogenic bacteria (MB) Visser (1995) indicated that fierce competition takes place for the same (carbon) substrate in an anaerobic reactor. The MB and the SRB both degrade acetate via methanogenesis and sulphate reduction, respectively. As the reactor pH exerts a strong effect on the competition between SRB (pH 8-8.5) and MB (pH 6.5-7.5), the reactor pH was maintained close to 8, during most of the experimental period.



#### *Sulphide/sulphate*

The experimental S<sup>2-</sup>/SO<sub>4</sub><sup>2-</sup>-ratio varied between 0.1 and 0.2. The theoretical value is 0.33 (mass ratio) when sulphate is reduced to sulphide (Reaction 1). The fact that the experimental values were less than the theoretical value of 0.33 supported the theory that a portion of the sulphate was converted to sulphur. Sulphur formation was due to either photosynthetic sulphur production (Reaction 3) or to aerobic sulphur production (Reaction 4). Due to the lower sulphide concentrations the process is more stable as high levels of sulphides are toxic to the sulphate reducing bacteria and thus can cause instability in the process.



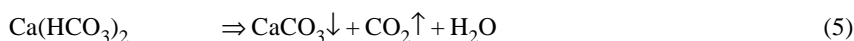
Another reason for the low sulphide/sulphate ratio can be explained by metal sulphide precipitation.

#### *Alkalinity/Sulphate*

The experimental alkalinity/sulphate-ratio varied between 0.39 and 1.04. The theoretical value is 1.04 (by mass) (Reactions 1 and 2). The experimental values being less than the theoretical value of 1.04 was explained by CaCO<sub>3</sub>-crystallization. The treated water became super-saturated with respect to CaCO<sub>3</sub> when CO<sub>2</sub> escaped from the water (Reaction 5).

**Table 3** Chemical composition of a.m.w, diluted a.m.w and treated a.m.w .

Parameter	Chemical composition of		
	A.m.w	Diluted A.m.w	Treated
Ammonia (mg/l N)	0.06	0	0
Nitrate (mg/l N)	0	0.73	0
Orthophosphate (mg/l P))	2.8	7.5	0.5
Calcium (mg/l Ca)	305	269	246
Magnesium (mg/l Mg)	178	157	141
Iron (mg/l N)	139	0.06	0.04
Aluminium (mg/l Al)	11.7	< 5	3.5
Manganese (mg/l Mn)	8.4	3.18	1.25
Copper (mg/l Cu)	0.35	0.01	0.01
Zinc (mg/l Zn)	113	3.1	3.1



### Sludge characteristics

The sludge settling rate was measured at 1.60 m/h, while the sludge achieved produced a maximum solids concentration of almost 3µg/l.

### Metal precipitation of acid mine water

The chemical composition of the acid mine water, the diluted acid mine water with the treated synthetic feed water (1: 1) and the treated acid mine water is given in Table 3. The results indicated that the macro nutrients (P and N) added to the feed were completely utilized. Iron and copper were removed completely and aluminium, manganese and zinc decreased to less than 4 mg/l. Aluminium precipitated as Al(OH)<sub>3</sub> and the other metals as metal sulphides.

### Conclusions

The single-stage process removed both sulphate and sulphide down to less than 200 mg/l consistently in a stable way when ethanol was used as carbon and energy source. The maximum sulphate reduction rate achieved was 8.4 g SO<sub>4</sub>/(2.d). The experimental COD/sulphate ratio was between 0.55 and 0.84 which is within 20% of the theoretical value (0.67). The lower value was due to reduction of sulphate to sulphide and to oxidation of sulphide to sulphur. This fact also resulted in an experimental sulphide/sulphate-ratio of less than the theoretical value of 0.33..The experimental alkalinity/sulphate-ratio was less than the theoretical value of 1.04 due to neutralization of acid water and CaCO<sub>3</sub>- precipitation. The metals, present in the a.m.w. were removed as metal sulphide precipitation. It was shown that a.m.w. mine water (pH 3.2) could be treated directly with the single-stage process to produce an effluent water of pH 7.9

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