

# Biological Sulphate Removal from Mining Effluents Utilizing Producer Gas as Energy Source

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## ABSTRACT

Acidic sulphate-rich effluents present a serious worldwide environmental pollution problem. A biological sulphate removal system consisting of a trickling filter and utilizing producer gas as energy source, was evaluated. Producer gas, a mixture of H<sub>2</sub>, CO, CO<sub>2</sub> and N<sub>2</sub> generated from coal, was shown to be an effective energy source for the autotrophic reduction of sulphate. The acidic effluent treated was simultaneously neutralized by alkalinity formed during the process. A volatile suspended solids (VSS) concentration of 3.7 g/l was present in the packing material of the anaerobic reactor.

## INTRODUCTION

High sulphate concentrations in water causes mineralization of surface water, salinity corrosion and scaling of equipment when associated with calcium. Sulphate in mine water originates from three sources; (i) bacterial oxidation of pyrite, (ii) the spent sulphuric acid used in metallurgical or chemical plants and (iii) in cooling systems due to evaporation. Solid waste in the form of gypsum, is also formed when sulphuric acid-containing effluents are neutralized with lime. This paper deals with sulphate pollution in the liquid phase.

Various processes for sulphate removal include: the slurry and precipitation reverse osmosis (SPARRO) process<sup>(1)</sup>, and the use of barium salts, such as barium carbonate and barium sulphide<sup>(2)</sup>. These processes, especially reverse osmosis and electrodialysis, are costly.

A promising biological sulphate reducing process<sup>(3)</sup> entails the reduction of sulphate to sulphide by sulphate-reducing bacteria in an upflow packed-bed reactor. Molasses was used as a nutrient source, which may not be available in sufficient quantities in the future, as it is used in other industrial processes; hence the need to investigate alternative energy sources.

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Hydrogen has been shown to be an effective electron donor for biological sulphate reduction<sup>(4,5,6)</sup>. Producer gas, also called synthesis gas, can be generated from any material containing carbon and hydrogen<sup>(7)</sup>. Some industries dispose of this gas as a waste product from heating plants. The most important industrial sources are: (i) from steam and methane, (ii) by the partial oxidation of fuel oil, or (iii) by coal gasification<sup>(8)</sup>. The resultant mixture of H<sub>2</sub>, CO, CO<sub>2</sub> and N<sub>2</sub> were put to a novel use as energy source for the sulphate reducing bacteria in an anaerobic trickling filter system.

The aim of this project was to develop a feasible sulphate-reducing process using (i) a trickling filter system and (ii) producer gas as energy source as an alternative to an upflow packed-bed system using molasses<sup>(3)</sup> as energy source.

### EXPERIMENTAL

#### Reactor description

The anaerobic reactor was constructed from a 14 cm internal diameter, 200 cm long transparent 'Perspex' cylinder as shown in Figure 1. Four circular deflection rings were inserted along the length of the reactor to ensure proper liquid distribution during downflow. The reactor was partially filled with 20 ℓ of ceramic rings with an internal diameter of 2 cm and a height of 2.5 cm, as bacterial support medium. It was inoculated with acclimatized biomass from an existing laboratory plant. Effluent for treatment was fed into the recirculation stream during continuous studies, which after trickling through the support medium, was collected in a 20 ℓ reservoir supplied with an overflow point. Producer gas was used as energy source and was pumped from a container under atmospheric pressure into the reactor. Loading rates of carbon monoxide, hydrogen and carbon dioxide were maintained at: 0.887, 0.0318 and 0.186 g/ℓ.d respectively throughout this project. The gas reservoir was refilled automatically from pressurized gas cylinders filled with waste gas from a local chemical company's ammonia plant. The composition of the producer gas is summarized in Table 1.

Table 1: Composition of the Producer Gas

Compound	Content (%)
H <sub>2</sub>	29.7
CO	59.1
CO <sub>2</sub>	7.9
N <sub>2</sub>	2.9
Ar + O <sub>2</sub>	0.4

Peristaltic pumps were used for feeding the water and producer gas to the reactor, while a centrifugal pump was used for recirculation of the water.

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### Operational procedures

The performance of the reactor and the kinetics of sulphate reduction were evaluated by means of continuous and batch studies. During continuous studies, the substrate solution was fed into the reactor at 5 and 10 l/d respectively and the producer gas at 20 ml/min. Batch studies were carried out by replacing half of the liquid contents of the reservoir with fresh feedstock at time zero, after which sulphate, alkalinity and pH were monitored as a function of time.

### Substrate

Feedstock consisted of a synthetic mine effluent with the following composition (g/l): Na<sub>2</sub>SO<sub>4</sub>, 2.96; CaCl<sub>2</sub>, 0.31; KH<sub>2</sub>PO<sub>4</sub>, 0.05; NH<sub>4</sub>Cl, 0.16; MgCl<sub>2</sub>·6H<sub>2</sub>O, 0.13. Tap water was used to fulfil the trace mineral requirements. Substrate was dosed continuously from a 60 l holding tank.

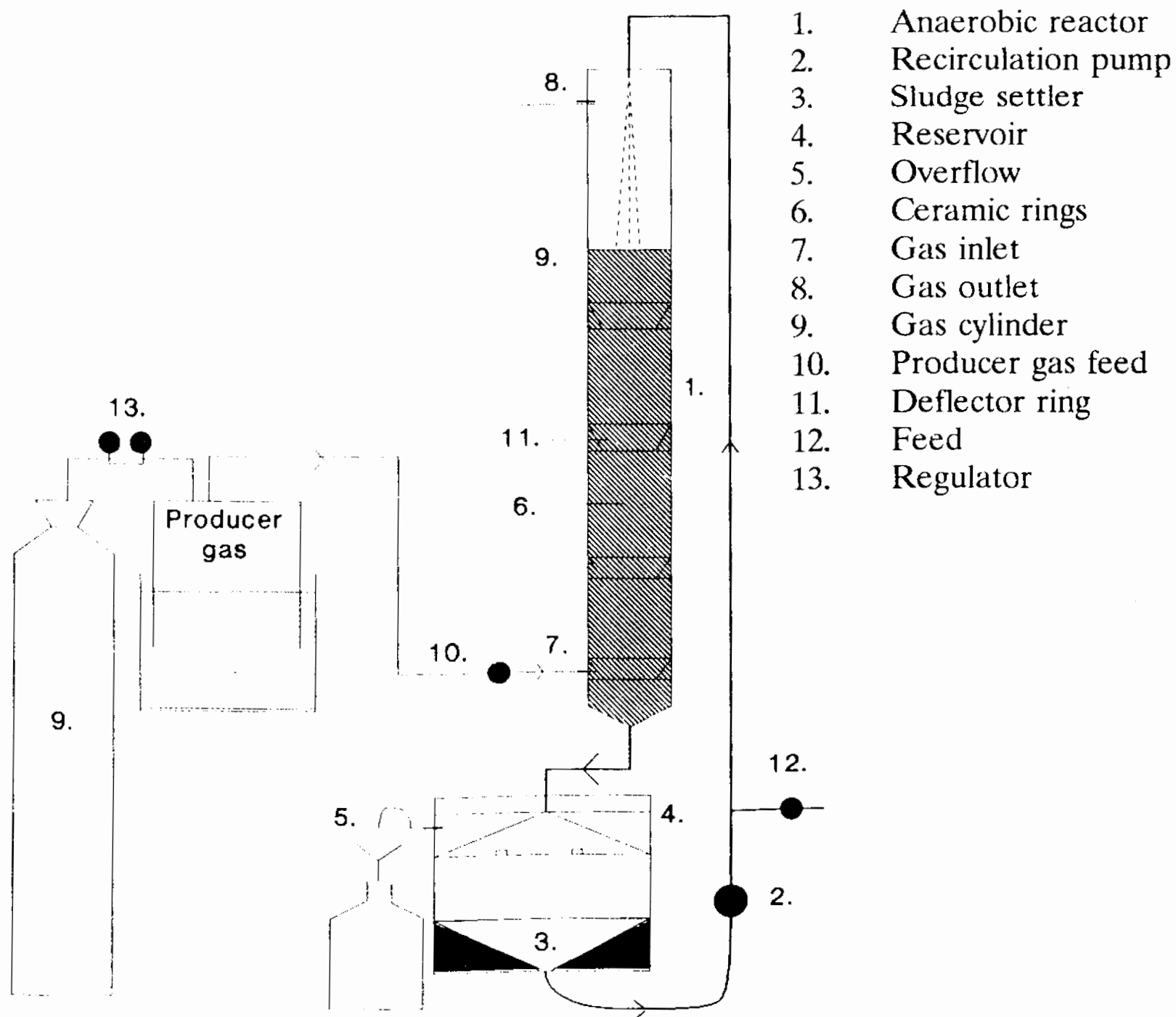


Figure 1: Schematic diagram of the laboratory-scale plant used for biological sulphate reduction.

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### Analytical

The parameters: pH, sulphate and alkalinity were monitored daily, while COD and volatile suspended solids (VSS) content were monitored weekly. VSS determinations were carried out by calculating the mass difference per unit volume after heating the medium samples to 105 and 500 °C respectively. Determinations of sulphate, alkalinity and pH were carried out according to analytical procedures as described in Standard Methods<sup>(9)</sup>. Gases were analyzed by gas chromatograph using a POROPAK column. The temperature of the column, injection port and TCD detector were 35, 250 and 150 °C respectively.

## RESULTS AND DISCUSSION

### Reactions

The results pertaining to the difference in gas composition before and after the anaerobic step are shown in Table 2 and a summary of the mean values is depicted graphically in Figure 2. Also shown in Table 2, is the gas composition after pure CO was dosed.

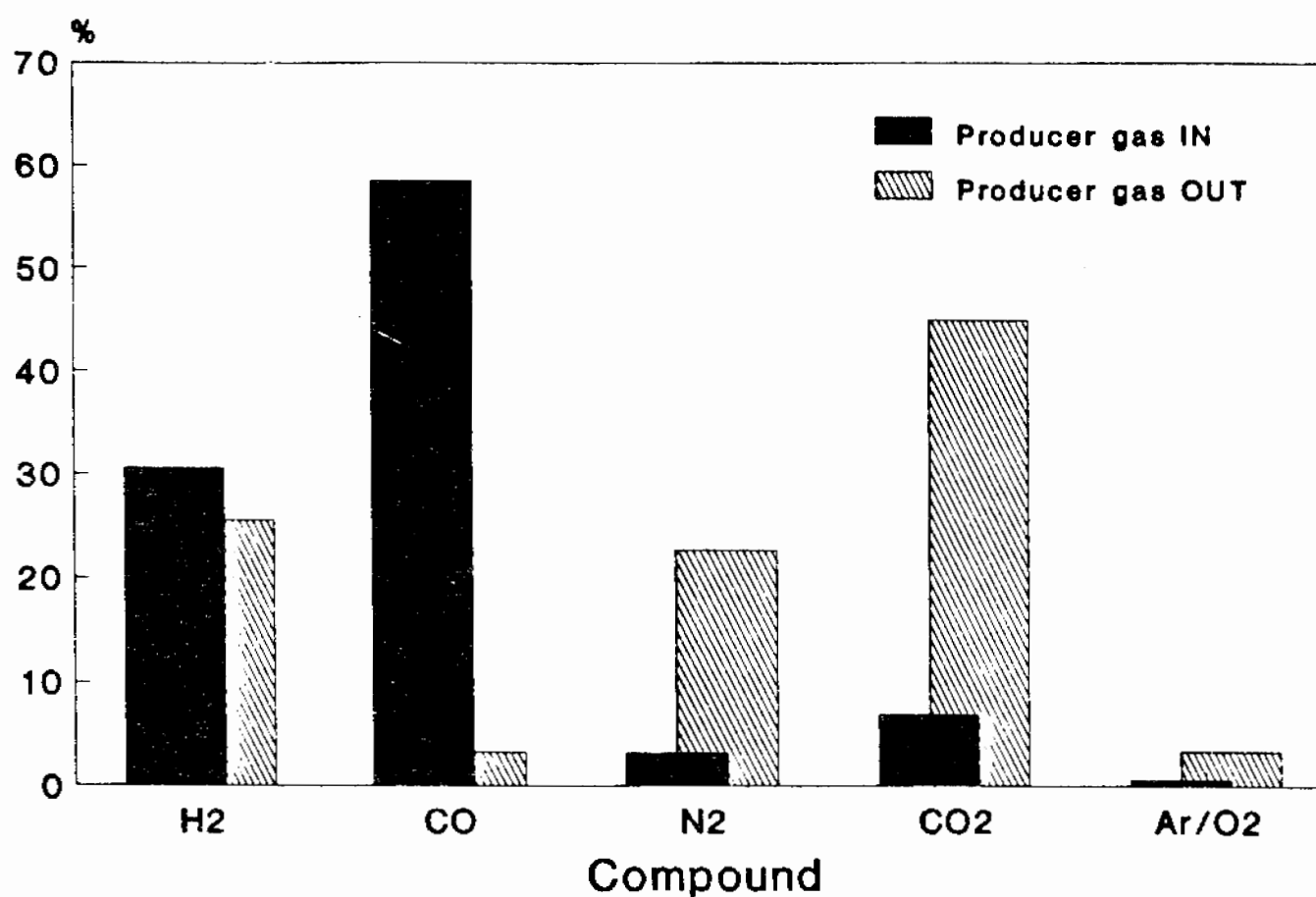


Figure 2: Producer gas composition before and after the anaerobic step.

The three main biological reactions occurring in the anaerobic reactor are:

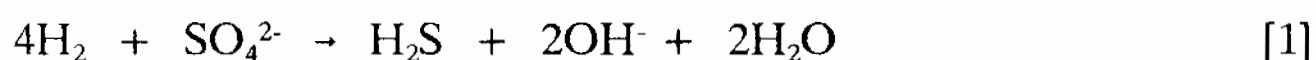
- \* The conversion of carbon monoxide and water to hydrogen and carbon dioxide
- \* Sulphate reduction with hydrogen as energy source
- \* Photosynthetic sulphur production from hydrogen sulphide.

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Table 2: Composition of the Producer Gas (PG) and CO before and after the anaerobic step.

Compound	H <sub>2</sub> (%)			CO (%)			N <sub>2</sub> (%)			CO <sub>2</sub> (%)		
	PG IN	31.8	30.6	29.5	59.3	56.2	60.1	2.3	5.2	2.1	6.2	6.5
PG OUT	23.8	23.9	28.9	3.2	3.8	3.0	25.8	17.0	25.3	41.8	53.1	40.2
CO IN	0			99.7			0.0			0		
CO OUT	Not detectable			3.0			22.8			>65		

The three reactions are represented by equations [1] to [3]:



It was surprising to see only a small decrease in the H<sub>2</sub> concentration since according to the literature, H<sub>2</sub> is supposed to be the primary energy source. The reason for this phenomenon as well as the sharp decrease in the CO concentration, can be attributed to the symbiotic lifestyle of sulphate-reducing bacteria and bacteria responsible for conversion of CO to H<sub>2</sub> as shown by equation [3]. Organisms that could be responsible for this reaction are *Rhodospseudomonas gelatinosa*<sup>(10,11)</sup> which belong to the group of purple non-sulphur bacteria.

In order to simulate conditions under which a fullscale plant will be operated, the reactor was run continuously for most of the time. Results pertaining to sulphate reduction are given in Figure 3.

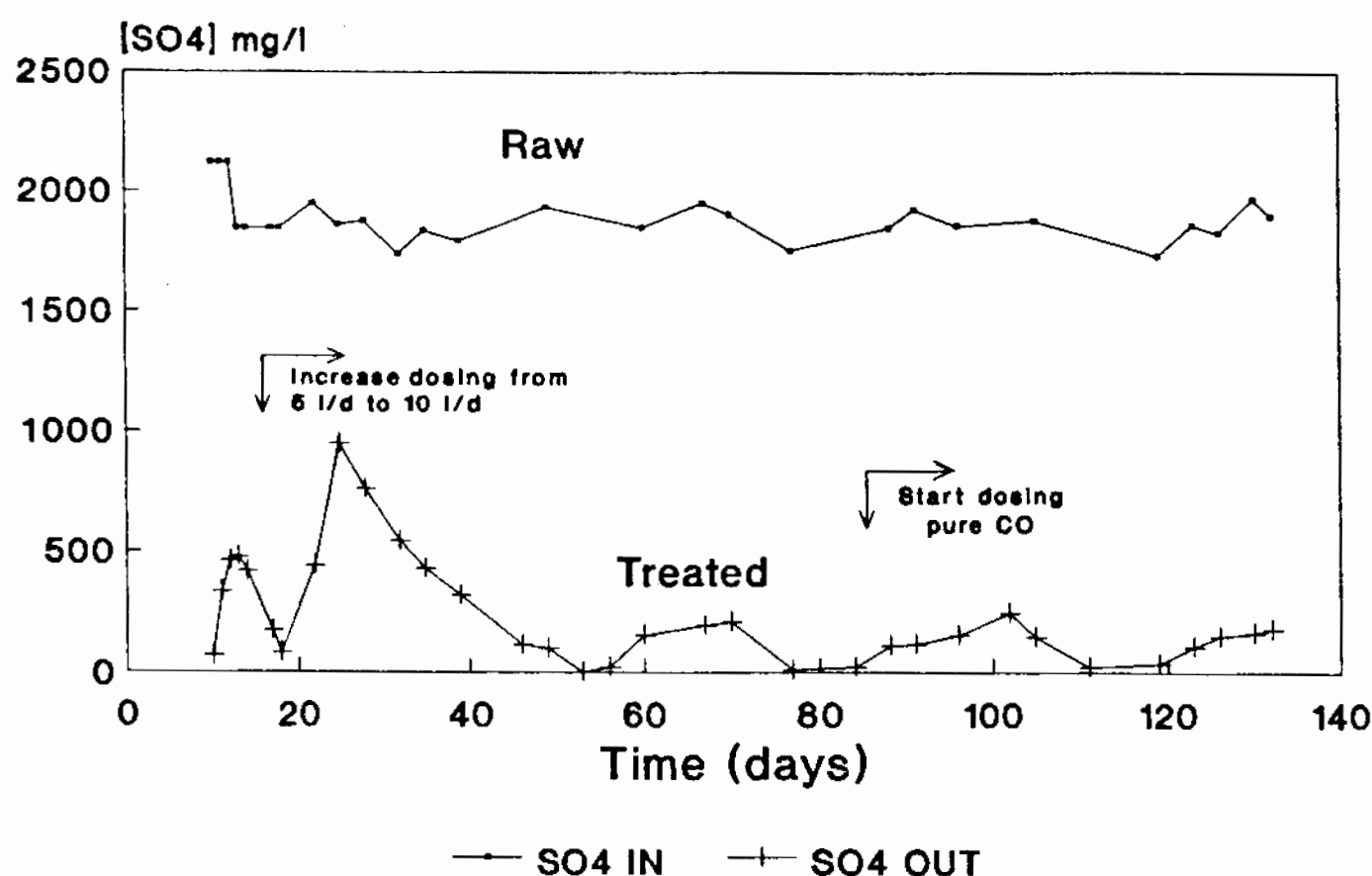


Figure 3: Temporal variation of sulphate concentration during anaerobic treatment in the trickling filter.

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Eighteen days after start-up, the liquid feed-rate was increased from 5 l/d to 10 l/d. It was possible to achieve stable conditions rapidly after start-up because the inoculum was obtained from acclimatized biomass from an existing laboratory unit. After 85 days the producer gas was replaced with pure carbon monoxide for 17 days to confirm our hypothesis of the symbiotic bacterial relationships previously discussed. Sulphate reduction was only very slightly affected by this change. Continuous sulphate reduction from 1 900 mg/l to below 200 mg/l was achieved throughout the duration of the project.

Underground acid minewater typically contains sulphuric acid and ferric sulphate in solution. The lime dosage required is therefore approximately equal to the sulphate content of the water. From stoichiometric considerations, it can be calculated that 1 465 mg/l of lime is required to neutralize acid mine water with a sulphate content of 1 900 mg/l. In the biological sulphate process, calcium carbonate can be produced internally, as shown by the increase in alkalinity of the treated water in Figure 4.

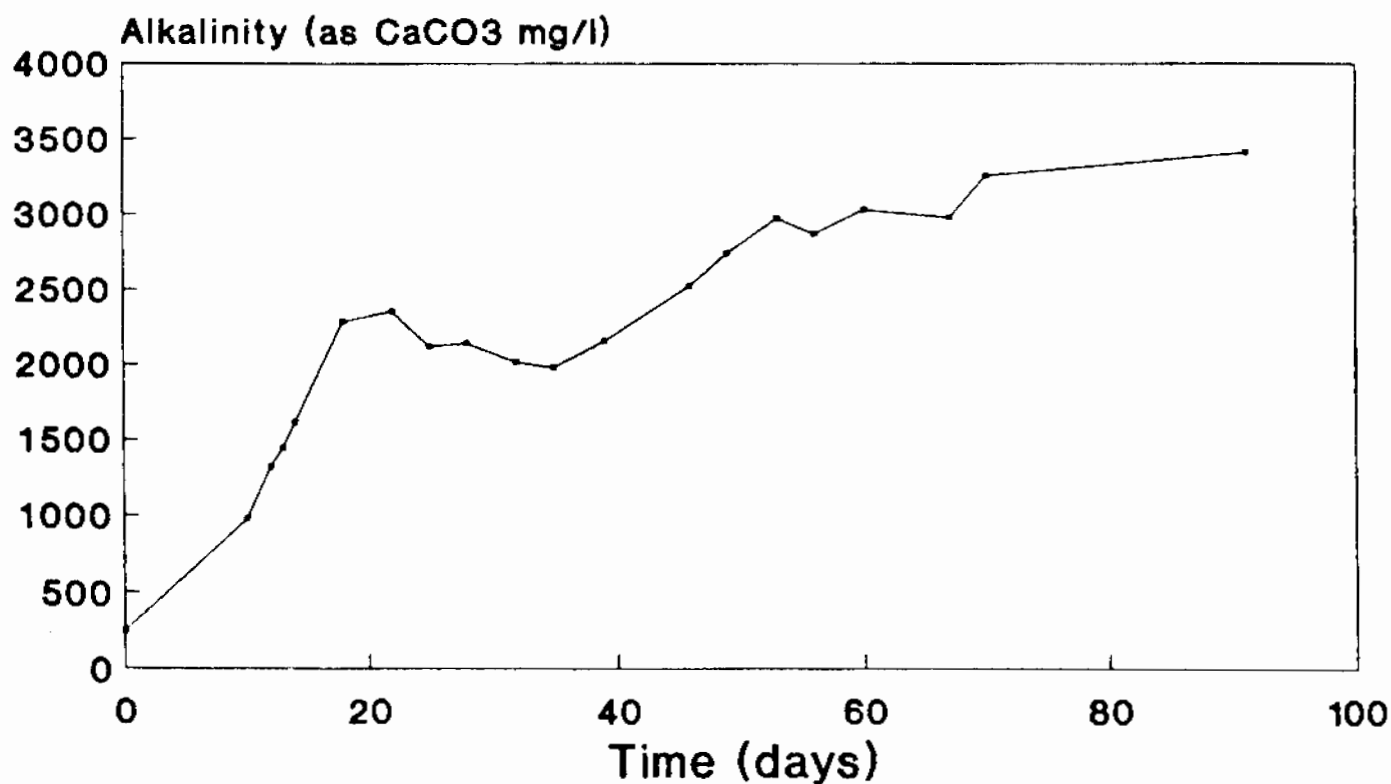


Figure 4: Alkalinity increase in the treated effluent as a function of time.

The alkalinity produced can be ascribed to equation [1]. The hydroxide ions formed were neutralized by the excess CO<sub>2</sub> present to produce bicarbonate (Equation [4]).



### H<sub>2</sub>S behaviour

Less sulphide was detected in the effluent than expected from the stoichiometric amount of sulphate reduced. Only 573 mg/l H<sub>2</sub>S (as SO<sub>4</sub>) was present in the effluent while 1 900 mg/l sulphate had been reduced. This can be explained as follows:

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- \* A fraction of the sulphide was stripped off automatically as a result of the low solubility of  $H_2S$  gas in solution
- \* Part of the sulphide content was converted to elemental sulphur due to the activity of photosynthetic sulphur oxidizing bacteria as shown by equation 2.

### Kinetics

In order to visualize the kinetics of sulphate reduction involved, a batch test was performed as described under Experimental. The results are summarized graphically in Figure 5. From reactions [1] and [4] it can be calculated that 1,04 g alkalinity is produced theoretically per 1 g sulphate reduced. This value compares favourably with the value of 1,004 which was determined experimentally from the batch experiment.

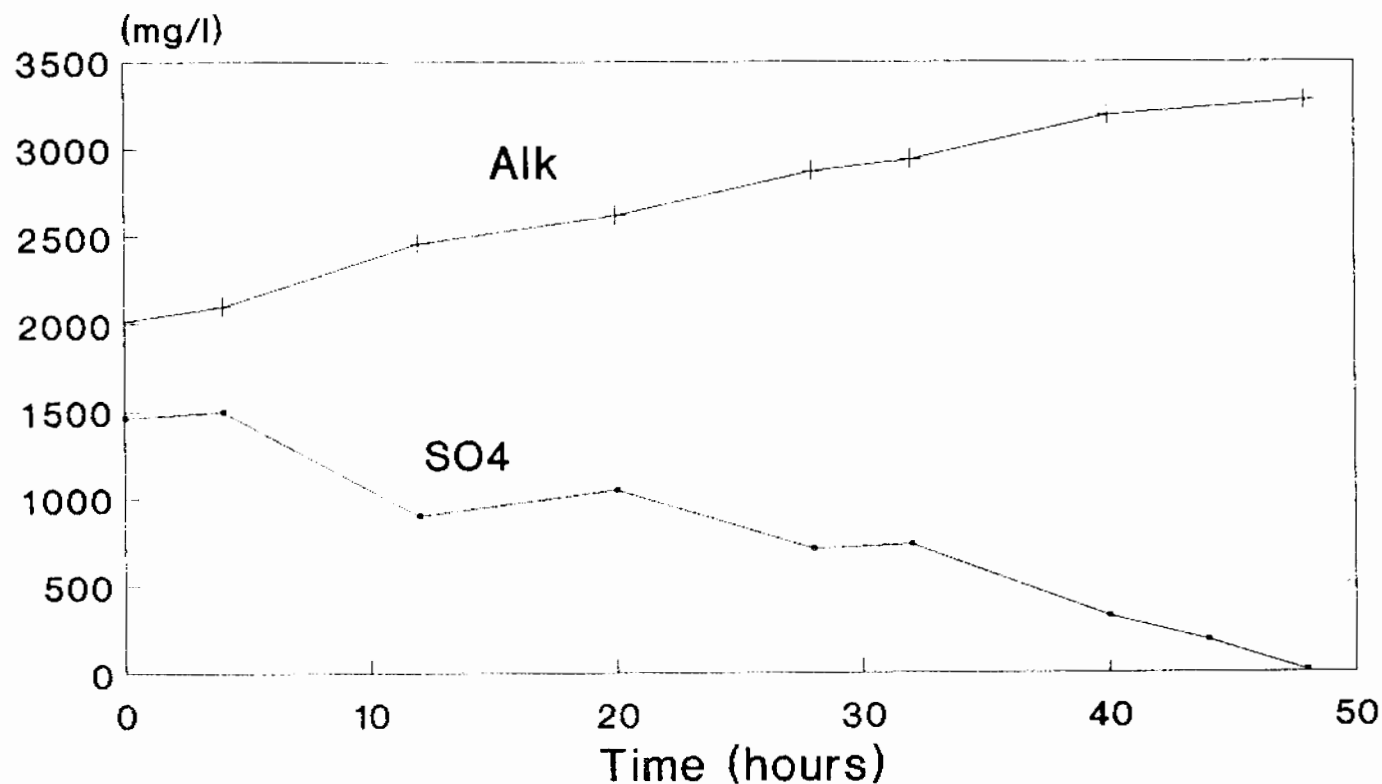


Figure 5: Sulphate reduction and alkalinity production as a function of time under batch conditions.

The reaction rate of sulphate reduction is influenced by, inter alia, the hydrogen, sulphate and biomass concentrations. The VSS value of 3.675 g/l was determined as described under Experimental, and this figure was used to calculate the specific and contact sulphate reduction rates at a producer gas feed rate of 20 ml/min.

(i) Continuous studies :

[SO <sub>4</sub> ] removed	=	1.7 g/l
Feedrate (q)	=	10 l/d
Active volume (V)	=	20 l
Contact time	=	2 days

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$$\begin{aligned} \text{SO}_4 \text{ reduction rate} &= [\text{SO}_4^-] \times q/V \\ &= 0.85 \text{ g SO}_4/(\ell.d) \\ \\ \text{Specific SO}_4 \text{ reduction rate} &= 0.85 \text{ g SO}_4/(\ell.d) \\ &= 0.231 \text{ g SO}_4/(\text{g VSS}.d) \end{aligned}$$

(ii) Batch study :

$$\begin{aligned} \text{SO}_4 \text{ reduction rate} &= 1.5 \text{ g SO}_4/\ell \text{ removed in 48 h} \\ &= 0.75 \text{ g SO}_4/(\ell.d) \end{aligned}$$

These results correspond with those of other researchers as shown in Table 3.

Table 3: Summary of biological sulphate reduction rates obtained by various researchers (Adapted from Maree *et al.*, 1991)

Reference	Reduction rate		Temp °C	Carbon source
	$\frac{\text{g SO}_4}{\text{g VSS}.d}$	$\frac{\text{g SO}_4}{\ell.d}$		
12	-	4.50	35	Primary sewage sludge
13	0.11	6.40	24	molasses; packed bed reactor
3	0.20	0.80	27	molasses; complete mix reactor
14	0.03	-	-	acetic acid
15	-	0.24	35	rubber waste effluent
16	-	10.20	35	cheese whey with stripping
16	-	1.50	-	cheese whey without stripping
17	0.11	1.20	35	waste activated sludge
18	-	2.79	-	sewage sludge
19	0.08	2.40	35	primary sewage sludge
20	0.15	-	35	primary sewage sludge
21	0.05	1.36	25	fermented molasses; packed bed

### CONCLUSIONS

- \* During anaerobic treatment of sulphate rich water in a trickling filter, influent sulphate was reduced from 1 900 mg/ℓ to less than 200 mg/ℓ .
- \* The alkalinity produced in the process resulted in the treatment of acidic effluents without pre-neutralization.
- \* It is concluded that both producer gas and pure carbon monoxide are viable energy sources for the biological sulphate process, which can be used for the treatment of acidic mine effluents.



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- \* No additional post-treatment scrubbing steps are needed as was the case with previous biological processes.

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