

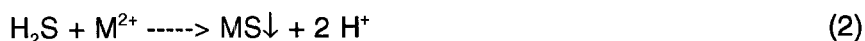
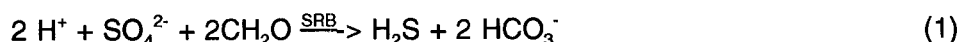
IN SITU TREATMENT OF ACID MINE DRAINAGE BY SULPHATE REDUCING BACTERIA IN OPEN PITS: SCALE-UP EXPERIENCES¹

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Abstract: Over the past three years, Noranda Technology Centre (NTC) has evaluated the feasibility of using sulphate-reducing bacteria (SRB) to treat acid mine drainage (AMD), in a pit or an underground mine. Following an initial study conducted in batch flasks that determined major process parameters (residence time, temperature effect, nutrients and substrate requirements), a conceptual flow sheet was developed. In order to confirm the concept for full-scale application, the present study included screening and selection of inexpensive nutrients and larger scale tests in a 280-L drum, a 160-L tall column and 5-L continuous reactors. The start-up conditions examined with drum tests included sediment formation (reactor inoculation methods and nutrient preconditioning), influent location and final effluent quality (e.g. metals, pH, BOD, COD, odor, etc.). The tall-column test (5 m) was conducted to define the reaction zone and the extension of H₂S dispersion in the pit. Nutrient utilization and S balance were estimated by monitoring off gases in 5-L continuous reactors as well as effluent quality. Due to the low SO₄ conversion rate found at low temperatures (e.g. 4 to 10°C), which is found in the bottom of the pit, the amount of nutrients required to treat moderate strength AMD with a high flow rate was determined to be very high, causing technical and economical difficulties in full-scale application of the process. The process was recommended for low loading situations.

Introduction

In general, sulphide precipitation offers some advantages over conventional hydroxide precipitation which is more commonly used for treating acid mine drainage (Bhattacharryya *et al.* 1981; Kuyucak *et al.* 1991). These advantages include a high degree of metal removal (e.g. Cu, Cd, Zn, Pb, As, Hg, Ni and Fe) at low pH (pH 3 to 6) and improved sludge characteristics, i.e. chemically more stable, denser and less voluminous sludges (Peters and Ferg 1987). However, the high cost of sulphides discourages their use in treating AMD. Several researchers have proposed the use of sulphate reducing bacteria to obtain inexpensive sulphide reagents, due to their ability to convert sulphate contained in AMD to H₂S (Hammack and Edenborn 1992). During the process, SRB utilize a carbon source and generate alkalinity (Kuyucak *et al.* 1991). The hydrogen sulphide generated reacts with metals to form insoluble metal complexes. The organic carbon is converted to carbonates. The reactions are shown below:



CH₂O represents the organic compounds used as nutrients and M represents metal ions.

¹Paper presented at the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29, 1994

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Several investigators have been exploring SRB processes as a possible basis for the development of cost-effective treatment for wastewaters, which have high acidity and contain sulphate and metal ions. Possibilities include passive systems for treating mine effluents (e.g. constructed wetlands, biotrenches and open pits) and reactor applications for treating metallurgical process effluents (Hedin and Nairn 1992; Kalin 1992; Wildeman 1992; Barnes *et al.* 1991; Béchard *et al.* 1991; Maree and Strydom 1987).

The results of earlier work (Phase I) at NTC, in which pure chemicals were used as nutrients, indicated that open pit application of the process would be technically feasible if the open pit could be well manipulated to be used as a large reactor (Kuyucak *et al.* 1991). The process economics would be basically dependent on the cost of nutrients and the degree of achieved treatment. Further research (Phase II) has, therefore, been undertaken to investigate alternative/inexpensive nutrient sources for SRB, and the parameters required for a successful process start-up and scale-up for field demonstration of the process. In addition, the technical and economical feasibility of the process were assessed and the key questions to be addressed were defined. The results of Phase II studies are discussed below.

Materials & Methods

Nutrients and Water. Selection of alternative nutrient sources was performed on two main groups of waste materials: cellulosic wastes and organic wastes. The cellulosic wastes consisted of: wood pulp, sawdust, bark, maple leaves, oat straw, fuel peat and horticultural peat. The organic wastes included: cow manure, distillers' dried grains, brewers' dried grains, dehydrated whey, molasses and starch. Combination of wood pulp, manure and brewers' dried grains was retained for all other tests. In control tests to assess the ability of the nutrient types to support SRB activity, chemical nutrients such as lactic acid (15 g/L), $(\text{NH}_4)_2\text{SO}_4$ (1.8 g/L) and K_2HPO_4 (0.35 g/L) were used. Moderate strength AMD (F-Group) was used for the tests (Kuyucak & St-Germain, 1994).

Substrate. In nutrient selection experiments, the substrate consisted of limestone and sand, in a mixture of 1:1. In scale-up parameters tests, the substrate was simply limestone. Materials examined as substrate alternatives in 2-L batch tests were: limestone, phosphate, limestone and sulphidic rocks in a ratio of 1:1, sulphidic rocks and wood chips. In another batch test, the position of nutrients vs substrate and its effect on the treatment efficiency was addressed. Mainly, three distributions were evaluated: nutrients on top of substrate, mixed and nutrients sandwiched between 2 layers of substrate.

SRB Inoculum. SRB enriched from mine sediments, as described earlier (Kuyucak *et al.* 1991), were used in all studies. The inoculum was 1% of the working water volume. In one batch test, which studied the effect of inoculum size on treatment efficiency, different inoculum proportions were added: 0.1, 1, 3, 5 and 10%. In parallel, two different inoculation techniques, i.e. pouring vs injection, were looked at. In this experiment only 0.1, 1 and 10% inoculum were studied.

Temperature. Effect of temperature on the process was addressed in two tests: at start-up, in 2-L batch tests where reactors were kept at either 20, 10 or 4°C, and 5-L continuous kinetic tests where reactors were kept at room temperature and 10°C.

Procedures

Different types of reactors and experimental modes were used in each study. All batch studies, including nutrient experiments and start-up parameters (solid substrate, inoculation technique and start-up temperature), were performed in 2-L reactors, usually for a 35-day period. Larger size reactors (e.g. 5-L, 280-L drum and a 5-m high, 160-L tall column) were used in continuous mode to investigate process kinetics and major parameters for process scale-up. All tests were run in duplicates. The pH was adjusted to 4.5-5, using $\text{Ca}(\text{OH})_2$. In general, reactors consisted in a gravel (limestone) sediment inoculated with SRB (1%

v/v) on which the nutrient was layered at the bottom of each reactor. The reactor, after filled with AMD, was left until the onset of SRB activities was confirmed by an increase in pH, decrease in ORP, dark color and distinct odor of hydrogen sulphide. Once the system was established, fresh AMD was added in a semi-continuous or continuous mode as required. Details of procedures and analytical methods are described elsewhere (Kuyucak and St-Germain, 1993).

Results

Nutrient Selection

Initial experiments involved investigations of cellulosic wastes as sole nutrients for SRB. Results indicated that cellulosic wastes alone would not sustain SRB growth. Therefore, use of a mixture of wood and organic wastes was considered. Subsequently, organic and cellulosic wastes were analyzed for their C, N, and P content and were mixed with each other in order to obtain optimum C:N:P ratio of 110:7:1, which would support high SRB activity (Gerhardt 1981). Several combinations of cellulosic and organic waste materials were examined.

The mixture of wood pulp, manure and brewers' dried grain exhibited the closest results to those obtained from the control tests containing lactic acid, ammonium sulphate, and potassium biphosphate salts as nutrients (Figure 1).

Process Parameters Investigated for Start-up

The optimal conditions required for a successful process start-up in the pit were investigated in conjunction with the use of natural nutrients (wood pulp, manure and brewers' dried grains). The parameters examined were: type of materials to be used and ways of preparing the sediment layer; need for SRB inoculum and the manner of addition; and effect of temperature and the possibility of acclimatization, as described by Ahonen and Tuovinen (1989).

Type of Sediment and Sediment Layer Preparation.

Phosphate rocks and limestone gravel proved to be preferable to wood chips or sulphidic rocks, but the latter can be used. When limestone was mixed with sulphidic rocks, the process was significantly improved. When wood chips and sulphidic rocks were used alone, the increase in pH was delayed by 16-18 days. However, as time went by, indicating that a wide range of materials, particularly with a large surface area, proper permeability, and buffering capacity can be used to form the sediment layer; the process is not limited by the type of material.

Effect of Inoculum Proportions and Inoculation Method. SRB inoculation would be essential to obtain positive measurable differences in process parameters in a reasonable time frame. Based on SO_4 removal and ORP results, the optimum SRB inoculum is 1% and injection of the SRB inoculum is better than pouring it.

Effect of Start-up Temperature. Only the tests initiated and performed at room temperature showed SRB activity after 42 days, as observed by relatively high SO_4 removal, as well as significant metal removal, as

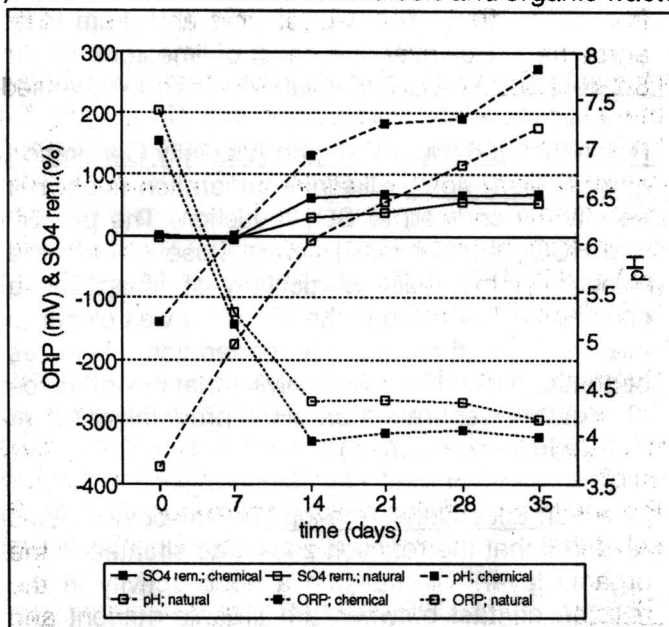


Figure 1 SO_4 and Zn removal and pH increase with the use of the mixture of woodpulp, brewers' dried grain and manure vs. lactic acid, ammonium sulphate and potassium biphosphate.

compared with results from 10 and 4°C incubation. Experimental results showed that start-up temperature was very important, as well as the incubation temperature of the inoculum, in facilitating the process start-up.

Investigations of Parameters for Process Scale-up (5-L Reactors, Drum and Tall Column Tests)

Rate of Sulfate Reduction and Effect of Temperature. The results showed that there is a relationship between rates of sulphate reduction, metal removal and dissolved organic carbon present in the system. Alkalinity generation could not be directly coupled to SO_4 -reduction, since in some cases no increase in pH was observed with the increase in net SO_4 removal. At steady state, SO_4 removal rates reached about 300 mmol/m³/d for a retention time of 280 days in the drum or 61 days in the nutrient bed. Only under reduced conditions were all metals, except Mn, removed to very low levels indicating S^{2-} precipitation. The total amount (mol) of SO_4 reduced was in excess of total amount (mol) of metals removed.

There was a decrease in SO_4 reduction rate of 43% reduction when the temperature decreased from 20 to 10°C. The total organic carbon (TOC) concentration was reduced by half by a decrease in temperature from 20 to 10°C. The 5-L reactors and drum test results with regard to sulphate reduction rates were in agreement. However, the effect of limestone on the overall process performance was more pronounced in 5-L reactors since AMD relatively uniformly passed through the gravel layer in those reactors.

Relationship Between S^{2-} and Alkalinity Generation and pH Behaviour. Alkalinity generation might not be directly coupled to SO_4 reduction. The pH, S^{2-} and HCO_3^- concentrations were closely monitored throughout the tests, particularly at steady state conditions. The trend in the pH curve was closer to the trend in the alkalinity generation curve as opposed to the S^{2-} curve, implying that the influence of alkalinity generation on pH is predominant over SO_4 reduction (Figure 2).

Reaction Zone Determination. The tall-column tests revealed that the reaction zone was situated in the organic layer. To maintain a good activity in the reactor, contact between the organic nutrient and water to be treated was required. Resuspension of the nutrient bed (Kuyucak & St-Germain, 1993), which also simulates turnover in pits, resulted in improved metal removal and homogeneous distribution of bacteria in the nutrient bed.

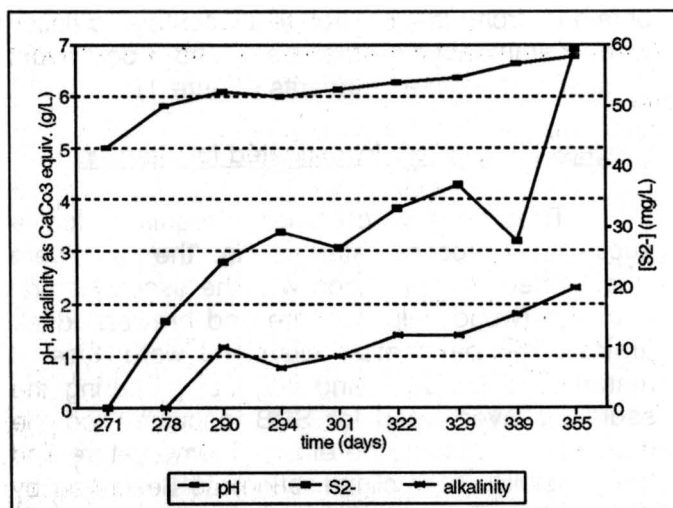


Figure 2 The relationship between pH, alkalinity and S^{2-} generation

Importance of Surface Area to Volume Ratio. The results showed that to get a true representation of the SO_4 reduction rate, retention time in the bed volume must be taken into consideration. However, when comparing drum with tall column tests, the maximal use of the nutrients can only be ensured by the presence of a large surface area (provides better contact for nutrients bacteria and AMD). In a small area and high depth case, uniform flow distribution within the nutrient bed cannot be maintained and the process efficiency declines.

Effect of Treatment on Water Quality. The effluent quality obtained from the SRB process for 14 months is summarized in Table 1. The concentration of Al, Fe and Zn fluctuated between non-detectable by ICP to 10-20 mg/L, depending on the conditions. Under oxidized conditions, the system would release Zn, Fe and Al. In particular, the Zn concentration follows the SO_4 reducing activity very closely. Mn removal was always poor. As, Cd and Cu were reduced to undetectable levels under all circumstances.

Table 1: Metal and sulphate concentrations in the effluent taken from the drum (operated for 14 months)

Parameter (mg/L)	Initial AMD (average)	Quality of effluent at different time intervals (days)										
		35	66	96	125	159	226	245	259	308	370	431
pH	2.5	6.8	6.6	6.6	6.4	6.2	5.2	4.8	5.4	6.3	6.8	6.4
Al	173	0.44	0.18	0.3	0.36	0.37	1.1	1.8	nd	nd	0.45	0.51
As	1.0	nd	0.09	nd	nd	nd	nd	nd	nd	nd	nd	nd
Cd	1.5	nd	nd	nd	nd	nd	0.05	0.04	0.04	0.04	nd	nd
Cu	47	nd	nd	nd	0.04	0.04	0.17	0.072	0.05	nd	nd	nd
Fe	160	0.74	0.19	0.69	0.76	4.77	2.66	8.99	1.12	0.19	0.54	0.13
SO ₄	4000	1682	1721	2837	3720	3360	3450	2989	2989	2490	2524	2460
Mn	38	1.11	6.99	13.5	21.5	23.6	21.1	25.3	26.0	24.3	21.8	19.5
Zn	350	0.38	nd	11.4	1.44	1.33	12.8	0.01	18	nd	0.27	nd

Organic indices such as TSS, VSS, BOD, COD, TOC, TKN and TP were also analyzed as described in Standard Methods (APHA, AWWA, WPCF. 1989) for the final effluent (Table 2). The comparison of results of the filtered vs, unfiltered samples for a few heavy metal ions showed that for all metals except Fe, the difference was not significant implying that metals are not in the colloidal form in the effluent and that additional filtration will not be required in full-scale applications.

Table 2: Effluent Quality in Terms of Organic Parameters

Time of sampling (days)	Organic Parameter as Concentration (mg/L)						
	TSS	VSS	BOD	COD	TOC	TKN	TP
257 ¹	156	35	30	79	27.2	28.1	< 0.05
319 ²	80	47	84	260	123	26	0.12

¹ quality of water before the addition of fresh nutrients

² quality of water after the addition of fresh nutrients

Effect of Influent Addition Method. The use of a baffle to introduce AMD over the sediment resulted in constant fluctuations in pH, with the general trend decreasing in the long-term. However, the baffle concept can be used, particularly on a pulsed flow. Adding influent through a tube (subsurface flow) in the sediment seemed to favor a more constant trend from day to day implying that better contact was provided between the influent, the nutrients and SRB.

Nutrient Consumption Rate. The C (available in the nutrient) utilized for the amount of sulphate reduced was computed per day using eq. 1. The theoretical nutrient consumption rate for the first 215 days at 20°C was 0.07%/d. Later, it decreased and stabilized around 0.05%/d. However, the actual value may be higher.

Composition of Off-Gases. The qualitative analysis of gases produced at 20°C showed that the gas was composed of 1.5% CO₂ and 98.5% N₂/O₂ on average. Minor amount of CH₄ (e.g. 0.023%) and no H₂S was detected. When the reactor was transferred at 10°C, CH₄ stopped being generated, indicating that activity

of methanogens was disturbed. The switch from batch to continuous mode resulted in an increasing trend in CO_2 and CH_4 concentrations and an inversely decreasing trend for N_2/O_2 content.

Discussion

General Concept. The increase in alkalinity and removal of metals from AMD with the SRB process are the result of several chemical and biological reactions. Synergism between three groups of microorganisms (acidogens, methanogens and sulphate reducers) and anaerobic conditions are essential for biochemically converting organic materials to organic acids (Tuttle *et al.* 1969; Westrich and Berner 1984; Holder *et al.* 1984; Maree and Strydom 1987; Kuhl and Jorgensen 1992; Scheeren *et al.* 1992). In addition to anaerobic and reduced conditions, oxygen may also be required to break down complex organics and oxidize CH_4 formed in the system (Morel 1983). The incorporation of additional limestone (even gypsum) into the reactors was suggested to boost the rate of alkalinity generation by buffering influent acidity, thereby allowing sulphate reduction to occur uninhibited at higher influent acidity loads (Hedin *et al.* 1991; Dvorak *et al.*, 1991). At low temperatures, the rates of chemical and biochemical reactions are reduced, resulting in less alkalinity and H_2S generation. The cellulose decomposers (methanogens) are mainly mesophilic microorganisms and, consequently, are more sensitive to low temperatures than SRB.

Critical Parameters at Process Start-up and During Operation. At process start-up, it is necessary to establish a correct start-up procedure (Scheeren *et al.* 1992; Wildeman 1992; Dvorak *et al.* 1991). The parameters considered to be important at start-up are: pH and reducing conditions; flow rate and composition of the influent, sufficient nutrients (e.g. C, N, P and SO_4), good contact of AMD with substrate and temperature. Scheeren *et al.*, (1992) stated that high pH (>6) and sufficient nutrients have to be maintained at start-up; however, as soon as methanogenic activity is detected (via methane gas production), the pH and dosage of phosphorous can be reduced. The concentration of an active microcosm is another critical factor. Since the sulphate reduction, CaCO_3 dissolution and sulphide movement processes are mainly diffusion controlled, the design should allow overcome of mass transfer limitations. Optimum amount of substrate and surface area, suitable substrate thickness and permeability and, even, gentle mixing should be considered (Morel 1983; Kuhl and Jorgensen 1992). Loading rates of acidity and metals are also critical. The actual temperature of the reservoir should be taken into account while designing the process.

Metals Removal. According to the literature (Hammack and Edenborn, 1992; Tarutis, *et al.*, 1992; Wildeman, 1992), copper, zinc, cadmium, iron, nickel and lead are retained within the reactors or wetlands as insoluble monosulphides, following their reaction with bacterially generated H_2S . Aluminum and manganese are hydrolyzed within the reactors and are retained as insoluble hydroxides or carbonates. Zinc may be retained in both carbonate and sulphide phases depending on pH and availability of S^{2-} species. Removal of some metals (e.g. Cu, Cd, As) to low levels under all circumstances was attributed to binding with organic matter and/or other oxide minerals (e.g. biocomplexation, bio-adsorption and precipitation).

Economics, Longevity. The economics of the process, which depend on the amount of nutrients required for the pit, have been calculated for a test case site and compared to the cost of conventional lime neutralization. The SO_4 reduction rate found (e.g. $0.3 \text{ molm}^{-3}\text{d}^{-1} \text{ H}_2\text{S}$ at 20°C or $0.15 \text{ molm}^{-3}\text{d}^{-1} \text{ H}_2\text{S}$ at 10°C) is in good agreement with the rates reported in the literature (Bolis *et al.*, 1991; Dvorak, *et al.*, 1992; CD&M, 1991). Assuming that AMD contains 20 mol/d metals, that a ton of substrate material costs \$40, and a **conservative rate** of H_2S generation ($0.15 \text{ molm}^{-3}\text{d}^{-1}$), the amount of substrate required and the total initial cost of the process have been estimated to be 40,000 tonnes and \$ 1.6 million (Canadian), respectively. For a pit with a surface area of 5000 m^2 , the substrate layer would be 8 m deep. Although the theoretical life expectancy of such a substrate layer is expected to be 120 y, the efficiency would be uncertain due to its thickness. In addition to the mass transfer limitations expected, temperature at the bottom of such a pit in Canada is $<10^\circ\text{C}$ all year round. **In conclusion**, loadings associated with open pits such as F-Group (Kuyucak and St-Germain, 1994) is too high for passive biological systems, but the concept is viable for

treating low load situations. Researchers need to search for easily degradable, yet inexpensive, nutrients and to overcome low temperature and mass transfer drawbacks.

Acknowledgements

The authors thank Mr. K. G. Wheeland for his support of this project and for his intensive review and comments provided during the course of the study.

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