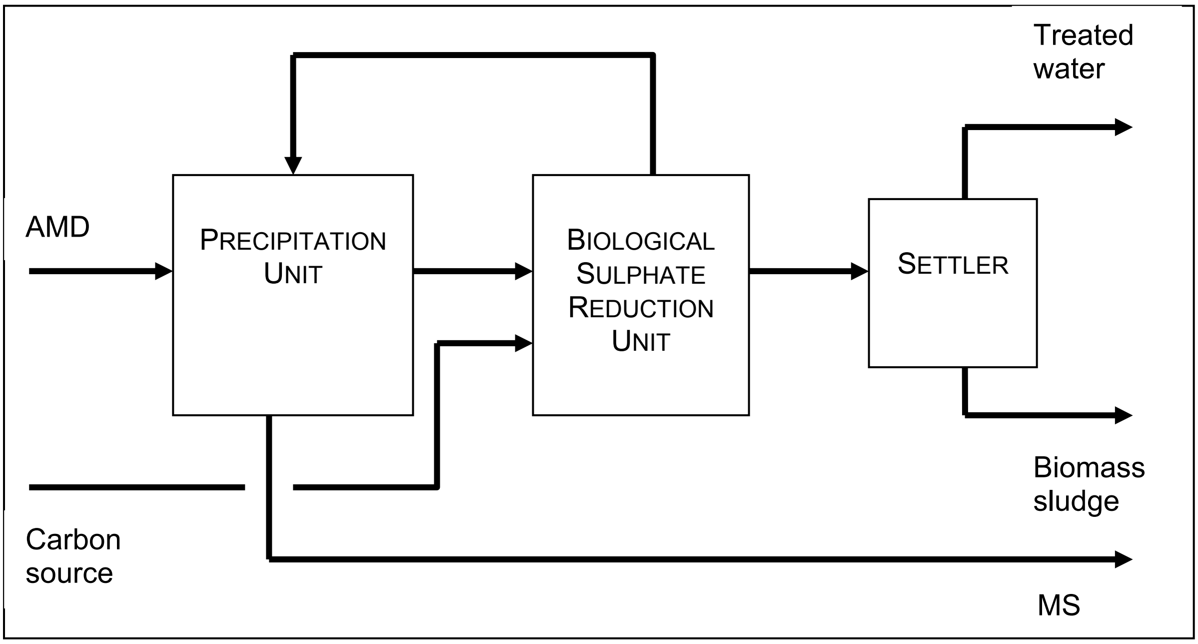
ABSTRACT

This project deals with an investigation into a remediation system based on the reduction of sulphate by sulphate reducing bacteria to treat water containing elevated concentrations of metals and sulphate typical in acid mine drainage (AMD). The process was investigated within the framework of the process flowsheet shown below, in which sulphide formed on biological sulphate reduction was recycled upstream to a precipitation reactor to precipitate metals from AMD as metal sulphides. In addition to metal sulphides, the products of the process were treated water, biological sludge and H_2S. Excess sulphide can then be converted into elemental sulphur or further metal sulphides (not included in present study).



The first aim of the project was based on the recognition of the need to extend the very simple systems studied previously to provide a deeper, more fundamental understanding of both the metal precipitation and the biological sulphate reduction processes through introducing more complexity into the operating environment, such as mixed metal precipitation, product inhibition and mixed microbial culture analysis.

The second aim was to improve the current simulation model for sulphate reduction by replacing the literature-based kinetics with kinetics measured in the laboratory in WRC project K5/1080.

The third aim was to carry out a process evaluation by generating an overall model of the biological treatment process. This would be used to investigate the viability of the process with respect to the carbon source and electron donor and to highlight bottlenecks in process application to guide future experimental work required.

Metal precipitation

- This aspect of the investigation showed that the thermodynamically based, commercial software packages used to predict metal speciation in aqueous solutions are not suitable tools to perform predictive modelling on metal precipitation from a complex stream under conditions where the system will not reach thermodynamic equilibrium.
- The copper sulphide system was extensively investigated and important differences between this and the original model system of nickel carbonate were identified. It was shown that the extremely insoluble nature of copper sulphide means that high global supersaturation must be avoided altogether if a reasonable precipitate is to be obtained. In addition, the formation of fines (a critical parameter for metal removal) must be avoided at the feed points as, unlike in the nickel carbonate system, these do not aggregate with time spent in the reactor. The sulphide to copper ratio is the most critical parameter affecting copper removal.
- The experimental studies showed that the precipitation of zinc from aqueous solution by a mixture containing sulphide and bicarbonate is dominated by the crystalline ZnS species. The iron and copper systems are characterised by the formation of amorphous metal sulphide precipitates and soluble metal polysulphide complexes. It is proposed that this phenomenon is related to sulphide species concentration, rather than total sulphide concentration, particularly in the case of copper.
- The use of anaerobic digester overflow resulted in effective copper precipitation over a wider range of metal to sulphide ratios than with synthetic solutions. This is attributed to the buffering effect of the soluble organic acids, which in turn affects the soluble sulphide speciation. While the use of digester overflow broadened the range over which significant iron precipitation occurred, the efficiency of iron precipitation did not exceed 75% under even the most favourable conditions. Efficient iron removal (>98%) was achieved in the synthetic system under a narrow range of conditions.
- It was recommended that pre-treatment of ferrous iron by oxidation be considered.
- The inability of the software packages to account for the formation of amorphous or colloidal precipitates, the absence of accurate thermodynamic data on some species and the fact that the predictions are only able to represent the system at thermodynamic

equilibrium, precluded the generation of an accurate model to predict both iron and copper precipitation in both the synthetic and biological systems.

Simulation of sulphate reduction

- This aspect of the investigation demonstrated that existing literature parameters are not applicable for simulation of sulphate reduction at high sulphate concentrations and with the carbon source in excess.
- Both the steady state and the dynamic simulations show that the measured kinetic parameters of Moosa et al. (2002, 2004) provide better predictions of the experimental data than literature data and thereby provide a contribution to the predictions required in estimating process performance and in reactor design.
- The temperature dependencies of the Moosa et al. (2004) parameters render them more applicable to a wider range of operating conditions.
- Sulphate inhibition plays a significant role in the accuracy of the dynamic prediction.
- H_2S inhibition has not been incorporated into the model, but is negligible under the conditions at which this data was collected;
- Application of the existing models to a steady state calculation for typical AMD conditions results in an underestimation in calculation of the reactor volume.
- The use of a reactor configuration supporting a long sludge retention time or high sludge age, such as the UASB reactor, is supported by the dynamic simulations.

Effect of sulphide on sulphate reduction

- This study found that, over the pH range of 6 to 7.5, the principal sulphide species inhibitory to the sulphate reducing bacteria is the undissociated H_2S. The maximum specific growth rate increased with increasing pH, owing to the changing speciation from H_2S to HS^- in the pH range of 6.0 to 7.5 studied. The operation of biological sulphate reduction reactors at pHs such that the presence of undissociated H_2S is minimised is thus recommended.
- At pH 7.8, the inhibition of sulphide with increasing concentration showed a decrease in the volumetric sulphate reduction rate with increasing sulphide addition to the feed stream at pH 7.8 over the concentration range 0 to 1.25 kg m^{-3}. The inhibition was observed through a decrease in the maximum specific growth rate and an increase in the death rate constant with increasing sulphide addition. Further the ratio of sulphate reduced to ethanol oxidised and of ethanol oxidised to acetate formed decreased with increasing inhibition. While the model based on the Contois equation could satisfactorily predict these observations for sulphide additions less than 1.0 kg m^{-3}, it failed to predict

observation at increased sulphide concentrations. The results suggest that a factor in addition to sulphide concentration and speciation requires consideration to complete the modelling satisfactorily. This may be the bioavailability of trace metals.

- Kinetic data for biological sulphate reduction using ethanol as carbon source and electron donor were gathered. These were described satisfactorily by the Contois-based model of Moosa et al. (2002). Further, the maximum specific growth rate obtained of 0.060 h^{-1} was similar to that obtained for the acetate system.
- Substrate inhibition was demonstrated at increased feed sulphate concentrations of 12.5 and 15.0 kg m^{-3}. While the latter led to reactor failure at a 10 day residence time of both the liquid and biomass fractions, the former illustrated inhibition through the onset of washout at a lower dilution rate, reduced sulphate conversion and a reduced volumetric sulphate reduction rate despite the increased sulphate loading rate. Hence, where necessary, recycle should be used to ensure feed sulphate concentrations to the biological sulphate reduction reactor are appropriate to avoid substrate inhibition.

Microbial speciation

By using the molecular technique described in this study, it was possible to detect different groups of SRB in the bioreactor across several genera. Using pure culture studies, the methodology used has been validated for the current system. The dominant genera were found to be *Desulfonema*, *Desulfobacteriaceae* and *Desulfobulbus*. *Desulfovibrionaceae* and *Desulfobacter* were the least dominant of the genera studied.

Preliminary studies suggest trends in dominant species with both changing carbon source (acetate vs ethanol) and changing sulphate concentration. On increasing the concentration of soluble sulphide added in continuous chemostat culture, a clear decrease in the prevalence of the *Desulfonema*, *Desulfobulbus* spp. and the *Desulfobacteriaceae* groups was shown. *Desulfobacter*, *Desulfotomaculum* and *Desulfovibrionaceae* were relatively unaffected by the range of sulphide concentration studied. Tools are thus in place to assist in the tailoring of microbial populations to provide increased resilience to process conditions and to overcome the negative impacts of process perturbation. The impact of microbial population dynamics on performance through process kinetics is the topic of ongoing study.

Using complex carbon sources as the electron donor

Review of the literature indicated that acidogenesis is affected by the presence of sulphide and metal ions. A limited pH range of 7.5 to 8.0 is proposed in which both acidogenesis and sulphidogenesis can operate satisfactorily, while methanogenesis is inhibited. Further, data on the effect of sulphate on acidogenesis is limited to sulphate concentrations of 4.0 kg m^{-3}

and less. Methanogenesis is inhibited in the presence of low sulphide concentrations. Hence, conditions for the optimisation of sulphidogenesis and acidogenesis with the concomitant inhibition of methanogenesis can be obtained; however, further data on impact of sulphate on acidogenesis at high sulphate concentrations will be valuable and is partially supplied by Ristow et al. (2004).

Factors governing the variable operating costs are dependent on the choice of carbon source. It was found that provision of a more complex carbon source (molasses) is cheaper than a simple carbon source (ethanol) while the disposal requirements for a complex carbon source are higher than for a simple carbon source. However, where use of the complex carbon source provides environmental burden reduction by avoiding its need for disposal, the assessment is changed. While a significant burden results on the use of primary sewage sludge (PSS), this can be offset against the reduced treatment required in the wastewater works providing a beneficial scenario. In order to assess PSS more fully, it is necessary to consider biomass retention within the anaerobic bioreactor, the use of a flocculating biomass system such as the UASB, enhanced dewatering of the biomass sludge and the potential need for subsequent treatment of the effluent water stream. It is recommended that these studies be undertaken.