SUMMARY

This project was initiated in order to provide a fundamental understanding of the mechanism and kinetics of the biological treatment of metal-sulfate-containing effluents such as acid mine drainage. It also has the objective of supporting process development investigations being carried out at other institutions, under Water Research Commission support. The results presented in this report cover the work outlined in the PhD thesis of S. Moosa and the MSc (Eng.) theses of N. E. Ristow and A. Knobel as well as the postdoctoral work of M. Nemati and M. R. Kosseva.

The conclusions of each investigation are summarised in detail at the end of each chapter, and Chapters 7 gives the overall conclusions and Chapter 8 the recommendations that have led to the further investigation being carried out in Project 1251.

The report covers four areas investigated in the project:

1. A review of the literature to define the state-of-the-art on the mechanism and kinetics of microbial sulfate reduction and provide rate equations for modelling bacterial sulfate reduction.
2. The development of two simulation models one using AQUASIM to predict the performance of the pilot plant for sludge hydrolysis and sulfate reduction developed by Rhodes University and the other a more general description of bacterial sulfate reduction.
3. Experimental investigations on the kinetics of bacterial sulfate reduction using, in one case, acetate and the other, ethanol.
4. Theoretical and experimental studies of metal precipitation.

The results of these areas of investigation can be summarised as follows:

1. The review of the literature provided a description of the pathway from complex organics through to sulfate reduction and methane formation. For most of the steps in these pathways, kinetic studies have been reported and rate equations and kinetic constants determined. However, in several of the steps the data was neither available nor applicable to the conditions applying in sulfate reduction. Rates of hydrolysis

were not well described and there was no published information on the effect of sulfate or sulfide and pH on the rates of hydrolysis. Through all the steps, the studies were aimed at anaerobic digestion and only included effects of sulfide inhibition at relatively low levels of sulfide. There is therefore the need to investigate the kinetics of acidogenesis, acetogenesis, and the kinetics of acetate utilising and hydrogen-utilising sulfate reducing bacteria at high concentrations of sulfate and sulfide. Investigation of the sulfate reducing bacteria at high sulfate loadings was initiated in this project. Further study of this as well as the other sub-processes will be investigated in WRC Project 1251.

2. In the development of the simulation models, it was decided to use published rate equations and kinetic parameters even though these were only available for low levels of sulfide inhibition. Two approaches were adopted in the modelling. Using the package AQUASIM developed for modelling wastewater treatment processes, a simulation model was developed for predicting the performance of the falling sludge bed bioreactor tested by Professor P. Rose of Rhodes University. This proved to be quite successful although the model could not be tested exhaustively due to the lack of steady state operating data from the pilot plant.

   The other simulation model, using a high level mathematical language, is more general and fundamental in nature, taking into account chemical and biological reactions as well as vapour-liquid equilibrium pertinent to the treatment systems. It was calibrated against steady state operating data published by Maree and co-workers. Neither simulation model was complete, and the work will be continued under 1251 both to refine and extend the model in terms of newly available information and to inform the experimental investigation.

3. Experimental investigations on the kinetics of bacterial sulfate reduction using acetate and using ethanol were carried out. The former was extensive based on chemostat culture in a well-mixed stirred tank. It investigated kinetics of sulfate reduction and bacterial growth as a function of sulfate loading (affected by both residence time and feed concentration) and temperature. The investigation using ethanol was only preliminary. Both showed that the kinetics are inhibited by sulfide and possibly by sulfate. For the case of the acetate-based sulfate reduction, the effect of sulfate concentration and temperature are reported and a rate equation describing the kinetics proposed.

4. Experimental precipitation studies showed that the pellet reactor is an appropriate technology for the precipitation of a metal hydroxy-carbonate salt from a synthetic nickel sulfate stream. The system produces no sludge, but rather, a dense precipitate, permitting easy solid-liquid separation and allowing reuse of the metal. The results suggest that fines are formed mostly by the spontaneous nucleation of solid phase in the liquid medium generated by a high supersaturation zone, often at the reactant inlet. The Patterson *et al.* (1977) solubility diagram can predict accurately the nickel conversion when two solid phases are taken into account: nickel hydroxide and nickel carbonate. The model is employed to determine the pH zone of the lowest soluble nickel concentration, i.e. the maximal conversion to solid nickel. The equilibrium model may not be used to predict removal efficiency, since it does not take into account fines formation. The kinetics of precipitation are fast, and the soluble species reach near equilibrium with the solid phase only after 20 centimetres of bed.

The recommendations of the investigations can be summarised as follows:

1. The possible inhibitory effect of high concentrations of sulfate *per se* on the sulfate reducing bacteria should be investigated

2. The literature review showed that while the kinetics of microorganisms involved in anaerobic digestion are available, there is very little kinetic information of the bacterial reduction of sulfate. In particular, little is reported on how the kinetics are affected by high concentrations of sulfide. It is recommended that this be thoroughly investigated.

3. The use of immobilisation to increase the concentration of sulfate reducing bacteria should be investigated.

4. The precipitation of iron carbonate and sulfide should be thoroughly investigated in the presence of sulfate reducing microorganisms.

5. The two simulation models are to be reconciled into a comprehensive modelling package including a kinetic description of all the microbial and physicochemical processes involved.

This will be undertaken in WRC Project 1251.