APPLICATION OF ELECTROCHEMICAL KINETICS TO ELUCIDATE THE LEACHING MECHANISM IN THE BIO-OXIDATION OF A SYNTHETIC NICKEL SULPHIDE

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I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Roberts

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Abstract

The importance of the direct and indirect mechanisms in the bacterial leaching of a synthetic nickel sulphide is investigated using an electrochemical leaching model. Sterile controls runs, in which only ferric leaching took place, are compared with runs in the presence of an active, adapted bacterial culture.

The direct mechanism occurs when bacteria attach to the sulphide mineral and catalyze the oxidation of the mineral, presumably with enzymes (biological catalysts). No evidence was found of the direct mechanism, in fact ferric leaching appeared to be inhibited as the bacterial presence increased due to growth. Considering evidence obtained by the fitting of the electrochemical model, it is tentatively suggested that leaching of the mineral is largely due to chemical ferric leaching, with the leaching role of bacteria restricted to re-oxidizing the resulting ferrous ions. Whether this is the case for other minerals remains to be established.

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CONTENTS Page

APPENDIX

List of Figures

Figure (page)

List of Figures (Continued...)

Figure (page)

List of Figures (Continued...)

Figure (page)

List of Figures (Continued...)

Figure (page)

List of Figures (Continued...)

Figure (page)

List of Figures (Continued...)

Figure (page)

List of Figures (Continued...)

Figure (page)

List of Tables

Table (page)

List of Tables (Continued...)

Table (page)

List of Tables (Continued...)

Table (page)

List of Tables (Continued..)

Table (page)

List of Tables (Continued...)

Table (page)

List of Tables (Continued...)

Table (page)

List of Tables (Continued...)

Table (page)

List of Tables (Continued...)

Table (page)

List of Symbols

Symbol	Quantity	Units
K	Equilibrium Constant	-
{i}	Activity of Species i	mol l^{-1}
$[i]_t$	Total Concentration of i	mol l^{-1}
[i]	Concentration of i	mol l^{-1}
γ_i	Activity Coefficient	-
A	Constant	$l^{1/2}mol^{-1/2}$
B	Constant	l angstroms^{-1}mol
A_0	Ion Size Parameter	angstroms
z(i)	Charge on ion i	-
E	Surface Mineral Potential and Redox Potential	mV
E^0	Standard Redox Potential	mV
R	Gas Constant	mJ K^{-1} mol^{-1}
T	Absolute Temperature	K
i	Current Density	C hr^{-1} m^{-2}
i_0	Exchange Current Density	C hr^{-1} m^{-2}
ß	Symmetry Factor	-
$E - E_e$	Overpotential	mV
F	Faraday Constant	C mol^{-1}
a	Particle Surface Area	m^2
t	Time	hr
m	Moles in a Particle	-
k_2	Electrochemical Constant	mV^{-1}
SF	Shape Factor	-
d	Particle Size	m
r	Particle Radius	m
v	Volume of a particle	m^3
ρ	Density of mineral	kg m^{-3}

List of Symbols (Continued...)

Symbol	Quantity	Units
k_1	Rate Constant	mol hr^{-1}
M	Moles in a Size Range	-
N	Number of particles in a Size Range	-
k_3	Modelling Constant	Mol hr^{-1}
k_4	Modelling Constant	mV hr^{-1}
k_5	Modelling Constant	mV

1. INTRODUCTION

In Section 1.1, background on organisms associated with bioleaching is presented. Literature on the bioleach process is presented in Section 1.2. In Section 1.3 certain by-products of bacterial leaching processes are described, and the importance of galvanic effects is discussed in Section 1.4.

In Section 1.5 the objective and scope of the dissertation is presented. Two tables are provided to act as a guide to the various sections of the work.

1.1. BACKGROUND ON BACTERIAL LEACHING

In 1947 Colmer and Hinkle[1] described a bacterium which was able to oxidize reduced ferrous and sulphur compounds. The bacterium was given the name *Thiobacillus ferrooxidans*, the generic name "*Thiobacillus*" referring to the sulphur oxidizing capability, and the epithet "*ferrooxidans*" indicating ferrous iron oxidation capability.

This organism features prominently in bacterial leaching processes, and is well adapted to acidic inorganic environments. More details on the nature of the organism and its growth requirements are supplied in Appendix A.1.1.

1.2. THE BIOLEACHING PROCESS

Two mechanisms operative in bacterial leaching have been presented in the literature: the direct and the indirect mechanisms. These are discussed in Sections 1.2.1 and 1.2.2 respectively. Comments from the literature on the relative importance of the mechanisms are provided in Section 1.2.3. In Section 1.2.4 some recent modelling developments are presented.

1.2.1. BIOLEACHING BY DIRECT MECHANISM

The direct mechanism refers to the situation in which the bacteria directly oxidize the sulphide entity of a mineral to sulphate, thereby simultaneously dissolving the metal moiety. Usually the bacteria are visualized to be in direct contact with the mineral sulphides being oxidized.

Tributsch[2] and Tributsch and Bennett[3] ascribed direct leaching of a mineral by bacteria to a kind of "molecular carrier" produced by the organism, which was thought to remove -SH groups from the sulphide surfaces. The resulting compound was then visualized to be reabsorbed into the cell, where the sulphide ion was oxidized. Tuovinen and Kelly[4], however, found it likely that sulphide minerals should at least enter the peripheral membranes of the bacterial cells. Lundgren and Tano[5] felt that the cell envelope, which forms the exterior of the bacteria, contained the necessary enzymes (biological catalysts) for sulphide oxidation.

Southwood and Southwood[6] observed tunneling in the bioleaching of pyrite. They suggested this to be partly due to direct action by bacteria, which attached preferentially to irregularities in the crystal structure of the sulphide.

Torma, Legault, Kougiomoutzakis and Quellet[7], Torma and Sakaguchi[8], and Tributsch and Bennett[3] found that there was a correlation between the solubility product of a given sulphide and the bacterial activity associated with it (a high solubility product resulted in more bacterial activity). Tributsch and Bennett[3] found one exception to this general trend: Sulphides having p-type conducting characteristics showed bacterial activity more enhanced than that expected by the mentioned general trend. They ascribed this to the large number of holes in the valence band, which are equivalent to a large number of broken bonds. In the presence of a S^{2-} acceptor, e.g. the molecular carrier postulated by the authors, the disssolution of the sulphide is accelerated.

It is clear that the direct mechanism could be of importance in bacterial leaching. The extent to which this mechanism operates seems to depend on the type of mineral being leached. Conditions in the leach could also have an influence.

1.2.2. BIOLEACHING BY INDIRECT MECHANISM

In the indirect mechanism ferric ions, known to be good oxidizing agents of metal sulphides, dissolve the metal moiety by oxidizing the sulphide ions in the mineral to

sulphur. Ferric ions are simultaneously reduced to their ferrous state. The ferrous ions formed may be oxidized back to their ferric state by bacteria (in this process bacteria obtain energy for growth, etc.). Thus a cycle is formed, and this process, where bacteria do not directly attack the mineral sulphide, is known as the indirect mechanism. Some viewpoints on the oxidation of ferrous ions by bacteria are presented in Appendix A.1.2.

Dry[9] leached a sulphide matte which consisted mainly of triolite (FeS), and Verbaan and Crundwell[10] leached a sphalerite concentrate. These authors found that the leaching behaviour in acidic iron sulphate solutions could be explained by an electrochemical mechanism.

1.2.3. RELATIVE IMPORTANCE OF DIRECT AND INDIRECT MECHANISMS

Tributch and Bennett[3] postulated that if suitable oxidizing agents are present, e.g. ferric ions, electrons may be extracted from the valence band of the mineral. This means that more broken bonds are formed in the sulphide lattice, leading to enhanced leaching. It is thought that this could imply that the indirect and direct mechanisms might interact: The action of the ferric ions, creating holes, could facilitate the direct attack of bacteria on the mineral. It is not known whether this conceptual combined effect would be equal to the sum of the two effects working individually.

Duncan, Landesman and Walden[11] bacterially leached chalcopyrite and pyrite minerals, and used selective