

## ACKNOWLEDGEMENTS

# DISSOLUTION OF SPHALERITE MINERALS FROM ROSH PINAH TAILINGS

by

Willem van der Merwe

submitted in partial fulfillment of the  
requirements for the degree of

Magister Scientiae

In the Faculty of Natural and

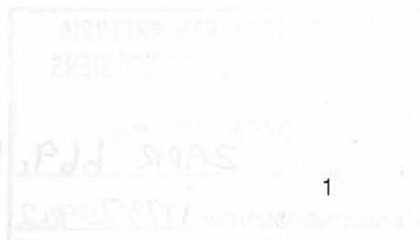
Agricultural Sciences

University of Pretoria

September 2003



University of Pretoria



## ACKNOWLEDGEMENTS

I would like to express my deepest gratitude towards the following people that contributed in making this study possible:

- Our Heavenly Father for the guidance time and perseverance to complete this study.
- Sincere thanks to my supervisor Professor C.A. Strydom all the help, her patience and valuable contributions.
- My wife Carina for moral support and encouragement.
- The contributions of HS du Preez and Leonie Reyneke are acknowledged and appreciated.
- JJ Oberholzer, KA Govender and Johan Swanepoel are thanked for performing the chemical analyses,
- Lourina de Beer en Pieter van Heerden are thanked for their literature searches.
- My manager Marinus du Plessis for his support and time made available.

## **Dissolution of Sphalerite Minerals from Rosh Pinah Tailings**

by

Willem van der Merwe

submitted in partial fulfillment of the requirements for the degree

Magister Scientiae

In the Faculty of Natural and Agricultural Sciences

Department of Chemistry

University of Pretoria

September 2003

### **ABSTRACT**

The aim of this study was to study the extraction of zinc from the mineral sphalerite, especially the leaching of concentrate recovered from the Rosh Pinah tailings by means of ferric chloride. To this end, the literature on zinc processing was surveyed and knowledgeable persons were consulted.

The study also addressed the leaching kinetics of an upgraded Rosh Pinah tailings dam concentrate as well as those of a synthetic zinc sulphide in a ferric chloride medium.

Valuable results were obtained, from the leaching of sphalerite concentrate in ferric chloride medium. An activation energy value of 45.82 kJ/mol was obtained, which compares well with what has been published in the literature.

A chemical control model and a diffusion control model were applied to the data obtained.

From neither of the models a straight-line relationship could be deduced over the leaching range. At  $t < 45$  minutes it seems that the process is controlled by chemical reaction at the interface; at  $t > 45$  minutes it seems that the process is controlled by diffusion through the product layer. It therefore seems that the rate-controlling step can be related to the process of diffusion through the product layer.

The mixed control model proposed by Huang and Rowson,  $[1-(1-x)^{1/3}+y/6[(1-x)^{1/3}+1-2(1-x)^{2/3}]]^2=kMt$ , was applied to data obtained during this study. The resultant graphical fit was near perfect, indicating that sphalerite leached in ferric chloride follows a mixed control mechanism for the conditions reported in the study. An activation energy of 20.71 kJ/mol was determined for this model by using the following equation:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

## SAMEVATTING

Die doel van hierdie studie was om die kinetika van sink uit 'n mineraal stienet te bestudeer, en in besonder die leeging van ferrichloried van 'n konsentraat variasie in materiaal van die Finab-sienet. Met hierdie doel is die literatuur oor swaermeting bestudeer en kennis op hierdie gebied geïdentifiseer.

Die studie het ook die leeg kinetika van sink uit 'n sifkdamkonsentraat en van 'n sintetiese sinkstienet in sink leeging aangespreek.

Waardevolle resultate is verkry met die leeging van die sifkdamkonsentraat in 'n ferrichloried medium, waarvoor 'n

## Oplossing van of Sfaleriet Minerale vanuit die Rosh Pinah Slikdam

deur

Willem van der Merwe

Voorgelê ter vervulling van deel van  
die vereistes vir die graad

Magister Scientiae

In the Fakulteit of Natuur- en Landbouwetenskappe

Departement Chemie

Universiteit van Pretoria

September 2003

### **SAMEVATTING**

Die doel van hierdie studie was om die ekstraksie van sink uit die mineraal sfaleriet te bestudeer, en in besonder die loging met ferrichloried van 'n konsentraat verkry uit materiaal van die Rosh Pinah-slikdam. Met hierdie doel is die literatuur oor sinkherwinning bestudeer en kenners op hierdie gebied geraadpleeg.

Die studie het ook die loog kinetieka van verbeterde slikdamkonsentraat en van 'n sintetiese sinksulfied in ferrichloried aangespreek.

Waardevolle resultate is verkry met die loog van die sfaleriet konsentraat in ferrichloried medium waaronder 'n



aktiveringsenergie waarde, vir die eerste gedeelte van die loogproses, van 45.82 kJ/mol, wat goed vergelyk met waardes wat in die literatuur gepubliseer is.

## NOMENCLATURE

Daar is gepoog om 'n model vir chemiese beheer en 'n model vir diffusiebeheer toe te pas op die data wat verkry is uit die toetswerk.

Uit nie een van die modelle kon 'n lineêre verwantskap afgelei word nie. By  $t < 45$  minute en  $80^{\circ}\text{C}$  en  $90^{\circ}\text{C}$  wil dit voorkom of die proses chemies op die oppervlak beheer word; by  $t > 45$  minute wil dit voorkom of die proses beheer word deur diffusie deur die produklaag. Dit skyn dus asof die tempobepalende stap verband hou met diffusie deur die gevormde produklaag.

Die gemengde beheermodel voorgestel deur Huang and Rowson,  $[1 - (1-x)^{1/3} + y/6[(1-x)^{1/3} + 1 - 2(1-x)^{2/3}]] = k_M t$  is toegepas op data wat verkry is uit hierdie studie. Die grafiese passing van die data op die vergelyking het 'n byna perfekte passing opgelewer. Daaruit kan afgelei word dat indien sfaleriet in ferrichloried geloog word onder die toestande in die studie vervat, 'n meganisme van gemengde beheer van toepassing is.

'n Aktiverings energie of 20.71 kJ/mol is bepaal vir hierdie model deur gebruik te maak van die volgende vergelyking:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$T$	Temperature, K
$t$	Reaction time, min
$V_1$	Velocity of the cathodic reaction
$V_2$	Velocity of the anodic reaction
$x$	Fraction leached
$\Delta G$	Gibbs free energy change

$\Delta G^\circ$ 

Difference between the free energies of the reactants and products when all components of the reaction are in their standard-state conditions.

**NOMENCLATURE**

Symbol/name	Description
$A_1$	Surface area of the cathodic zone
$A_2$	Surface area of the anodic zone
Anhedral Grains	Granular minerals without the expression of crystal shapes
E	Electrode potential
$E^\circ$	Standard electrode potentials
$E_A$	Activation energy, $\text{kJ} \cdot \text{mol}^{-1}$
$E_h$	Oxidation / reduction potential (ORP) measured in volts, millivolts or $E_h$ ( $1E_h = 1\text{mV}$ ).
F	Faraday constant
$k_1$	Velocity constant at the cathodic zone
$k_2$	Velocity constant at the anodic zone
$K_S, k_D, k_M$ and $k_C$	Apparent rate constants
R	Universal gas constant, $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Subhedral Crystals	Occurs as crystals which tend to exhibit a recognizable crystal shape
T	Temperature, K
t	Reaction time, min
$V_1$	Velocity of the cathodic reaction
$V_2$	Velocity of the anodic reaction
$\alpha$	Fraction leached
$\Delta G$	Gibbs free energy change

---

$\Delta G^\circ$	Difference between the free energies of the reactants and products when all components of the reaction are present at standard-state conditions.
Tutty	A yellow or brown amorphous substance obtained as a sublimation product in the flues of smelting furnaces of zinc, and consisting of a crude zinc oxide (Webster's Revised Unabridged Dictionary (1913))
Orichalcum	A yellow bronze, alloy of copper and zinc, resembling gold when new. Its name comes from two Greek words: oros meaning mountain, and chalkos, brass. The Romans made two coins made of orichalcum: the sestertius and the dupondius. ( <a href="http://www.artlex.com">http://www.artlex.com</a> 1996-2003, Michael Delahunt)
White vitriol	Zinc sulphate (Webster's Revised Unabridged Dictionary, © 1996, 1998 MICRA, Inc)
Calmia	Closest reference: calamine $(ZnOH)_2SiO_3$ (Palache, C. (1936): The Minerals of Franklin and Sterling Hill, Sussex County, New Jersey <i>USGS Professional Paper 180</i> )

---



## Table of Contents

Chapter.....	Page
Acknowledgements.....	2
Abstract.....	3
Samevatting .....	5
Nomenclature .....	7
Table of Contents .....	9
CHAPTER 1 .....	14
Introduction .....	14
1.1 Historical background.....	14
1.2 Mineral forms of zinc.....	15
1.3 Chemistry of zinc.....	18
1.4 Mintek study of Rosh Pinah tailings dump samples .....	19
1.4.1 Background .....	19
1.4.2 Conclusions from Report 1 (Mintek) .....	20
1.4.3 Conclusions from Report 2 (Mintek) .....	21
1.4.3.1 Flotation.....	22
1.4.3.2 Gravity concentration.....	22
1.5 Mineralogy .....	23
1.6 Aim of this study .....	24
1.6.1 Why ferric chloride? .....	24
CHAPTER 2 .....	26
Zinc Processing.....	26
2.1 Extraction of zinc from its ores .....	26
2.2 The retort processes .....	27

2.3	The roasting-leaching-electrowinning route .....	27
2.4	Pressure leaching process .....	29
2.4.1	The Sherritt Zinc Process .....	30
2.5	The Sherritt Zinc Integrated Process .....	34
2.6	Advantages of the Sherritt process .....	36
2.7	Ferric Ion as leaching agent .....	38
<b>CHAPTER 3 .....</b>		<b>40</b>
<b>Previous work.....</b>		<b>40</b>
3.1	Kinetics of the metallurgical processes .....	40
3.1.1	Porosity .....	40
3.1.1.1	Criteria of porosity .....	40
3.1.2	Sphericity.....	41
3.1.3	Electrochemical action.....	42
3.1.4	Generalised Rate Equation .....	46
3.2	Sulphides .....	49
<b>CHAPTER 4.....</b>		<b>51</b>
<b>Source and geological setting .....</b>		<b>51</b>
4.1	Introduction.....	51
4.2	Source .....	51
4.3	Geology .....	51
4.4	Sampling .....	53
4.4.1	V-trench.....	53
4.4.2	Reverse circulation drilling.....	54
<b>CHAPTER 5.....</b>		<b>56</b>
<b>Theoretical background.....</b>		<b>56</b>
5.1	Thermodynamics.....	56
5.1.1	Applications of half-reaction potentials .....	56

5.1.2	Nernst equation .....	59
<b>5.2</b>	<b>Reduction potential .....</b>	<b>59</b>
5.2.1	Pourbaix diagram .....	60
<b>5.3</b>	<b>Chemical kinetics .....</b>	<b>61</b>
5.3.1	Reaction rate .....	62
5.3.1.1	Definition of rate and rate laws .....	62
5.3.2	Rate constants.....	63
5.3.3	Reaction order .....	64
5.3.4	Determination of the rate law.....	64
<b>5.4</b>	<b>Integrated rate laws .....</b>	<b>64</b>
5.4.1	First-order reactions .....	65
5.4.2	Second-order reactions .....	66
<b>5.5</b>	<b>Rate equations and half lives .....</b>	<b>67</b>
<b>5.6</b>	<b>Arrhenius theory.....</b>	<b>68</b>
5.6.1	Activation energy .....	70
5.6.2	Rate-controlling step.....	70
5.6.3	Three-dimensional diffusion.....	70
5.6.4	Chemical reaction controlled .....	72
5.6.5	Diffusion controlled .....	72
5.6.6	Mixed control .....	72
5.6.7	Rate-controlling step.....	73
<b>CHAPTER 6</b>	<b>.....</b>	<b>75</b>
<b>Experimental.....</b>	<b>.....</b>	<b>75</b>
<b>6.1</b>	<b>Materials.....</b>	<b>75</b>
<b>6.2</b>	<b>Sample and particle size analysis.....</b>	<b>75</b>
<b>6.3</b>	<b>Leaching experiments.....</b>	<b>77</b>
6.3.1	Set-up.....	77

6.3.2	Experimental procedure .....	78
<b>6.4</b>	<b>Analysis.....</b>	<b>79</b>
6.4.1	Elemental analysis.....	79
6.4.2	Fe(II) determinations .....	80
6.4.2.1	Reagents for Fe(II) determination.....	81
6.4.2.2	Procedure .....	82
6.4.3	Eh to measure cell potential .....	82
6.4.4	pH measurement.....	83
<b>CHAPTER 7</b>	<b>.....</b>	<b>84</b>
<b>Results and Discussion</b>	<b>.....</b>	<b>84</b>
7.1	E <sub>h</sub> and pH determination.....	84
7.2	Calculation of E <sub>h</sub> values.....	84
7.3	Leach tests.....	88
7.4	Results and discussion of the zinc part of the reaction ..	90
7.5	Scanning Electron Microscope Investigation .....	93
7.6	Barium extraction .....	93
7.7	Kinetic tests .....	95
7.7.1	The method of initial rates .....	95
7.7.2	Phase boundary controlled reaction .....	101
7.7.3	Three-dimensional diffusion.....	102
7.7.4	The mixed control model .....	103
<b>CHAPTER 8</b>	<b>.....</b>	<b>107</b>
<b>Conclusions</b>	<b>.....</b>	<b>107</b>
8.1	Determination and calculation of E <sub>h</sub> values.....	107
8.2	Leach tests.....	107
8.3	Kinetic tests .....	108
8.3.1	Reaction rates .....	108



8.3.2	Activation energy .....	108
8.3.3	Rate-controlling step.....	108
8.3.4	Application of the technique .....	109
<b>References</b> .....		<b>110</b>

## INTRODUCTION

### 1.1 Historical background

Peter van der Krug (2003) reports that centuries before zinc was recognised as a distinct element, zinc ores were used for making brass. Tubak-Cain, seven generations after Adam, is mentioned as being an "instructor of every artificer in brass and iron."

Habashi (2000) mentions that in the latter part of the thirteenth century, Marco Polo described the manufacture of zinc oxide in Persia and how the Persians prepared tufia (a solution of zinc vitriol) for healing sore eyes.

Habashi (2000) reports that the Roman writer Strabo (66 B.C. – 24 A.D.) mentioned in his writings that only the Cyprian ore contained "the cadmian stones, copper vitriol, and tuffa," that is to say, the constituents from which brass can be made. It is believed that the Romans first made brass in the time of Augustus (20 B.C. to 14 A.D.) by heating a mixture of powdered calamine, charcoal and granules of copper. Roman writers observed that coins made from orichalcum were indistinguishable from gold.

Gowland (1912) reported that pure zinc was not known until quite modern times, the ore employed being calamine, which is an impure zinc carbonate rich in silica. Mixing ground calamine ore with copper and heating the mixture in a crucible produced the earliest brass. The heat applied was sufficient to reduce the zinc to the metallic state, but