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Catalysed Aeration of Reduced Ilmenite

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I wish to dedicate this thesis to the
memory of Dr Robert Becher (1913 to 1997)
Through his optimism and eagerness to explore
and share his ideas many have benefited.

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Abstract

A study has been conducted on the aeration of reduced ilmenite with emphasis on increasing the aeration speed and understanding the mechanism of the aeration based on laboratory scale experiments. These issues were highlighted by comparing the currently operating Becher process which incorporates the use of an ammonium chloride catalyst in the aeration process.

The speed of production of synthetic rutile from the Becher process is currently dictated by the time the reduced ilmenite remains in the aeration tank. As these times can vary greatly for no obvious reason, experiments were conducted to find which parameters could be changed to increase the speed of leaching. It was found that by increasing the oxygen content to 100 per cent the aeration time was reduced by at least half.

By replacing ammonium chloride with various other amine compounds as the catalyst it was found there was a relationship between pK_a and aeration time. It was also found that the more sterically hindered the amine group, the slower the leaching. The use of ethylenediammonium chloride has shown that, when used at two thirds of the ammonium chloride concentration, aeration can be completed an hour (17%) faster than with the ammonium chloride catalyst. Furthermore, when ethylenediammonium chloride was used with a 100 per cent oxygen gas flow the aeration time was reduced by two thirds.

Other compounds that did not contain amine groups were also investigated as catalysts in reduced ilmenite aerations. Of those tested only a citric acid / trisodium citrate mixture managed to aerate the reduced ilmenite substantially faster than the standard ammonium chloride catalyst. Other compounds with similar structure to the citrate ion failed to aid the aeration at all.

Table of contents

Chapter One	
Introduction	Page
1.1 Processing ilmenite to pigment grade titanium dioxide	1
1.1.1 Titanium resources	1
1.1.2 World titanium requirements	2
1.2 Methods of upgrading ilmenite to synthetic rutile	4
1.2.1 The Becher process	4
1.2.2 Beneficiated slag	5
1.2.3 The Benelite process	5
1.2.4 The Ishihara process	5
1.2.5 The Murso process	5
1.2.6 The Summit process	6
1.3 Methods of processing synthetic rutile to pigment grade titanium dioxide	6
1.3.1 The sulfate process	6
1.3.2 The chloride process	7
1.4 The Becher process	9
1.4.1 Process description	9
1.4.2 The Becher process mechanism	12
1.5 Significance of the research	14
1.6 Objectives	15
1.6.1 Mechanistic study of the Becher process	15
1.6.2 Effect of temperature	15
1.6.3 Effect of pH	16
1.6.4 Effect of oxygen partial pressure	16
1.6.5 Effect of solution composition	16
1.6.5.1 The concentration of ammonium chloride	17
1.6.5.2 Substitution of ammonium chloride with other leaching media	17
Chapter Two	
Materials and experimental methods	
2.1 Materials and reagents	18
2.1.1 The reduced ilmenite samples	18
2.1.2 Gas and water supplies	19
2.1.3 Leaching reagents	20
2.2 Reactor design	21
2.2.1 The 5.0 litre aerator design	21
2.2.2 The inverted cone aerator design	23
2.3 Experimental procedures	27
2.3.1 Experimental procedures for the 5.0 litre aerator	27
2.3.2 Experimental procedures for the inverted cone fluidised bed aerator	27
2.4 Methods of analysis and calibration of data	28
2.4.1 SATMAGAN analysis	28
2.4.2 Metallic iron analysis	29
2.4.3 Total iron analysis	29
2.4.4 Iron oxide analysis	30
2.4.5 Manganese analysis	30

Chapter Three

Ammonium chloride as a catalyst in the Becher process

3.1 Introduction	31
3.2 Aeration at differing air flow rates	31
3.2.1 Low pulp density tests	31
3.2.2 High pulp density tests	33
3.2.3 Iron oxides produced	35
3.3 Changes in aeration related to the pulp density of the slurry	36
3.3.1 Removal of metallic iron as a function of pulp density	36
3.3.2 Iron oxides produced	39
3.4 The effect of ammonium chloride concentration	39
3.4.1 Removal of metallic iron as a function of concentration	39
3.4.2 Iron oxides produced	41
3.5 Aeration as a function of temperature	42
3.5.1 Removal of metallic iron as a function of temperature	42
3.5.2 Iron oxides produced	45
3.6 Changes in aeration caused by altering the pH of the slurry	45
3.6.1 Removal of metallic iron as a function of pH	45
3.6.2 Iron oxides produced	50
3.7 Changes in aeration by altering the oxygen partial pressure	50
3.8 Mineralogy of reduced ilmenite	53
3.8.1 Metallic iron detected in the titanium dioxide matrix	54
3.8.2 Sulfur and manganese detected in the titanium dioxide matrix	65
3.9 Reproduction of results for ammonium chloride aerations	65
3.10 Conclusions	67

Chapter Four

Substitution of ammonium chloride with other electrolytes in the Becher process

4.1 Introduction	70
4.2 The use of sodium salts as catalysts for aeration reactions	70
4.2.1 Sodium chloride as an aeration catalyst	70
4.2.2 Sea water as an aeration catalyst	72
4.2.3 Sodium acetate as an aeration catalyst	75
4.2.4 Sodium sulfate as an aeration catalyst	77
4.2.5 Sodium perchlorate as an aeration catalyst	79
4.2.6 Sodium nitrate as an aeration catalyst	81
4.3 The use of ammonium salts as catalysts in aerations	83
4.3.1 Ammonium perchlorate as an aeration catalyst	83
4.3.2 Ammonium nitrate as an aeration catalyst	85
4.3.3 Ammonium sulfate as an aeration catalyst	87
4.4 Conclusions	89

Chapter Five

Other amine compounds as catalysts in the Becher process

5.1 Introduction	91
5.2 Methyl substituted ammonium chlorides	91
5.3 Aniline hydrochloride as an aeration catalyst	95
5.4 Aniline hydrochloride derivatives as aeration catalysts	98
5.4.1 Chloro- substituted aniline hydrochloride	99
5.4.2 Nitro- substituted aniline hydrochloride	101
5.4.3 Methyl- substituted aniline hydrochloride	103
5.5 Ethylene diammonium chloride	108
5.5.1 Introduction	108
5.5.2 Effect of air flow rate on aeration	109
5.5.3 Aeration as function of the catalyst concentration	111
5.5.4 Effect of temperature on aeration	114
5.5.5 The effect of pH on aeration	116
5.5.6 The effect of oxygen partial pressure on aeration	120

5.5.7 Reproducibility of results using ethylene diammonium chloride	124
5.6 Conclusions	126
Chapter Six	
Other organic catalysts for the Becher process	
6.1 Introduction	129
6.2 The use of citric acid and its salts as aeration catalysts	129
6.2.1 Changes in the aeration rate caused by varying pH	130
6.2.2 Iron oxides produced through varying the citric acid / trisodium citrate composition	137
6.3 Ammonium chloride and citric acid mixtures as aeration catalysts	138
6.3.1 The effect of a mixed composition	138
6.3.2 Iron oxides produced	142
6.4 Tartaric acid and its salts as aeration catalysts	143
6.4.1 The effect of pH	143
6.4.2 Iron oxides produced	147
6.5 Ammonium chloride and tartaric acid mixtures as aeration catalysts	148
6.5.1 The effect of varying the mixture composition on aeration rates	148
6.5.2 Iron oxides produced for the different mixtures	152
6.6 Oxalic acid and its salts as aeration catalysts	153
6.6.1 Changes in the aeration rate caused by varying pH	153
6.7 Ammonium chloride and oxalic acid mixtures as aeration catalysts	157
6.7.1 The effect of a mixed composition	157
6.8 Conclusions	161
Chapter Seven	
Inverted cone aerator	
7.1 Introduction	163
7.2 Aeration at different pulp densities	163
7.3 Aeration at different air flow rates	166
7.4 Aeration as a function of temperature	168
7.5 Aeration as a function of oxygen partial pressure	172
7.6 Citric acid / trisodium citrate mixture as a catalyst	175
7.6.1 Aeration with 20 grams of solids	175
7.6.2 Aeration with 100 grams of solids	177
7.7 Ethylene diammonium chloride as a catalyst	179
7.8 Conclusions	181
Chapter Eight	
Reduced ilmenite from alternative sources	
8.1 Introduction	182
8.2 The influence of using reduced ilmenite from different producers	182
8.2.1 Comparison between the different reduced ilmenite under four different aeration conditions against a standard	183
8.2.2 Direct comparison between the four different reduced ilmenite under four different sets of aeration conditions	190
8.3 Conclusions	193
Chapter Nine	
The products from acid washing of reduced ilmenite after aeration	
9.1 Introduction	195
9.2 Removal of impurities from the upgraded ilmenite by acid leaching	196
9.3 Iron removal by acid leaching	197
9.4 Manganese removal by acid leaching	198
9.5 Conclusions	200

Chapter Ten	
Summary and further work	
10.1 Concluding Summary	202
10.2 Suggestions for further work	204
References	206

List of Figures

<u>Figure</u>	<u>Page</u>
1.1 A diagrammatic representation of the six stages of the Becher process	9
2.1 Schematic diagram of the 5.0 litre aerator	22
2.2 A diagram of the original inverted cone aerator	23
2.3 Modifications to the air inflow of the inverted cone aerator	24
2.4 Continuous solution flow aerator	25
2.5 The final design of the inverted cone fluidised bed aerator	26
3.1 The effect of air flow rate on the removal of metallic iron in a reduced ilmenite slurry consisting of 100 grams RI, 1.8 litres of water and 9.0 grams of ammonium chloride at 70-80 degrees	32
3.2 The effect of air flow rate on the removal of metallic iron in a reduced ilmenite slurry consisting of 300 grams RI, 1.8 litres of water and 9.0 grams of ammonium chloride at 70-80 degrees	34
3.3 The effect of pulp density on the removal of metallic iron from reduced ilmenite under standard conditions	37
3.4 The effect of ammonium chloride concentration, 0.0 M to 0.19 M, on the removal of metallic iron from reduced ilmenite slurry (14.28 per cent)	40
3.5 The effect of varying the temperature, from 40 to 90 degrees, on the removal of metallic iron from reduced ilmenite	43
3.6 Effect of pH variations on the removal of metallic iron from reduced ilmenite, as determined by SATAMAGAN	47
3.7 Changes in the pH of experimental slurries over the course of a 7.0 hour leaching trial	48
3.8 The effect of oxygen partial pressure on the leaching of metallic iron from reduced ilmenite using ammonium chloride as an aeration catalyst	51
3.9 Rate of metallic iron removal as a function of the amount of oxygen supplied	52
3.10 A Backscatter (A) and EDXRA SEM images of a reduced ilmenite sample prior to leaching showing the iron (B), manganese (C) and sulfur (D) distributions	57
3.11 A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 1 hour of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions	58
3.12 A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 2 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions	59

3.13 A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 3 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions	60
3.14 A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 4 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions	61
3.15 A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 5 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions	62
3.16 A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 6 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions	63
3.17 A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 7 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions	64
3.18 The ammonium chloride slurry experiment under optimum conditions repeated four times to assess the reproducibility of the experiment	66
4.1 Sodium chloride (0.1 M) and ammonium chloride (0.1 M) used as aeration catalysts to remove metallic iron from reduced ilmenite	71
4.2 Sea water, sodium chloride (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the leaching of metallic iron from reduced ilmenite	73
4.3 Sodium acetate (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron	76
4.4 Sodium sulfate (0.1 M), sodium chloride (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron	78
4.5 Sodium perchlorate (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron	80
4.6 Sodium nitrate (0.1 M), sodium perchlorate (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron	82
4.7 Ammonium perchlorate (0.1 M), sodium perchlorate (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron	84
4.8 Ammonium nitrate (0.1 M), ammonium perchlorate (0.1 M), ammonium chloride (0.1 M) used as catalysts to remove metallic iron, and a non catalysed aeration of reduced ilmenite	86
4.9 Ammonium sulfate (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron	88

5.1 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using ammonium chloride, methylamine hydrochloride, dimethylamine hydrochloride (in duplicate), trimethylamine hydrochloride (in duplicate) and tetramethylamine hydrochloride (in duplicate) as catalytic reagents	93
5.2 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using ammonium chloride (0.1 M) and aniline hydrochloride as catalytic reagents	97
5.3 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using aniline hydrochloride, <i>para</i> -chloroaniline hydrochloride, <i>meta</i> -chloroaniline hydrochloride and <i>ortho</i> -chloroaniline hydrochloride as catalytic reagents	100
5.4 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using <i>para</i> -nitroaniline hydrochloride, <i>meta</i> -nitroaniline hydrochloride, <i>ortho</i> -nitroaniline hydrochloride and aniline hydrochloride as catalytic reagents	102
5.5 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using <i>para</i> -toluidine hydrochloride, <i>meta</i> -toluidine hydrochloride and <i>ortho</i> -toluidine hydrochloride as catalytic reagents	105
5.6 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using <i>para</i> -toluidine hydrochloride, <i>para</i> -chloroaniline hydrochloride and <i>para</i> -nitroaniline hydrochloride as catalytic reagents	107
5.7 The effect of the air flow rate on the catalytic action of EDAC	110
5.8 The effect of concentration of EDAC (and ammonium chloride) on the leaching rate of metallic iron in reduced ilmenite	112
5.9 The effect of temperature on the leaching of reduced ilmenite with the use of EDAC as catalyst	115
5.10 Variations in the leaching of metallic iron from reduced ilmenite using EDAC as a function of initial pH	117
5.11 The pH profiles for the leaching trials using EDAC as a leaching agent with various values of initial pH	119
5.12 The removal of iron from reduced ilmenite at various oxygen partial pressures at a total gas flow rate of 1.0 litre per minute, using EDAC as the catalyst	121
5.13 The effect of the oxygen partial pressure on iron removal at a constant total gas flow rate of 1.0 litre per minute, using ammonium chloride as the catalyst	123
5.14 The ethylene diammonium chloride experiment under optimum conditions repeated four times to assess the reproducibility of the experiment	125

6.1 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using ammonium chloride, citric acid, trisodium citrate and mixtures of citric acid and trisodium citrate as catalytic reagents	131
6.2 Graph of time vs pH in the aeration of reduced ilmenite using ammonium chloride, citric acid, trisodium citrate and mixtures of citric acid and trisodium citrate as catalytic reagents	133
6.3 A comparison between the leaching ability of freshly made catalyst solution (Virgin) and reused catalyst solution (Recycled), where 0.05 M citric acid and 0.05 M trisodium citrate is used as the catalyst in both cases.	135
6.4 A pH profile of freshly made catalyst solution (Virgin) and reused catalyst solution (Recycled), where 0.05 M citric acid and 0.05 M trisodium citrate is used as the catalyst in both leaching trials	136
6.5 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using mixtures of ammonium chloride, citric acid and trisodium citrate as catalytic reagents	139
6.6 Graph of time vs a ratio of the extent of leaching with 0.1 M ammonium chloride to the extent of leaching with 0.05 M ammonium chloride with and without citric acid	141
6.7 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using ammonium chloride, tartaric acid, disodium tartrate and mixtures of tartaric acid and disodium tartrate as catalytic reagents	144
6.8 Graph of time vs pH in the aeration of reduced ilmenite using ammonium chloride, tartaric acid, disodium tartrate and mixtures of tartaric acid and disodium tartrate as catalytic reagents	146
6.9 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using mixtures of ammonium chloride, tartaric acid and disodium tartrate as catalytic reagents	149
6.10 Graph of time vs a ratio of the extent of leaching with 0.1 M ammonium chloride to the extent of leaching with 0.05 M ammonium chloride with and without tartaric acid	151
6.11 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using ammonium chloride, oxalic acid, disodium oxalate and mixtures of oxalic acid and disodium oxalate as catalytic reagents	154
6.12 Graph of time vs pH in the aeration of reduced ilmenite using ammonium chloride, oxalic acid, disodium oxalate and mixtures of oxalic acid and disodium oxalate as catalytic reagents	155
6.13 Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using mixtures of ammonium chloride, oxalic acid and disodium oxalate as catalytic reagents	158

6.14 Graph of time vs pH in the aeration of reduced ilmenite using mixtures of ammonium chloride, oxalic acid, disodium oxalate as catalytic reagents	160
7.1 Graph of time vs percentage metallic iron using different pulp densities in ammonium chloride slurries	165
7.2 Graph of time vs percentage metallic iron using different air flow rates for standard ammonium chloride slurries	167
7.3 Graph of time vs percentage metallic iron of reduced ilmenite aerations at different temperatures using standard ammonium chloride slurries	169
7.4 Graph of temperature vs residual metallic iron level (after 5.0 hours) for standard aerations run at temperatures between 30 and 90 degrees	171
7.5 Graph of time vs percentage metallic iron for four standard ammonium chloride slurries that were aerated at different oxygen partial pressures	173
7.6 Graph of oxygen percentage vs rate of reaction for four separate trials	174
7.7 A combined graph of time vs percentage metallic iron and time vs pH for the aeration of 20 grams of reduced ilmenite with a citric acid / trisodium citrate catalyst and an air flow of 1.0 L / min	176
7.8 A combined graph of time vs percentage metallic iron and time vs pH for the aeration of 100 grams of reduced ilmenite with a citric acid / trisodium citrate catalyst	178
7.9 Graph of time vs percentage metallic iron comparing an ethylene diammonium chloride slurry to an ammonium chloride slurry	180
8.1 Four standard slurries using ammonium chloride with air, ethylenediammonium chloride, 0.05 M citric acid / 0.05 M sodium citrate and ammonium chloride with oxygen as aeration catalysts with reduced ilmenite sample S1	184
8.2 Four standard slurries using ammonium chloride with air, ethylenediammonium chloride, 0.05 M citric acid / 0.05 M sodium citrate and ammonium chloride with oxygen as aeration catalysts with reduced ilmenite sample S2	185
8.3 Four standard slurries using ammonium chloride with air, ethylenediammonium chloride, 0.05 M citric acid / 0.05 M sodium citrate and ammonium chloride with oxygen as aeration catalysts with reduced ilmenite sample S3	187
8.4 Four standard slurries using ammonium chloride with air, ethylenediammonium chloride, 0.05 M citric acid / 0.05 M sodium citrate and ammonium chloride with oxygen as aeration catalysts with reduced ilmenite sample S4	189

8.5 Four different reduced ilmenite samples all aerated with an ammonium chloride catalyst with an air gas flow. Graph A shows percentage metallic iron vs time While graph B shows absolute percentage metallic iron vs time	191
8.6 Four different reduced ilmenite samples all aerated with a 0.05 M citric acid / 0.05 M sodium citrate catalyst with an air gas flow	192
8.7 Four different reduced ilmenite samples all aerated with an ethylene diammonium chloride catalyst with an air gas flow	192
8.8 Four different reduced ilmenite samples all aerated with an ammonium chloride catalyst with an oxygen gas flow	193

List of Tables

<u>Table</u>	<u>Page</u>
1.1 The formula and titanium composition of titanium bearing rock types	2
1.2 The production of titanium bearing ores and processed products in 1996 for Australia and the ore producing states of Western Australia (WA), Queensland and New South Wales (NSW)	3
2.1 The composition of the standard reduced ilmenite used in most of the work.	18
2.2 Concentrations of species in Perth scheme water	19
2.3 Table of the leaching agents use in this work, and their suppliers	20
3.1 Table of oxygen utilisation for different pulp densities to convert metallic iron to iron (II) or iron (III)	38
3.2 The remaining amounts of iron in a reduced ilmenite sample after being leached at different temperatures for 7.0 hours	44
3.3 The effect of temperature on the oxides produced	45
3.4 Metallic iron and total iron contents for the final reduced ilmenite products of slurries leached with different initial solution pH	49
5.1 Table to compare the rates of removal of metallic iron from reduced ilmenite by a series of substituted amine compounds	94
5.2 Table of ammonium ions used for aeration and their pK_a values at 348 K	95
5.3 Nitrogen concentrations in solution before and after leaching with ammonium chloride and EDAC	113
6.1 Table of the iron oxides produced by various aeration catalysts	137
9.1 The metallic iron (Fe(m)) and total iron (Fe(t)) content of six aerated samples before and after acid leaching with hydrochloric acid	197
9.2 The metallic iron (Fe(m)) and total iron (Fe(t)) content of six aerated samples before and after acid leaching with sulfuric acid	198
9.3 The manganese (Mn) content of six aerated samples before and after acid leaching with hydrochloric acid	199
9.4 The manganese (Mn) content of six aerated samples before and after acid leaching with sulfuric acid	200

Chapter One

Introduction

1.1 Processing ilmenite to pigment grade titanium dioxide

1.1.1 Titanium resources

Titanium, listed as being the ninth most abundant element in the earth's crust, is found in two mineral forms that are of commercial importance - rutile and ilmenite (Roberts, 1971). Rutile contains approximately 95 percent titanium dioxide (TiO_2) while ilmenite, which is mainly ferrous titanate (FeOTiO_2), has an approximate composition of 52 per cent titanium dioxide. The composition of ilmenite varies due to weathering of the ilmenite-containing rock. This variation in composition of the ilmenite can change the titanium dioxide percentage from 33 to 65 per cent (Roberts, 1971).

As titanium is recorded as constituting 0.86 per cent of the earth's crust it is considered to be one of the major elements. Titanium is found in rocks as oxide and silicate materials. The minerals that account for most of the titanium in rock structures are listed in Table 1.1 (Force, 1991).

Table 1.1: The formula and titanium composition of titanium bearing rock types

Mineral	Theoretical Formula	TiO ₂ Content (%)
Oxides		
Rutile	TiO ₂	> 95
Anatase	TiO ₂	> 95
Brookite	TiO ₂	> 95
Ilmenite	FeOTiO ₂	52 **
Altered Ilmenite	FeOTiO ₂	33 - 65
Leucoxene	FeOTiO ₂	> 70
Perovskite	CaOTiO ₂	59 **
Magnetite	Fe ₃ O ₄	0 - 15
Silicates		
Sphene	CaTiSiO ₅	41 **
Melantic garnet	Ca ₃ Fe ₂ SiO ₁₂	0 - 17
Biotite	K ₂ (Mg,Fe) ₄ (Fe,Al) ₂ Si ₆ - Al ₂ O ₂₀ (OH,F) ₄	0 - 6
Calic Amphiboles	(Na,K)Ca ₂ (Mg,Fe,Al) ₅ - Si ₆ Al ₂ O ₂₂ (OH,F) ₂	0 - 10
Augite	Ca(Mg,Fe)(Si,Al) ₂ O ₆	0 - 9

** Stoichiometric value

Although titanium minerals can be mined from hard crystalline rocks, weathered rocks and unconsolidated sediments, presently over half the world's titanium is mined from shoreline placer deposits. The shoreline placer deposits supply rutile and variably altered ilmenite. The majority of the remaining mines are magmatic ilmenite deposits which supply unaltered ilmenite (Force, 1991). The deposits found in Western Australia are located in ancient beach lines well inland along the west coast (Stewart, 1993).

1.1.2 World titanium requirements

Titanium bearing ore is processed to produce titanium dioxide and titanium metal. The titanium dioxide is produced mainly for use as a pigment. The titanium metal produced is used as a structural material. The pigment industry consumes 90 per cent of all titanium sources that are mined - most of the remaining resources go into the making of metallic titanium.

The use of titanium dioxide in the pigment industry has come about because pure white titanium dioxide has a high refractive index, in the order of 2.6 to 2.9. As titanium dioxide is non toxic it has almost completely replaced lead oxides in the pigment industries. Pigment grade titanium dioxide is used in the paint, plastic, ceramic and paper industries, not only to produce white colouring but also for addition to other colours to create a larger range of colours (Force, 1991).

After conversion of titanium dioxide into its metallic form, the titanium has the following properties: a high strength to weight ratio, high temperature resistance and high corrosion resistance. As a result of these characteristics titanium metal is used extensively as an aircraft material, and as a component of heat exchangers and desalination plants (Force, 1991).

The world wide production of mineral sand ores was approximately 9,326,000 tonnes in 1996. This was broken up into 338,000 tonnes of rutile, 7,976,000 tonnes of ilmenite and 1,012,000 tonnes of zircon (ABARE, 1997a). Australia produced 25.4 per cent of the world's titanium ores in 1996, the breakdown of production is given in Table 1.2.

Table 1.2: The production of titanium bearing ores and processed products in 1996 for Australia and the ore producing states of Western Australia (WA), Queensland and New South Wales (NSW)

Mineral	W. A.	Queensland	N.S.W	Australia Total
Ilmenite Concentrate	1871 kt	191 kt	10 kt	2071 kt
Rutile Concentrate	95 kt	61 kt	33 kt	189 kt
Leucoxene Concentrate	29 kt	-	-	29 kt
Synthetic Rutile	517 kt	-	-	517 kt
Titanium Dioxide Pigment	185 kt	-	-	185 kt

(ABARE, 1997a) (ABARE, 1997b). (kt = 1000 tonne)

Of the data presented in Table 1.2 Western Australia produced most of Australia's titanium bearing ore in 1996. At export prices of \$93, \$673, \$664, \$490 and \$2557 a tonne of ilmenite, rutile, leucoxene, synthetic rutile and titanium dioxide pigment respectively, the titanium industry was worth over 1.065 billion dollars to

Australia in 1996. Forecasts predict the price of these exports to increase in the coming years (ABARE, 1997b).

1.2 Methods of upgrading ilmenite to synthetic rutile

As most of the titanium ores mined at present are rutile, altered ilmenite or ilmenite, the upgrading processes now in use take these ores as their feed material. In different parts of the world the titanium industry has developed to account for these different types of ore and for local conditions such as co-economics of byproduct usage from nearby industries. As a result there have been several different processing techniques developed to upgrade the percentage of titanium dioxide in the ore to a higher level feed stock (synthetic rutile) for final processing into pigment grade material. Some of these processes are currently used in industry while others have yet to pass the developmental stage. Most of these processes produce a product, with high titanium dioxide content, which is intended as a feed stock for conversion to pigment grade titanium dioxide.

1.2.1 The Becher process

The Becher process, developed and used solely in Western Australia, upgrades ilmenite from approximately 55 to 95 per cent titanium dioxide. This process uses coal in a rotary kiln at high temperatures (1150 degrees Celsius) to reduce all the iron oxides to metallic iron. The iron is then leached out of the reduced ilmenite grain, in an aerator, with the use of oxygen from compressed air. Ammonium chloride is used to accelerate the oxidation and assist the removal of the oxidised iron from the titanium dioxide grain (Becher *et al*, 1965). The final product is then used as a feed stock for the chloride process to produce pigment grade titanium dioxide.

1.2.2 Beneficiated slag

Beneficiated slag, which consists of ilmenite that has been smelted in an electric arc furnace with coal, is used to produce metallic iron and titania slag that contains approximately 72-80 per cent titanium dioxide (Sinha, 1988). The process involves high power, capital and maintenance costs but does produce iron as a by-product. The slag is then used as the starting product in the sulfate process to make pigment grade titanium dioxide.

1.2.3 The Benelite process

The Benelite process, using ilmenite as a feedstock, involves a partial reduction of iron(III) to iron(II) through the use of coal in a rotary kiln. The iron(II) is then pressure leached with 18-20 per cent hydrochloric acid to produce 93-94 per cent titanium dioxide (Kahn, 1984).

1.2.4 The Ishihara process

The Ishihara process also involves the use of a partial reduction of iron (III) in ilmenite to iron (II). This reduction is then followed by a leaching stage with waste sulfuric acid, from the sulfate process, to produce synthetic rutile (95 per cent titanium dioxide). This synthetic rutile is then used as a feed stock for fluidised bed chlorinators (Yamada, 1976).

1.2.5 The Murso process

The Murso process requires the ilmenite to be oxidised; this converts all the iron present to an iron (III) form at 900 to 950 degrees Celsius. The oxidised ilmenite is then reduced back to iron (II) at 800 to 850 degrees Celsius and under reducing conditions. The effect of the oxidation and reduction makes the ilmenite far more reactive to 20 per cent hydrochloric acid leaching in reflux conditions. The end product contains greater than 95 per cent titanium dioxide. In addition manganese,

magnesium, aluminium and vanadium impurities are removed (Sinha, 1988). This process is not in commercial use at present.

1.2.6 The Summit process

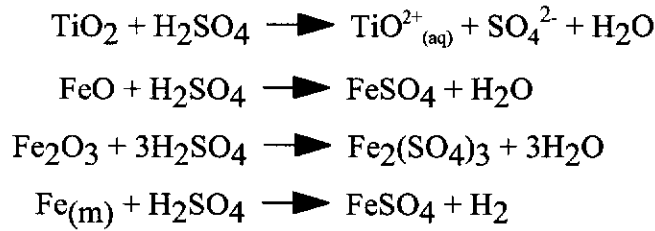
The Summit process was designed to use reduced ilmenite, that had been produced in a kiln at high temperatures, with a leaching stage involving ferric chloride. The ferric chloride is regenerated by oxidising ferrous chloride solution, which is produced during the leaching. This process produces an end product of 94 per cent titanium dioxide (Sinha, 1988). This process is not in commercial use due to the high capital and operating costs.

1.3 Methods of processing synthetic rutile to pigment grade titanium dioxide

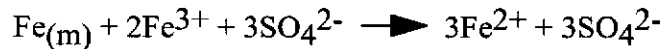
As most of the processes described in section 1.2 produce 94-95 per cent synthetic rutile, a further stage is required to create pigment grade titanium dioxide (greater than 99%). The two processes available to do this are: 1. The sulfate process; and 2. The chloride process.

1.3.1 The sulfate process

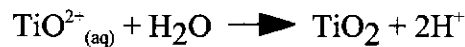
The sulfate process uses ilmenite and converts this to a product of pigment grade titanium dioxide. The procedure begins by mixing titanium ore (ilmenite) and concentrated sulfuric acid. This slurry is then agitated with air and heated by steam. As the agitation and heating take place the titanium and any other metals present are dissolved. The iron, in either metallic or oxide form, is dissolved to form ferric or ferrous sulfate while the titanium forms a titanium (IV) sulfate.



The ferric sulfate is then reduced to ferrous sulfate by the addition of scrap iron.



As the solution is cooled down ferrous sulfate begins to precipitate. Once the ferrous sulfate has precipitated the solids are separated from solution. The solution is then hydrolysed and titanium dioxide is reformed with a much higher purity.



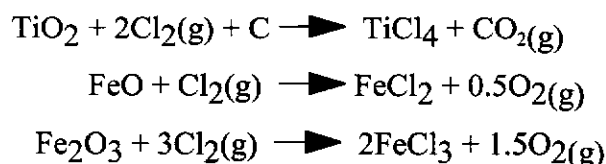
The solid titanium dioxide is then filtered and washed. The remaining solution is then stored as a waste product. The solids are finally calcined to give pigment grade titanium dioxide (Yamada, 1976).

The raw material used in the sulfate process can be as low as 33 per cent in titanium dioxide but as the impurities in the titanium ore increase, more sulfuric acid is needed to dissolve the excess of impurities, which creates more waste. The other waste material in the process is the acidic ferrous sulfate which can not be recycled or used for any other purpose, and represents the major disadvantage of the sulfate process.

1.3.2 The chloride process

The chloride process was developed as a route to pigment grade titanium dioxide in 1954, by DuPont. The upgraded ilmenite or rutile used as feed for this process is

chlorinated in a fluidised bed reactor with petroleum coke as the reductant at a temperature of 900-1000°C.



All the metals present are transformed to their chlorides.

The next stage in the process is the purification stage where titanium tetrachloride (TiCl_4) is separated from all the other impurities such as iron chlorides, vanadium chlorides and silicates. Purification is achieved by distillation and fractionation of the titanium tetrachloride from the impurities.

The titanium tetrachloride fraction is then oxidised in a high temperature flame or plasma reactor to produce the high purity titanium dioxide,



and chlorine gas which is recycled to the beginning of the process (Sinha, 1988).

The chloride process creates a high purity titanium dioxide final product (99.99 per cent), which is better than the sulfate process can produce, and no major waste products are created. The disadvantage is that a high grade raw material is required, with no more than 5 per cent impurities, whereas the sulfate process can operate with as much as 30-50 per cent impurities.

1.4 The Becher process

1.4.1 Process description

In practice the Becher process is used in conjunction with a kiln reduction, an acid leach and drying stage to make the upgraded feed stock, synthetic rutile (SR), for the subsequent pigment grade titanium dioxide production.

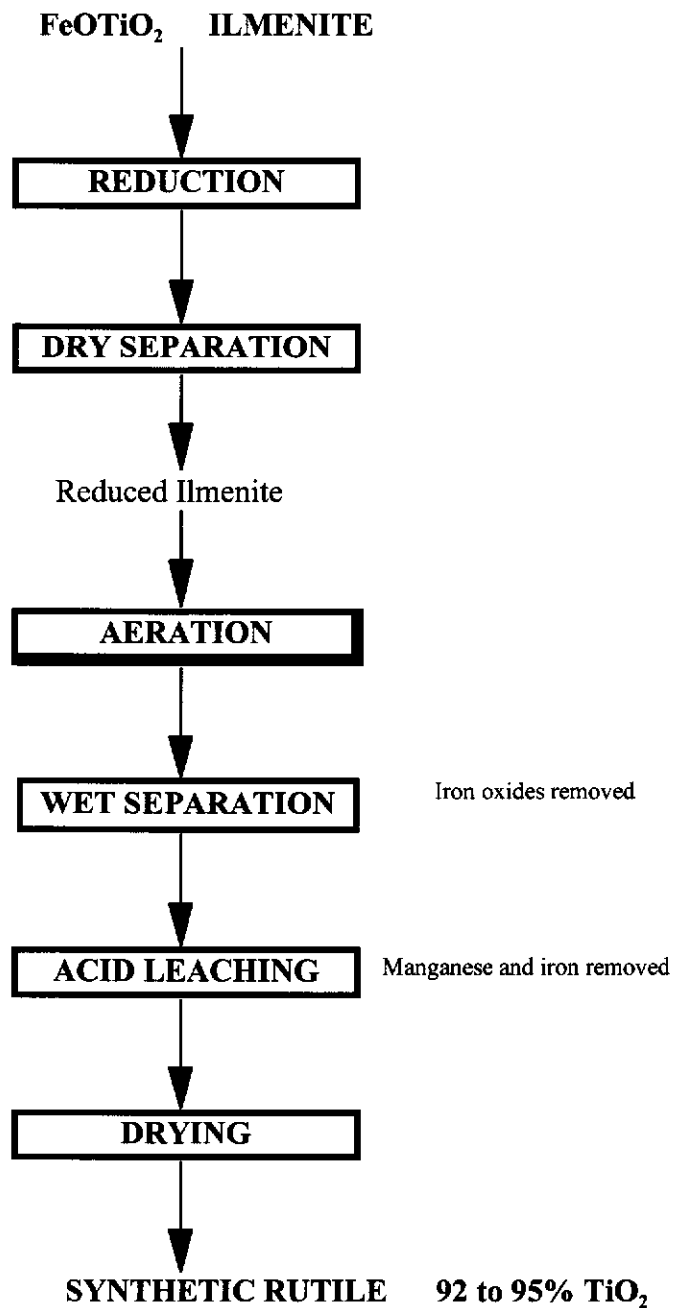


Figure 1.1: A diagrammatic representation of the six stages of the Becher process.

As can be seen in Figure 1.1 there are six stages in the ilmenite upgrading process. The raw material for this process is ilmenite (FeOTiO_2) which is separated with other heavy mineral sands from silicate materials in the beach sands by using a series of spirals. To separate the ilmenite from the other heavy mineral sands electrostatic and magnetic separators are used.

The first stage of the ilmenite upgrading is the reduction stage. The reduction of ilmenite occurs in a rotary kiln at 1150 degrees Celsius using coal and char as reductants (Palmer, 1990). The retention time of ilmenite in the kiln is between 13 to 16 hours, during which time the iron oxides present are reduced to metallic iron.

The second stage of the upgrading is the dry separation stage. Here the “reduced ilmenite” (RI) is separated from the char by the use of magnetic separators to give a final product which can be represented by the formula FeTiO_2 .

The third stage of the process is the aeration stage; this is in essence the Becher process. The reduced ilmenite is placed in an aerator tank (typically of the order of 100 m^3) with a one per cent ammonium chloride solution. The solution is stirred by a propeller with air pumped into the bottom of the tank at a rate of 2000 to 4000 m^3 per hour. In the aerator the metallic iron is oxidised by oxygen to ferrous ion and removed from the grain to precipitate as iron oxides outside the reduced ilmenite grain. This process typically takes 14 to 20 hours for a 20 tonne batch of reduced ilmenite.

The wet separation stage, the fourth stage, uses a series of cyclones to separate the denser upgraded ilmenite from the less dense iron oxides.

The fifth stage of the process is an acid leach. The stage uses sulfuric acid to remove any accessible metallic iron that may be left in the grains and to remove manganese sulfide and other soluble impurities from the grains.

The final stage is a drying stage that incorporates the use of a rotary kiln to dry the final product. The final product is called synthetic rutile and has a composition of 92-95 per cent titanium dioxide.

Since the inception of the Becher process several changes have been made to the original process. The first was the use of a preoxidation stage to convert all the ferrous content to a fully oxidised ferric form (Becher *et al*, 1965). This stage was in place because previous work by Lloyd and Amundson (1961) had shown that hematite (a ferric oxide) structure was easier to reduce than magnetite (a mixed iron oxide) structure. The preoxidation stage is no longer in use at any of the synthetic rutile production plants in Western Australia. This arose from the cost of the preoxidation stage, plus the time taken to complete the stage, being too high when compared to the cost of leaving the ilmenite in the reduction kiln (without preoxidation) for longer periods to reduce the ilmenite.

Developments were also made in the reduction stage of the process to improve the quality of the product through the work of Reid, Grey and Jones, at CSIRO, Melbourne, in the field of chemical, structural, thermodynamic and phase equilibria in Fe-Ti-O and Fe-Mn-Ti-O systems (Jones, 1973; Grey and Reid, 1974; Grey, *et al*, 1974). This work also incorporated the kinetics and mechanisms of reduction of natural and synthetic ilmenites using both carbon monoxide and solid carbon (Sinha, 1988).

The other change to the Becher process has been the introduction of sulfur additions in the reduction process. Rolfe (1973) discussed the use of sulfur in the reduction stage of the Becher Process. His work showed that adding sulfur at approximately 1 to 2 per cent of the weight of ilmenite led to the formation of soluble transition metal sulfides at temperatures close to 1050 degrees Celsius. As a result of these reactions several advantageous effects were found. 1: A significant increase in the degree of metallisation occurred. 2: The lowering of kiln temperatures to 1150 degrees Celsius from temperatures as high as 1700 degrees Celsius (Merk and

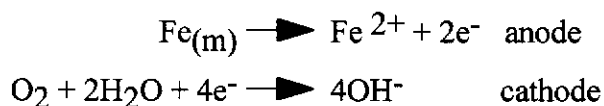
Pickles, 1988) reduced the cost in fuel. 3: The removal of manganese and iron during the aeration and mild acid wash is enhanced by the formation of metallic sulfides.

Later, Li and Merrit (1990) went on to investigate the effects of reduction temperature, reduction time and oxygen fugacity in a kiln on the grade of synthetic rutile produced. In these experiments sulfur was added to the reduction stage and was found to create manganese sulfides to some extent. The extent of reaction was dependent on reduction temperature, the reduction time and oxygen fugacity. They also found that there was an optimum temperature below which the reduction was no longer improved. This finding was in contrast to the prediction by Rolfe (1973) based on laboratory experiments.

1.4.2 The Becher process mechanism

The research work for the upgrading of ilmenite ore in Western Australia began in the early 1960's when Robert Becher began to develop a process to produce titanium dioxide pigments from local beach sands. The first publication by Becher and his associates at the W.A. Government Chemical Laboratories was in 1963 (Becher, 1963). This was the patent for the process, and then in 1965 another paper was released giving a description of the full process (Becher *et al*, 1965). This paper described the initial laboratory and pilot scale plant tests carried out on the Becher process.

The second stage of the Becher process, the aeration stage, was claimed to consist of two half reactions.



which can give a complete equation for the formation of ferrous hydroxide



However, this equation does not explain how the ferrous hydroxide (or ferrous ion) is transported out of the reduced ilmenite grain and then precipitated in the bulk solution. The rate determining step that was suggested by Becher *et al* (1965) involved the diffusion of oxygen through the solution to the iron in the grains.

Becher *et al* also stated in their 1965 paper a possible rationale behind the use of a 0.5 per cent w/v ammonium chloride solution in the aeration stage. The rationale was, in part, explained through the work of Denholm (1962) which showed that chloride ion prevented the creation of a protective iron oxide layer around the reduced ilmenite grain, so that metal dissolution occurred faster. The other part of the reasoning came from Mandyczewsky (1964) who suggested that precipitation of ferrous hydroxide would be expected to take place close to, or within, the grain where there was a localised build up of hydroxide ions (from the reduction of oxygen which accompanies the oxidation of iron). It was suggested that ammonium ions would buffer this localised system so there would not be immediate precipitation. These factors, combined with the fact that ammonium chloride is relatively inexpensive, made it an ideal reagent. It has also been shown that ammonium chloride is most effective at concentrations of 0.5 to 1.0 per cent w/v.

An actual mechanism of the aeration procedure was not fully described until Farrow and Ritchie (1985) suggested that the rate determining step involves the diffusion of oxygen to the reduced ilmenite grain (Farrow *et al*, 1987).

The suggested mechanism is as follows :

(i) The oxygen contacts the porous reduced ilmenite grain and oxidises the metallic iron to the iron (II) ion, also producing hydroxide ions.

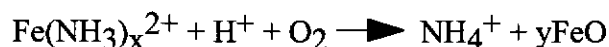
(ii) The soluble ionic iron is then able to move through the grain as the ammonium chloride is acting as a buffer to prevent immediate precipitation of ferrous hydroxide



It is then suggested that the ionic iron forms a stable complex with the ammonia species at the localised pH.



(iii) As the complex ions move out of the localised pH within and around the grain into the bulk solution, which is more acidic, the complex ion becomes unstable and breaks apart allowing the ammonia to react with acid to form ammonium ions and iron (II) ions which can subsequently form iron(II) oxides and/or iron(III) oxides (Ward *et al*, 1989; Ward, 1990).



This mechanism is based on a substantial amount of evidence, and is consistent with the results from previous research (Farrow and Ritchie, 1985) (Farrow *et al*, 1987) (Schick and Uhlig, 1964), but lacked conclusive proof until research was completed on the existence of iron - ammonia complexes. Lewis (1994) built on earlier work, (Isaev *et al*, 1990), (Jones and Hackerman, 1968), (Klocke and Hixson, 1972), (Leussing and Kolthoff, 1953), (Mironov *et al*, 1992), (Osseo-Asare, 1981), (Queneau and Weir, 1986) to prove the existence of the iron - ammonia complex in the pH range of 6 to 8.

1.5 Significance of the research

Although the Becher process is used exclusively in Western Australia it creates an export market of over 253 million dollars per annum with the export of synthetic rutile alone. Added to this, the industry also produces over 127,000 tonnes of pigment grade titanium dioxide each year, worth around 2,557 dollars per tonne.

With the commercial application of the Becher process being restricted to Western Australia, mainly because the type of ore and the type of coal produced locally make the process viable here, there has been very little research conducted on the process elsewhere apart from at the CSIRO in Victoria. Much of the research

work that has been carried out has been done within the industry, where the objectives relate to process improvements. In addition, results from much of this work remain in house as commercial secrets.

There is a need for research to be conducted in this area to develop a greater understanding of the mechanism of the Becher process chemistry and the kinetics of the reactions so that more effective processing conditions can be found from logical prediction.

1.6 Objectives

1.6.1 Mechanistic study of the Becher process

From the previous sections it is obvious that the titanium industry is a major export earner for Western Australia. It is also apparent that little research has been conducted into the mechanism of the Becher process. It is the aim of this work to further research the mechanism of the removal of metallic iron from reduced ilmenite in the Becher Process stage for the upgrading of reduced ilmenite to synthetic rutile.

1.6.2 Effect of temperature

When dealing with the effect of temperature on removal of metallic iron from reduced ilmenite, there are two main factors to consider. The first is that oxygen solubility decreases as the temperature increases (Crisafio *et al*, 1994). The second is that temperature increases the rate and energy of collisions by imparting more energy to a molecule to move through solution (diffusion) and so the intrinsic rate of reaction will increase.

Industry has chosen to use a temperature between 70 to 80 degrees Celsius for a combination of reasons, and this appears to be the most effective temperature for the removal of metallic iron.

The objective of this segment of research is to look at the effect of the temperature in terms of leaching capability and the final products.

1.6.3 Effect of pH

In an unmodified system the pH will be approximately 6.7 due to the ammonium chloride buffering action. Industry at the moment uses the natural pH created by the reduced ilmenite and its leaching agents to remove the metallic iron. A little work has been carried out in this area by Farrow and Ritchie (1985) but this was on a very small scale and was only a preliminary investigation. The objective of this section is to look at a wider range of pH.

1.6.4 Effect of oxygen partial pressure

Industry, at present, uses air as the source of oxygen for the aeration stage. The oxygen partial pressure in air is approximately 20 per cent of the total pressure. An increase in the partial pressure of oxygen in the gas stream feeding into the aerator could prove to be a major benefit as it is quite possible that the oxidation rate may increase. This could be of major importance as it is the oxygen diffusion through the solution to the slurry that is presently thought to be the rate determining step (Farrow *et al*, 1987)

The objective of this section is to study the effect of varying the partial pressure of oxygen on the leaching rates. It is also important to determine the extent of improvement in leaching compared with the cost of enriching the gas supply with oxygen.

1.6.5 The effect of solution composition

There are two separate investigations that come under this heading. The first is the effect of the concentration of ammonium chloride and the second the effect of

substituting other leaching media for ammonium chloride.

1.6.5.1 The concentration of ammonium chloride

At present industry uses a concentration of approximately 1 per cent ammonium chloride solution, but little research has gone into the optimum concentration of ammonium chloride. The ammonium chloride influences two aspects of the solution chemistry. The first, positive aspect, is that it buffers the pH, prevents oxide layers forming on the reduced ilmenite grain surface and possibly complexes with ferrous ion at high pH. The second, negative, aspect is that the more concentrated the solution the less soluble oxygen becomes. The aim of this section of work is to find the optimum ammonium chloride concentration for maximum leaching rates.

1.6.5.2 Substitution of ammonium chloride with other leaching media

Ammonium chloride has been used in the Becher process because of its buffering action, prevention of oxide layers forming and its possible complexing capabilities. Many other chemical reagents have some of these properties but none has been found, so far, to work as well.

The objectives of this section are to examine other leaching systems. This may lead to a better understanding of how ammonium chloride promotes the aeration process. From this, superior alternatives to ammonium chloride may be found.

Chapter Two

Materials and experimental methods

2.1 Materials and reagents

2.1.1 The reduced ilmenite samples

The reduced ilmenite samples used in this study were obtained from within the mineral sands industry in Western Australia. Nearly all of the work was carried out on reduced ilmenite from a single batch. This sample has a composition of 28.7 per cent total iron and 66.9 per cent titanium dioxide. The exact make up of the sample is presented in Table 2.1.

Table 2.1: The composition of the standard reduced ilmenite used in most of the work.

Compound	Percentage	Method of Analysis
Metallic Fe	27.5%	Volumetric Analysis
Total Fe	28.7%	Volumetric Analysis
MnO	1.33%	XRD
TiO ₂	66.9%	XRD
SiO ₂	1.0%	XRD
ZrO ₂	0.08%	XRD
P ₂ O ₅	0.09%	XRD
Al ₂ O ₃	1.1%	XRD
S	0.46%	XRD

This sample was supplied in 20 kilogram batches from a larger sample kept on site at one of the synthetic rutile plants. The analysis of each individual 20 kilogram batch sometimes varied slightly, but the overall analysis for the entire sample is adequately represented in Table 2.1.

2.1.2 Gas and water supplies

The air used in all the experiments was introduced through an electrical air compressor. An electrical air compressor was used as it is free of exhaust carbon dioxide contamination that is found in mechanical compressors. Any other gases, such as oxygen and nitrogen, were supplied from compressed gas bottles from BOC Gases. Other special gas mixtures, eg 50 per cent oxygen - 50 per cent nitrogen, were prepared at BOC Gases Australia Ltd. and supplied in compressed cylinders to minimise the need for mixing of gases.

Water used in these experiments is common local tap water. Tap water was used instead of distilled water because the exclusion of the minerals and ions from the water could have a minor effect on the results in the form of aeration time and the aeration product. Some industrial plants use recycled process liquor that contains a large quantity of soluble materials that could have a minor effect on the leaching whilst other plants use fresh water obtained from the water supply. The use of deionised water in these experiments was therefore deemed inappropriate, as tap water is a close approximation to the process water in plants using fresh water. Typical species concentrations in local tap water are shown in Table 2.2.

Table 2.2: Concentrations of species in Perth scheme water (Henderson *et al*, 1991)

	Mean	Minimum	Maximum
pH	7.0	5.7	9.8
Turbidity	0.6	0.1	6.2
Colour	3	< 1	11
Conductivity	53.3	17	93
Total Filterable Solids	300	100	570
Sodium	70	24	167
Potassium	4	1	11
Calcium	16	2	89
Magnesium	7	2	16
Chloride	118	42	244
Sulfate	21	2	71
Alkalinity *	38	2	202
Hardness **	66	15	264
Silica	10	2	37
Fluoride	0.85	0.14	1.3
Nitrate	0.9	< 0.4	7.5
Filterable Organic Carbon	2.8	0.5	11.2
Iron	0.041	< 0.005	0.39
Manganese	< 0.005	< 0.005	0.069
Aluminium	0.05	< 0.01	0.54

(All values are mg / L) * as Calcium Carbonate, ** as Calcium Carbonate

2.1.3 Leaching reagents

The various leaching reagents used in the aeration trials, and their sources, are listed in Table 2.3.

Table 2.3: Table of the leaching agents used in this work, and their suppliers.

Leaching Agent	Grade	Supplier
m-Aminobenzoic Acid	98 % Purity	Aldrich
Ammonium Chloride	Analytical Reagent	Ajax Chemicals
Ammonium Nitrate	Analytical Reagent	Ajax Chemicals
Ammonium Perchlorate	Laboratory Reagent	Ajax Chemicals
Ammonium Sulfate	Analytical Reagent	Ajax Chemicals
Aniline Hydrochloride	Laboratory Reagent	BDH Chemicals
m-Chloroaniline Hydrochloride	Guaranteed Reagent	Tokyo Chemical Industry
o-Chloroaniline Hydrochloride	Extra Pure Reagent	Tokyo Chemical Industry
p-Chloroaniline Hydrochloride	Guaranteed Reagent	Tokyo Chemical Industry
Citric acid	Analytical Reagent	BDH Chemicals
Dimethyl Ammonium Chloride	Technical Reagent	Ajax Chemicals
Disodium Oxalate	Analytical Reagent	Ajax Chemicals
Disodium Tartrate	Analytical Reagent	Ajax Chemicals
Ethylene Diammonium Chloride	>99 % Purity	Fluka
Glycine	Analytical Reagent	BDH Chemicals
Hydrochloride Acid	32 % w/w	Ajax Chemicals
Methyl Ammonium Chloride	>99 % Purity	Merck
m-Nitroaniline Hydrochloride	Guaranteed Reagent	Tokyo Chemical Industry
o-Nitroaniline Hydrochloride	Extra Pure Reagent	Tokyo Chemical Industry
p-Nitroaniline Hydrochloride	Guaranteed Reagent	Tokyo Chemical Industry
Oxalic Acid	Analytical Reagent	Ajax Chemicals
Sodium Acetate	Analytical Reagent	BDH Chemicals
Sodium Chloride	Analytical Reagent	BDH Chemicals

Leaching Agent	Grade	Supplier
Sodium Hydroxide	Analytical Reagent	Rowe Scientific
Sodium Nitrate	Analytical Reagent	Ajax Chemicals
Sodium Perchlorate	Laboratory Reagent	Ajax Chemicals
Sodium Sulfate	Analytical Reagent	BDH Chemicals
Tartaric Acid	Analytical Reagent	Ajax Chemicals
Tetramethyl Ammonium Chloride	98 % Purity	WAKO Pure Chemicals
m-Toluidine	>99 % Purity	Fluka
o-Toluidine Hydrochloride	>98 % Purity	Fluka
p-Toluidine Hydrochloride	Laboratory Reagent	BDH Chemicals
Trimethyl Ammonium Chloride	95 % Purity	WAKO Pure Chemicals
Trishydroxymethyl Aminomethane	>99 % Purity	Merck
Trisodium Citrate	Analytical Reagent	BDH Chemicals

2.2 Reactor design

2.2.1 The 5.0 litre aerator design

Leaching experiments were conducted in a 5.0 litre modified autoclave, shown in Figure 2.1.

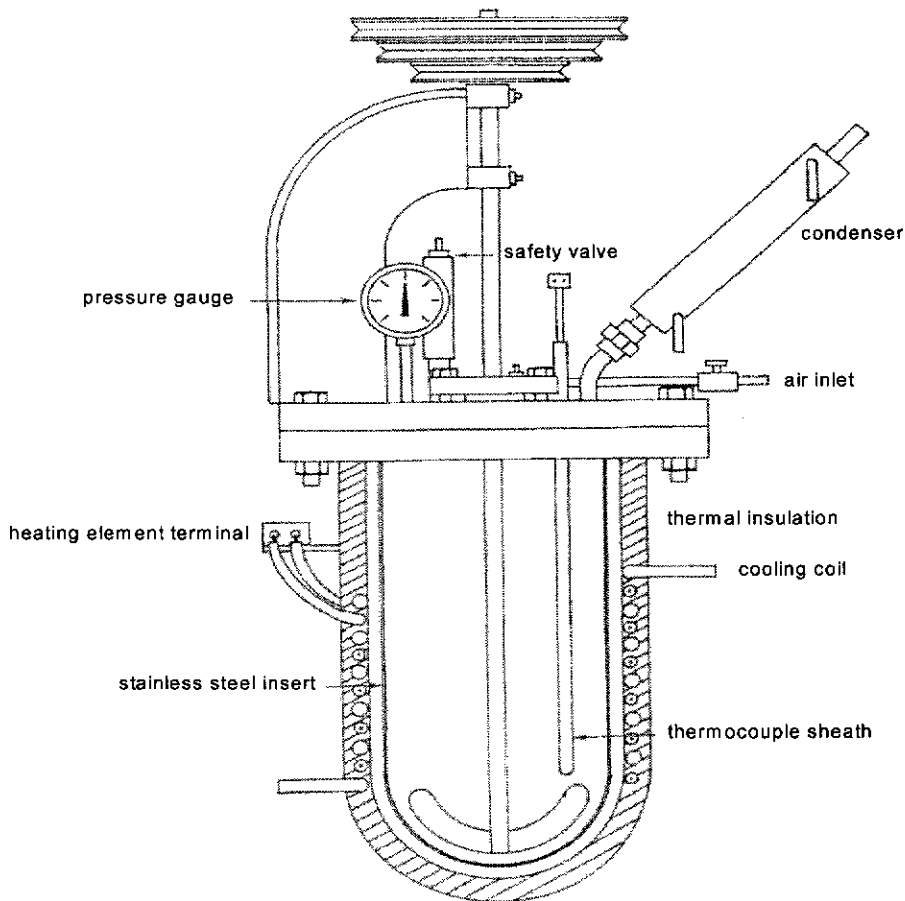


Figure 2.1: Schematic diagram of the 5.0 litre aerator

The autoclave contains a stainless steel insert allowing the reaction mixtures and products to be easily removed and therefore retained. There are two additional features of the apparatus that are not shown in Figure 2.1. The first of these was that the air was introduced into the pulp via a thin metal tube that extends the same distance as the thermocouple sheath into pulp; that is just above the propeller. The hole at the end of the air tube was approximately 5 millimetres in diameter and was covered by a flexible piece of hose such that the air could go into solution but the pulp could not enter the air tube. The second feature consists of two baffles, 1.0 centimetre wide, placed on opposite sides of the main stainless steel insert to assist mixing.

2.2.2 The inverted cone aerator design

Laboratory scale leaching experiments were also conducted in a one litre inverted cone aerator. In the design of the inverted cone reactor two factors were considered: firstly, to aerate a sample of reduced ilmenite faster than the 5.0 litre aerator and secondly, to be able to use a quantity of 20 grams of solids or higher.

The design tests began by using an inverted cone vessel designed from the specifications of the inverted cone used by Farrow and Ritchie (1985), which is represented in Figure 2.2. This simple design allowed a small sample of 30 grams of reduced ilmenite to be suspended in the solution by means of air being introduced through the bottom of the vessel.

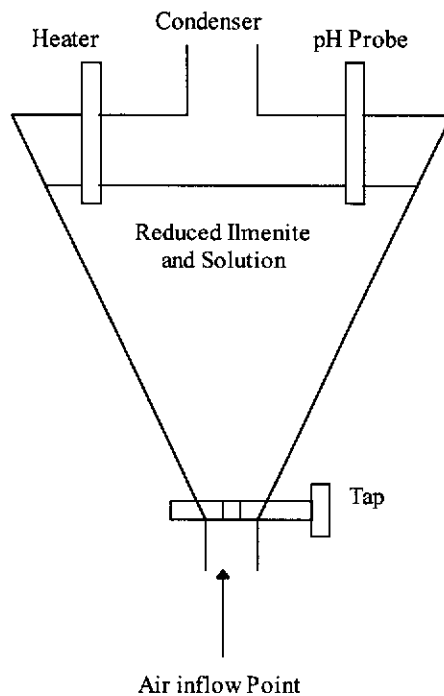


Figure 2.2: A diagram of the original inverted cone aerator

The aerator shown in Figure 2.2 was unable to treat charges of reduced ilmenite greater than 30 grams because the only force used to suspend the solids came from the air flowing through the inflow hole. As this hole was large, the air was

dispersed, thereby decreasing the force used to suspend the solids. A series of taps with smaller holes was tested but it was found that, although larger amounts of solids could be suspended, a dead space was created on either side of the inflow hole, and so solids would settle in this dead space.

To overcome these problems the tap system was removed and replaced with a direct line to the air inflow with a one way valve in the flow line as shown in Figure 2.3.

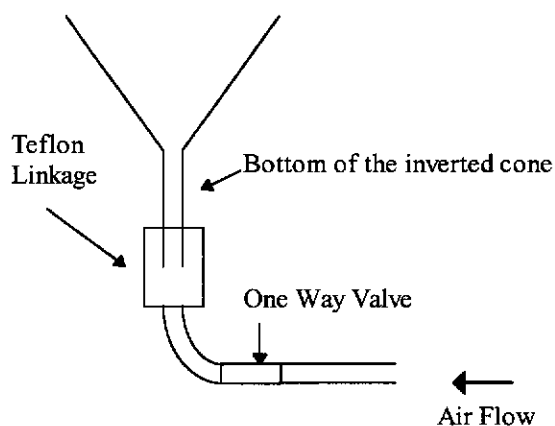


Figure 2.3: Modifications to the air inflow of the inverted cone aerator.

Through the improvements shown in Figure 2.3 the aerator was able to hold 40 to 50 grams of reduced ilmenite in suspension. Although progress had been made in suspending more solids, the whole system relied upon a high air flow rate to sustain the solids in suspension. This therefore meant that any experiments at low air flow rates could not be conducted. As these limitations were not acceptable, the concept idea of using the air inflow as the means to suspend the solids was revised.

A new design that involved the use of a circulating solution as the means of suspending the solid was introduced. In this system the leaching solution was pumped into the bottom of the inverted cone and pumped out of the inverted cone at the top with a peristaltic pump fitted with a variable speed controller. To achieve this the glass cone vessel itself was reshaped so that a volume at the top of the cone would contain mainly liquid, ie the majority of the coarse solids would remain in the

lower part of the vessel. This was required because any solids passing through the pump would be crushed and therefore ruin the integrity of the experiment. The method used to segregate the solids and liquids was to employ two different gradients in the cone as can be seen in Figure 2.4. The air in the new system was introduced into the line below the suspended solids to allow the oxygen to dissolve and continue the leaching. To achieve this the air inflow line was joined to the line pumping the solution into the bottom of the cone (see Figure 2.4).

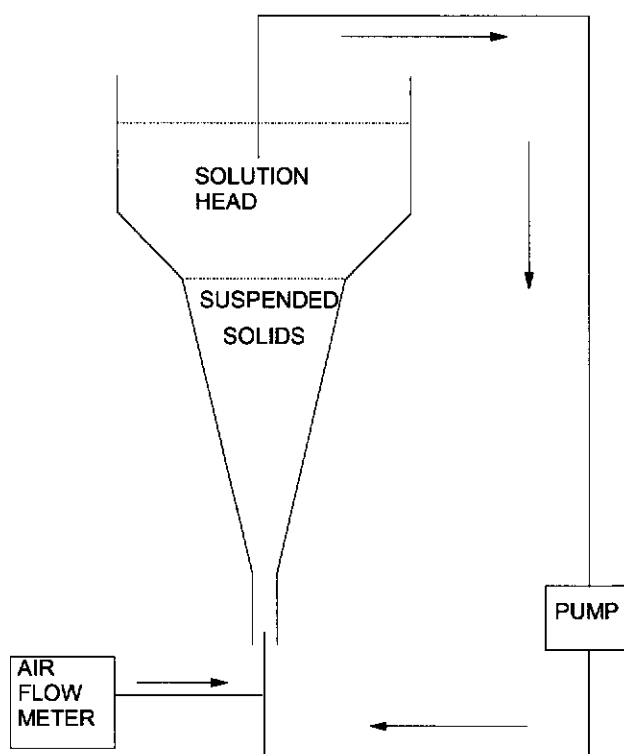


Figure 2.4: Continuous solution flow aerator

By using the apparatus shown in Figure 2.4 the solids were suspended in the lower section of the cone while a liquid head was maintained in the higher section through the use of a continuous solution flow creating a fluidised bed. The air flow could then be adjusted to lower levels without causing the solids to settle out. Additionally, by using a pump with variable speeds, 100 grams or more of solids were able to be suspended. The final change to the system was the removal of the heating rod, which disturbed the inflow of the solution. The heating element was

replaced by a heated water jacket, with hot water supplied from a circulating water bath.

The final design for the glass inverted cone aerator is shown in Figure 2.5. The aerator was a glass vessel with a steeply sloped area, in which the solids would be suspended, and a broader section that would allow a liquid head to form. The cone shape itself was encased in a glass sheath so that heated water from the water bath could be used to heat the system. The leaching solution within the cone was circulated by a Cole Parmer peristaltic pump and solid state speed controller, with a Masterflex 7015-20 head attached. The air flow was introduced into the solution circulation line through either of two Fisher and Porter air flow meters, allowing for different flow rates. All linkages for lines to the aerator, pump or air flow were completed with Swagelok stainless steel connections. The reactor is open to the atmosphere as there are no air seals on the three upper most ports.

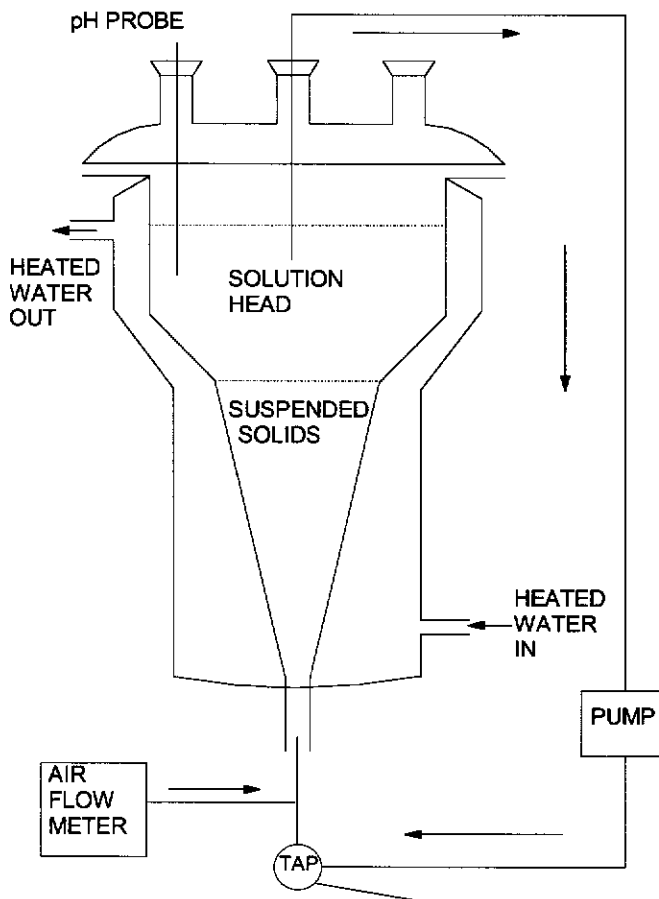


Figure 2.5: The final design of the inverted cone fluidised bed aerator.

2.3 Experimental procedures

2.3.1 Experimental procedures for the 5.0 litre aerator

In all experiments the initial reaction mixture, which was placed in the stainless steel insert, comprised 1.8 litres of hot water, a measured amount of reduced ilmenite (RI) and a measured amount of aeration catalyst. The reagents were raised to the temperature of experiment using the electrical heater of the autoclave. Once the slurry had reacted the required temperature the gas flow was then started at the required rate and the stirrer was turned on to a constant 220 revolutions per minute.

The pH was measured initially at room temperature (20 – 30°C) before the solution was heated to the experimental temperature. Once at experimental temperature (eg 70 – 80°C) the reduced ilmenite was added and the pH immediately remeasured. Thereafter the pH was measured at the experimental temperature.

After the individual tests were completed the autoclave was dismantled and the stainless steel insert was removed. The contents of the insert were then washed through a 38 micron sieve. The liquid and minus 38 micron solids were collected in a bucket and allowed to settle for at least 12 hours. After the settling period the excess water was decanted off, the remaining solids were washed into a tray and placed in an oven to dry. The dry solids comprised iron oxides produced during aeration, along with minor impurities. The plus 38 micron solids (the upgraded ilmenite) were oven dried as above.

2.3.2 Experimental procedures for the inverted cone fluidised bed aerator

In all experiments using the inverted cone the water bath controlling the temperature of the cone was set to the temperature of the experiment and allowed to begin heating. While the temperature was rising, 1.0 litre of hot tap water was

measured out and the set amount of aeration catalyst was dissolved into the water. The air flow, from the air flowmeters, was then allowed to begin passing through the cone. The 1.0 litre of catalyst solution was then added to the cone and finally the required amount of reduced ilmenite was added to the cone. Once the reduced ilmenite had settled below the head area of the reactor, the peristaltic pump was switched on. The temperatures of the water bath and the solution within the cone were constantly monitored. The slurry was then aerated for a set amount of time or until the aeration was completed.

After the individual tests were completed the inverted cone was emptied by switching the peristaltic pump off and opening the tap in the circulation line to allow the contents of the cone to drain out. The contents of the cone were then washed through a 38 micron sieve. The liquid and minus 38 micron solids were collected in a bucket and allowed to settle for at least 12 hours. After the settling period the excess water was decanted off, the remaining solids were washed into a tray and placed in an oven to dry. The dry solids comprised iron oxides produced during aeration, along with minor impurities. Due to the small sample size the dried minus 38 micron product was insufficient for analysis. The plus 38 micron solids (the upgraded ilmenite) were oven dried as above.

2.4 Methods of analysis and calibration of data

2.4.1 SATMAGAN analysis

The progression of the aeration experiments was followed by taking a solids sample (reduced ilmenite) at regular intervals. The solids were then washed, dried, then ground in a mortar and pestle and finally analysed for their metallic iron content. These analyses were carried out by the use of a Saturated Magnetic Analysis balance (SATMAGAN). As the results obtained from the SATMAGAN are dimensionless a calibration graph of SATMAGAN values against the percentage of metallic iron

determined by chemical analysis was used to calculate the actual percentage metallic iron.

2.4.2 Metallic iron analysis

The percentage metallic iron content of samples used for the calibration of the SATMAGAN was determined by a wet chemical method at the Chemistry Centre (W.A.). Firstly, the ilmenite samples were ground in a tungsten carbide ring mill and then treated with a copper sulfate solution. The solution was then filtered and acidified with sulfuric acid. Aluminium fines were then added to the boiling solution to reduce the remaining copper (II) ions to copper. After complete removal of the copper (II), the solution was cooled and filtered. The solution remaining was diluted to 300 mL and then combined with phosphoric acid and three drops of barium diphenylamine sulfonate indicator. The solution was then titrated with potassium dichromate to a purple end point. From these titrations the percentage metallic iron was determined and then used to calibrate the SATMAGAN results.

2.4.3 Total iron analysis

The total iron analysis of the reduced ilmenite samples was conducted by a wet chemical technique. The samples were first ground in a tungsten carbide ring mill then the samples were decomposed by a fusion with sodium peroxide. The fused solid was then dissolved in dilute sulfuric acid. The resulting solution was then treated with stannous chloride followed by mercuric chloride. The solution was then diluted and titrated with potassium dichromate with barium diphenylamine as the indicator. The results of the titrations gave a total percentage value for all iron present as metallic iron or any form of iron oxide.

2.4.4 Iron oxide analysis

The iron oxides formed during the aerations were separated and dried. The dried oxides were then made into a pressed powder disk and then analysed on a Phillips PW1710 X-ray diffractometer. After the scans were completed the data were matched using peak search software. A semi-quantitative analysis was carried out by comparison of relative peak intensities and further supplemented with SEM / EDXRA to give an approximate concentration.

2.4.5 Manganese analysis

Manganese content, in a reduced ilmenite sample, was analysed after fusion with sodium borate to dissolve all elements in the sample into the glass. The glass was then dissolved in hydrochloric acid and analysed with an ARL 3410 simultaneous inductively coupled plasma spectrometer.

Chapter Three

Ammonium chloride as a catalyst in the Becher process

3.1 Introduction

As discussed in Chapter One, the Becher process uses ammonium chloride in the aeration solution to assist in the removal of the metallic iron from the reduced ilmenite grains. Once in the bulk solution the iron can be oxidised further to form iron oxides (Ward *et al*, 1989). The ammonium chloride is said to have three properties that make it so important. These are its ability to buffer the solution (Farrow and Ritchie, 1985), to prevent passive iron oxide films from forming on the surface of the metallic iron in the reduced ilmenite grains (Marinovich *et al*, 1995) and its ability to form a stable complex with the iron (II) ions in the grains (Lewis, 1994). This complex is then able to break apart on entering the bulk solution due to a differing pH.

3.2 Aeration at differing air flow rates

3.2.1 Low pulp density tests.

An initial charge of 100 grams of reduced ilmenite, with 9 grams of ammonium chloride and 1.8 litres of water was held at 70 - 80 degrees Celsius for a 5.0 hour period. The air flow rates evaluated varied between 0.0 to 1.0 litre per minute. Periodic samples of the reduced ilmenite were taken for metallic iron analysis and these results are shown in Figure 3.1.

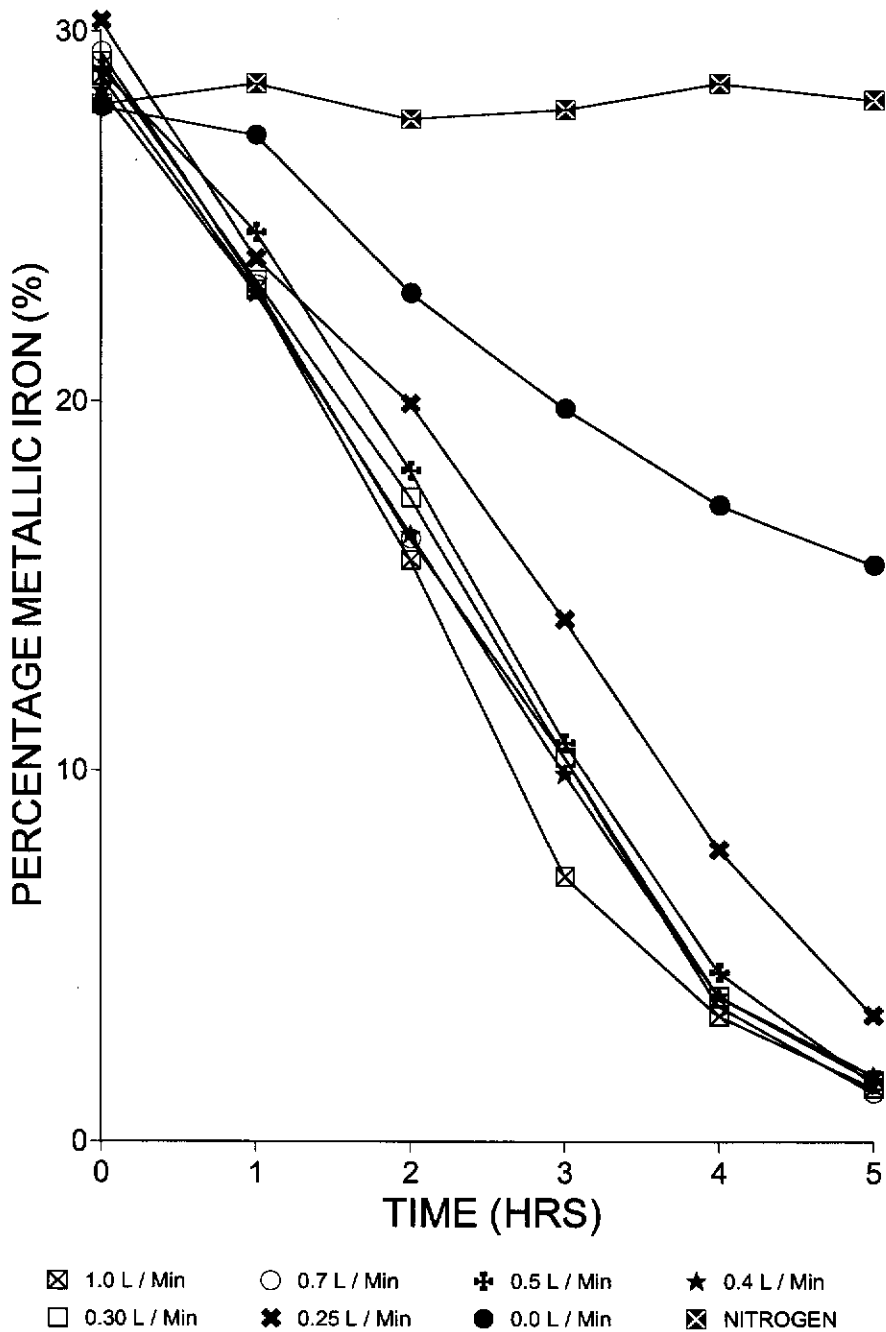


Figure 3.1: The effect of air flow rate on the removal of metallic iron in a reduced ilmenite slurry consisting of 100 grams RI, 1.8 litres of water and 9 grams of ammonium chloride at 70-80 degrees

From Figure 3.1 it can be seen that at air flow rates of 0.30 litres per minute and above, the reduced ilmenite was leached at a similar rate. This produces a residual metallic iron level of 1.3 to 1.7 per cent after 5.0 hours. The removal of metallic iron occurs at a fairly constant rate for the first 4 hours and then slows down in the last hour. This would seem to indicate that the leaching of the readily

accessible iron was essentially complete. The small amount of residual metallic iron as measured by the SATMAGAN was assumed to be a combination of iron that was inaccessible to the leaching reagents or possibly due to the presence of other magnetic species.

The test utilising 0.0 litres per minute of air had approximately 10 grams or 40 per cent of the available metallic iron leached out after 5.0 hours, while no detectable iron was leached when using a nitrogen purge for the same amount of time. As very little oxygen is soluble in water, at 70 degrees Celsius, this iron removal cannot be attributed to oxygen originally present in the solution. It is possible that the bulk solution, being at a slightly acidic pH could have dissolved the iron by consumption of the acid from the ammonia - ammonium equilibrium. The ionic iron would then be transported in the usual way to the bulk solution. However, since no iron dissolved under a nitrogen atmosphere, and only 10 litres of air would be required to dissolve the ten grams of iron, it seems more probable that the stirring and sampling procedures led to the introduction of a certain amount of air.

To assess the completion of the reaction another sample was aerated at 0.75 litres per minute of air for a 24 hour period. The residual metallic iron level after the initial 5.0 hour aeration was found to be 1.3 per cent. At the end of 24 hours that level had dropped to 1.1 per cent metallic iron. As there was only a small difference in these percentages and accounting for experimental error, it can be concluded that the reaction was essentially completed in 5.0 hours.

3.2.2 High pulp density tests.

The second series of experiments used 300 grams of reduced ilmenite corresponding to approximately half the pulp density used in plant practice. All other conditions were kept identical to the low pulp density tests (section 3.2.1) and observed over a 7.0 hour period. The results of these tests are shown in Figure 3.2.

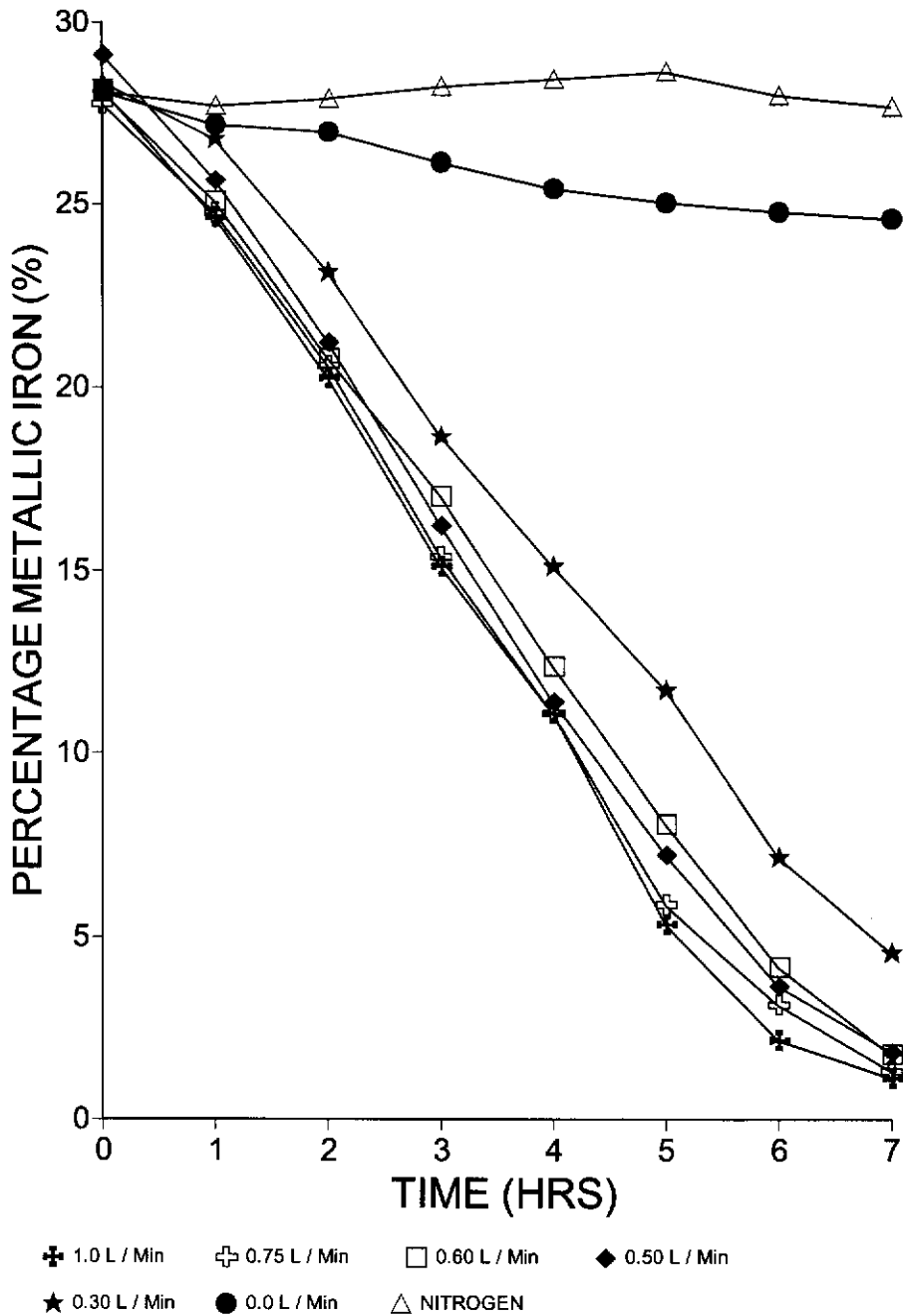


Figure 3.2: The effect of air flow rate on the removal of metallic iron in a reduced ilmenite slurry consisting of 300 grams RI, 1.8 litres of water and 9 grams of ammonium chloride at 70-80 degrees

The data plotted in Figure 3.2 indicate a similar residual iron level being approached after 7.0 hours at air flow rates exceeding 0.5 litres per minute. This residue contains in the region of 1.1 to 1.7 per cent metallic iron. It also appears that as the air flow rate increases the rate of reaction increases moderately.

Air flow rates below 0.50 litres per minute resulted in less iron removal after

7.0 hours. Another reaction mixture was made up and aerated at 0.3 litres per minute of air for 20 hours. At the end of this period the residual metallic iron level was 1.3 per cent, the same level reached after 7.0 hours in the pulps that used 0.5 litres per minute or higher air flow rates.

The data recorded for leaching 300 grams of reduced ilmenite at 0.0 litres per minute air, or under nitrogen differ in the same way as was found in tests using 100 grams of reduced ilmenite. It is instructive to note that irrespective of the mass of reduced ilmenite, a loss of around 10 grams of metallic iron resulted from both tests at 0.0 litres per minute of air, while no metallic iron was leached under the nitrogen purge. This evidence confirms that the metallic iron was dissolved by adventitious oxygen, since the total amount (but not percentage) of iron loss is essentially identical for each charge of reduced ilmenite as would be expected from a steady ingress of oxygen.

3.2.3 Iron oxides produced

The final products from the series of aerations at different air flow rates gave either a black or brown coloured oxide after 5.0 or 7.0 hours of aeration. In most cases the colour of the oxide appeared to be a dark brown colour after the first hour of aeration. The lower pulp density experiments typically remained this colour for the remainder of the leaching time. In the case of the higher pulp density experiments the colour of the oxide had changed to black by the second hour and then remained so for the rest of the aeration time. The final product of the 0.5 litre per minute aeration, for both pulp densities, was judged to be a typical example of this series. As there are 13 different known iron oxides, oxyhydroxides and hydroxides (Schwertmann and Cornell, 1991) visual inspection can not be used alone in the determination of the oxide type. Therefore, the 0.5 litre per minute aerations were analysed by X-ray diffraction techniques to establish the type of oxide/s created under these conditions. The results of the oxide analyses showed that the 0.5 litre per minute flow rate using a lower pulp density produced a dominant amount (greater than 50 %) of haematite ($\alpha\text{-Fe}_2\text{O}_3$), a minor amount (5 - 25 %) of lepidocrocite ($\gamma\text{-FeO(OH)}$) and a minor

amount of goethite ($\alpha\text{-FeO(OH)}$). The results for the same air flow rate at a higher pulp density indicated that a dominant amount of magnetite (Fe_3O_4) and a minor amount of haematite were produced. The cause of the production of different types of oxides was thought to be the variation in the availability of oxygen. Although, in both cases, the same amount of oxygen was flowing through the slurry, the different amounts of solids in the slurry would have affected the amounts of soluble oxygen in the vicinity of the iron (II) ions. In the case of the lower pulp density there would have been more dissolved oxygen present so an oxide with a higher oxygen to iron ratio would have been created compared with a higher pulp density with less soluble oxygen present. As these leaching trials follow the same colours as the rest of their series, it is reasonable to assume that similar quantities of the same oxides were created throughout the same series.

Other factors that control the type of oxide produced include temperature, pH, iron (II) concentration, the anions and cations present (eg. chloride ion) and the presence of dissolved gases (Cornell and Schwertmann, 1996). It must also be noted that almost every iron oxide can be converted, under the appropriate conditions, to at least two other oxides (Cornell and Schwertmann, 1996). These conditions mainly concern temperature and whether the environment is oxidising or reducing. Therefore, during the course of the aeration, an oxide may be transformed, for example, from magnetite to haematite, in the presence of air (oxidant). This would be more probable in the lower pulp density trials where there is a comparatively higher level of available oxygen.

3.3 Changes in aeration related to the pulp density of the slurry

3.3.1 Removal of metallic iron as a function of pulp density

In earlier work the pulp density utilised was substantially below that used in industrial practice. Before this work could be elaborated to examine the effect of

leaching medium, it was necessary to establish that the behaviour observed was related to the higher pulp density used in industry. Consequently, aerations were conducted using pulp densities equivalent to those used commercially.

The leaching tests carried out to assess the effect of pulp density used the same slurry conditions as described in section 3.2.2 but used a range of pulp densities. The pulp densities used in these experiments were 5.26 per cent w/v, ie 100 grams of reduced ilmenite, 14.28 per cent w/v, ie 300 grams of reduced ilmenite and 25 per cent w/v, ie 600 grams of reduced ilmenite. The results of these three experiments are presented graphically in Figure 3.3.

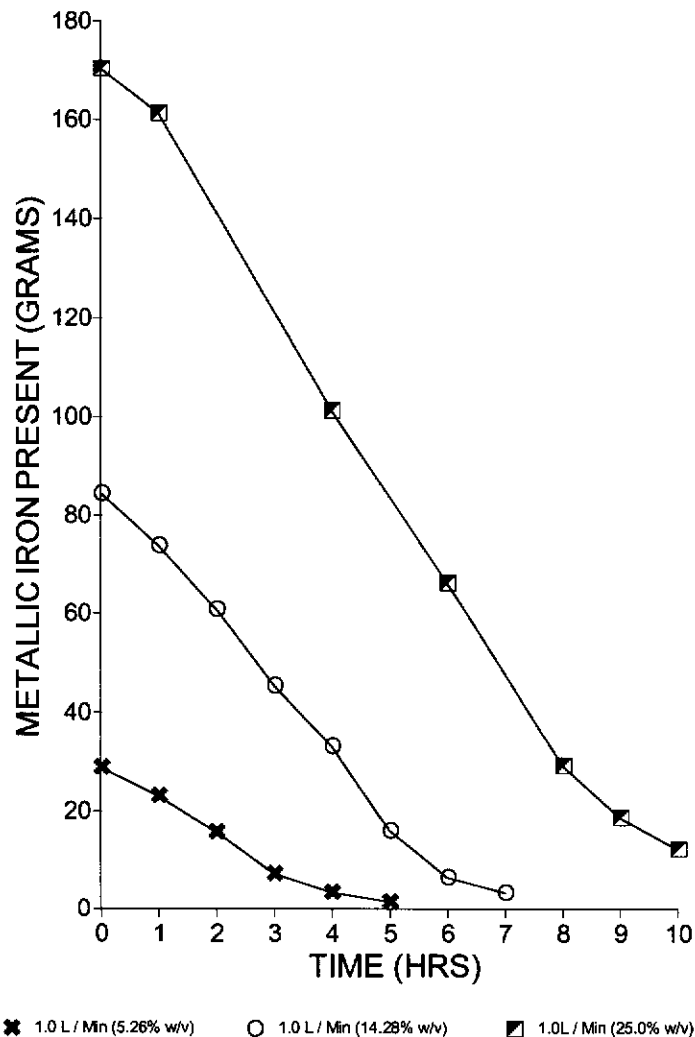


Figure 3.3: The effect of pulp density on the removal of metallic iron from reduced ilmenite under standard conditions

Figure 3.3 shows that the leaching test using a 25 per cent pulp density finished leaching all the available metallic iron in a 10.0 hour period, which was only 3 hours longer than the test with a 14.28 per cent pulp density. When comparing the test involving a 25 per cent pulp density to that for the 5.26 per cent pulp density it is evident that complete leaching took only twice as long for the higher pulp density as it did for the lower pulp density. The higher pulp density test (25 per cent) contained six times more metallic iron than the lowest pulp density (5.26 per cent) so it is clear that the oxygen utilisation was substantially more efficient. The efficiency of the gaseous oxygen consumption is shown in Table 3.1.

Table 3.1: Table of oxygen utilisation for different pulp densities to convert metallic iron to iron (II) or iron (III).

Pulp Density	Charge of RI	n(O ₂) moles	n(Fe) moles	O ₂ efficiency for Iron (II) production	O ₂ efficiency for Iron (III) production
5.26%	100g	2.45	0.462	9.4 %	14.1 %
14.28%	300g	3.43	1.387	20.2 %	30.3 %
25.0%	600g	4.91	2.774	28.2 %	42.3 %

From the data presented in Table 3.1 the increasing oxygen utilisation and hence, rate of reaction, as the pulp density increased can be attributed to several factors. The first was the reactor design itself. The air introduced into the system was delivered above the propeller blade such that the air bubbles were not broken up efficiently and therefore the mass transfer was lower (bubbles were less reactive) due to less surface area. The air bubbles must therefore rely on solids to break them up. This agrees with the comments of Nigam and Schumpe (1996) in their discussion of three phase reactors.

The second factor being that the increased pulp density resulted in a more viscous slurry. As an air bubble slowly moves up through the slurry the greater level of solids present causes more collisions between the air bubble and solids. These collisions will assist in breaking the bubble up and dispersing the oxygen though the

slurry. As the air bubble is broken up more oxygen in the air is able to interact with the solution due to increased surface area, leading to a greater rate of oxygen dissolution. Thus more oxygen is able to move into the solution to oxidise the metallic iron from the reduced ilmenite grains.

3.3.2 Iron oxides produced

The oxides produced by these three tests also vary in composition. At the lowest pulp density of 5.26 per cent, a red brown oxide was produced, which, when analysed by XRD, was found to be predominantly (greater than 50 %) haematite (α - Fe_2O_3) with a minor amounts (5 - 25 %) of lepidocrocite (γ - $\text{FeO}(\text{OH})$) and goethite (α - $\text{FeO}(\text{OH})$). The high pulp densities of 14.28 and 25.0 per cent produced black oxides that were found to be predominantly magnetite (Fe_3O_4) with traces (less than 5 %) of haematite (α - Fe_2O_3). Again the differences in the oxide composition can be explained by the amount of soluble oxygen present in each slurry. The higher the pulp density, the less dissolved oxygen will be present, so the oxygen to iron ratio will decrease as the solids in the slurry increase resulting in preferential products of magnetite over haematite.

3.4 The effect of ammonium chloride concentration

3.4.1 Removal of metallic iron as a function of concentration

The standard amount of ammonium chloride used in all previous tests was 0.093 M (9 grams per 1.8 litres of water). The concentration was varied in order to determine if any rate advantage could be obtained for the leaching of the metallic iron.

A series of tests was carried out using ammonium chloride additions ranging from 0.0 grams per 1.8 litres to 18 grams per 1.8 litres (0.19 M), with 300 grams of

reduced ilmenite. All other conditions remained unchanged as described in section 3.2.2. These results are presented graphically in Figure 3.4.

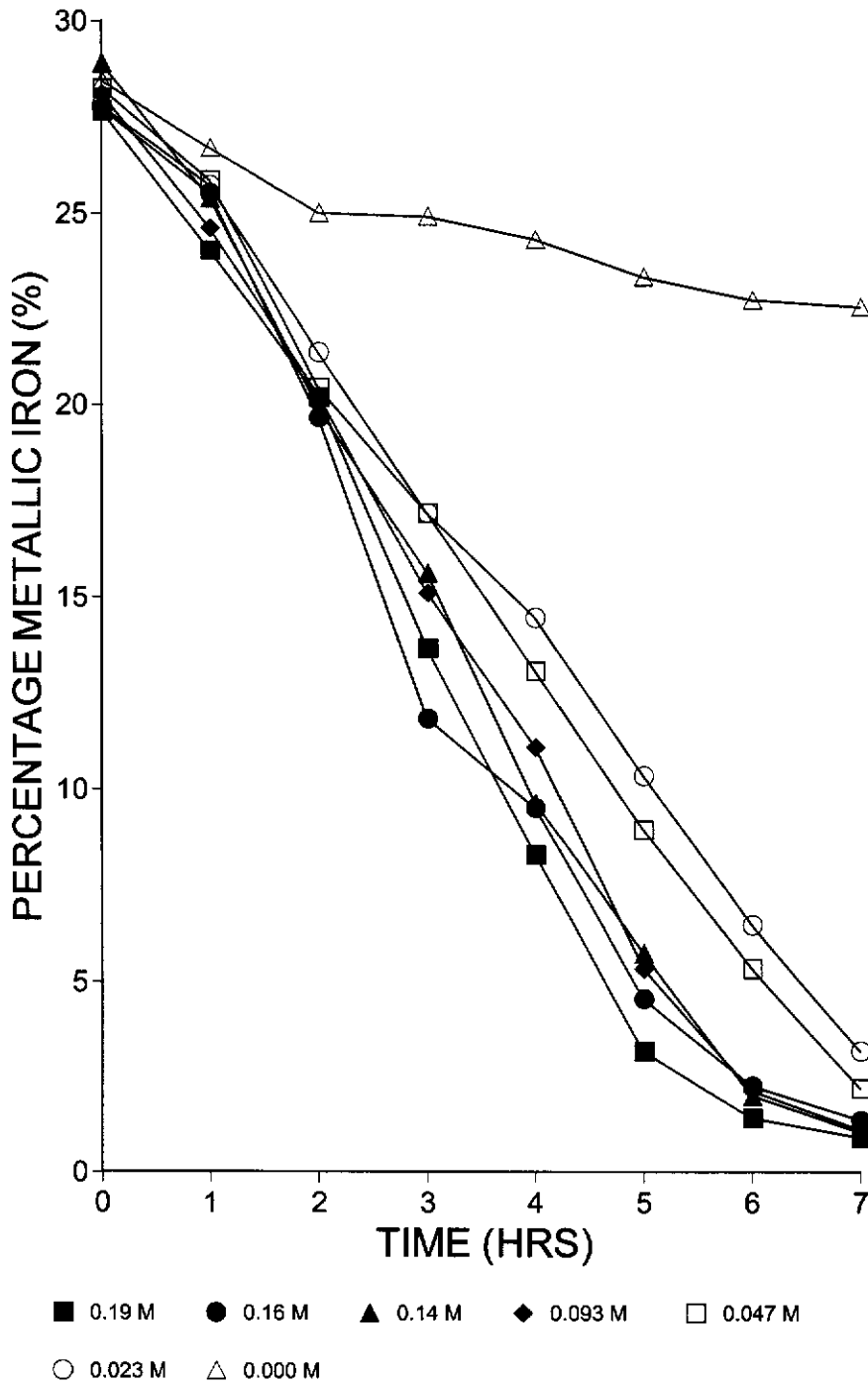


Figure 3.4: The effect of ammonium chloride concentration, 0.0 M to 0.19 M, on the removal of metallic iron from reduced ilmenite slurry (14.28 per cent)

The results shown in Figure 3.4 fall in two groups. Reaction mixtures with more than 0.047 M ammonium chloride leach better than those with less than or equal to 0.047 M. The two leaching experiments with 0.023 M and 0.047 M

ammonium chloride did not achieve such low residual metallic iron as the four reaction mixtures with higher ammonium chloride concentrations. Reaction rates were also greater for the aerations using higher concentrations of ammonium chloride.

There appears to be a general but small increase in rate of reaction as the ammonium chloride concentration increases above 0.093 M but this effect is not as marked as that observed between 0.093 M and the lower two values of 0.047 M and 0.023 M. This observation agrees with previous results discussed by Becher *et al* (1965), who concluded that the optimum ammonium chloride concentration was 0.5 percent w/v (0.093 M). Substantial increases in ammonium chloride over 1.0 per cent w/v (0.19 M) begin to hinder the reaction, the reason put forward being that higher ammonium chloride concentrations lead to a decrease in the oxygen solubility (Bracanin *et al*, 1972; Crisafio *et al*, 1994). The present study confirms that suggestion and also supports the industrial practice of using 0.5 - 1.0 per cent w/v ammonium chloride.

3.4.2 Iron oxides produced

All the oxides produced in this series of experiments were black in colour after seven hours of aeration. A typical example was taken for analysis and was found to contain a dominant (greater than 50 %) amount of magnetite (Fe_3O_4) with traces of haematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeO(OH)}$).

3.5 Aeration as a function of temperature

3.5.1 Removal of metallic iron as a function of temperature

The industry has found the temperature range of 70 to 80 degrees Celsius to be part of the optimum leaching conditions, and important in the creation of suitable oxides to allow facile separation. The best oxide is magnetite because of its large particles and its settling abilities.

In the following series of experiments the temperature was varied from room temperature to 90 degrees Celsius. The temperature will be denoted in 10 degree intervals (eg 70-80 degrees Celsius). The reason for the temperature being quoted in a 10 degree range was that the heating element was manually controlled. So far as possible, the temperature was held at the midpoint of the range. The other point to note is that the initial temperature of the solution was 50 degrees Celsius (the temperature of the hot water) and within the first hour the temperature is brought up to the required temperature range.

The experimental conditions of the slurries used, apart from the temperature, are the same as in section 3.2.2. The results of these tests are shown in Figure 3.5.

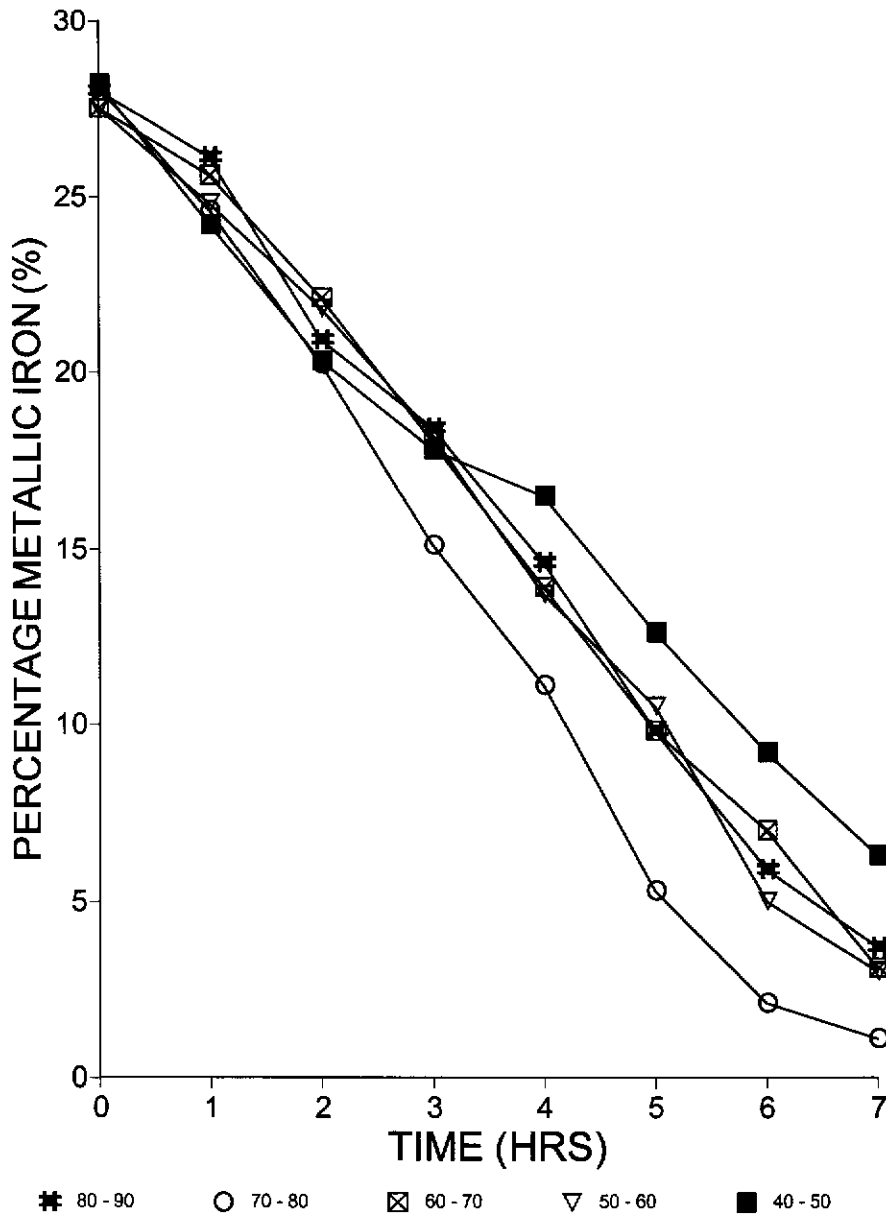


Figure 3.5: The effect of varying the temperature, from 40 to 90 degrees, on the removal of metallic iron from reduced ilmenite

From the results shown graphically in Figure 3.5 it can be clearly seen that the 70-80 degrees Celsius temperature range removes the most metallic iron. Further details of the products of the aeration (the oxides and reduced ilmenite) can be seen in Tables 3.2 and 3.3. The reduced ilmenite products were analysed by two titration methods, the first employed a gentle oxidation so that only the metallic iron would dissolve to give the metallic iron value, the second method used a much more potent reagent (hydrochloric acid) to dissolve all the iron present to give a total iron value. To assess an approximate value of the iron remaining as iron oxides the metallic iron

value was subtracted from the total iron value. The oxide products for each temperature range were analysed by X-ray fluorescence.

Table 3.2: The remaining amounts of iron in a reduced ilmenite sample after being leached at different temperatures for 7.0 hours

Temperature (°C)	Metallic Iron	Iron Oxides
15 to 40	3.31%	5.80%
40 to 50	5.03%	4.76%
50 to 60	2.80%	4.51%
60 to 70	2.02%	4.92%
70 to 80	0.59%	4.45%
80 to 90	1.09%	5.18%

The results in Table 3.2 demonstrate a trend between the removal of metallic iron and increasing temperature. As the temperature increases from 15 to 80 degrees Celsius more metallic iron was oxidised to iron (II) ions. Once 80 degrees Celsius was reached the amount of metallic iron being oxidised lessened. Again, using the same samples the iron oxide content was assessed by subtracting the metallic iron percentage from the total iron analysis value. In all the samples the iron oxide content appears to be high at approximately 5.8 to 4.4 per cent, but the lowest values here are found in the 70-80 degrees Celsius range. These high values for iron oxides seem to indicate the process of *in situ* rusting occurring. This *in situ* rusting seems more pronounced for those temperatures outside the 70 to 80 degrees Celsius optimum range.

3.5.2 Iron oxides produced

The results of the oxide analyses for the leaches at different temperatures are collated in Table 3.3.

Table 3.3: The effect of temperature on the oxides produced

Temperature	Dominant	Major	Minor	Trace
15 to 40		Lepidocrocite	Haematite	
40 to 50	Lepidocrocite		Magnetite	
50 to 60		Lepidocrocite and Magnetite	Goethite	Haematite
60 to 70		Goethite and Magnetite	Haematite	Lepidocrocite
70 to 80		Magnetite	Haematite	Goethite
80 to 90		Magnetite	Haematite	

goethite α -FeO(OH) - Burnt Yellow

haematite α -Fe₂O₃ - Burnt Red

magnetite Fe₃O₄ - Black

lepidocrocite γ -FeO(OH) - Brown

Dominant > 50%

Major 25 - 50%

Minor 5 - 25%

Trace > 5%

Table 3.3 indicates a progression with increases in temperature of the types of iron oxide found as the end product from aeration. Lepidocrocite was the major product at temperatures ranging from 15 to 60 degrees Celsius. As the temperature range was set at 60 to 70 degrees Celsius goethite was the major product. At higher temperatures (70 degrees and above) the major iron oxide produced was magnetite. The oxide most desired by the industry is magnetite because of its fast settling properties.

3.6 Changes in aeration caused by altering the pH of the slurry

3.6.1 Removal of metallic iron as function of pH

As has already been discussed, the buffering qualities of the ammonium chloride catalyst have been considered to be very important. This was due to the

ability of ammonium chloride to buffer the creation of hydroxide ion formed during the oxidation of the metallic iron in the reduced ilmenite grain. Without this action the hydroxide ion would react with oxidised iron (II) ion to form a solid iron oxide that would block the pores in the grain and stop any further oxidation of metallic iron (this is known as *in situ* rusting).

The purpose of this series of experiments was to elucidate the effect of changing the pH of the ammonium chloride slurry and define the limitations of the pH range in which the Becher process can work efficiently. All the slurries were made up by adding 9.0 grams of ammonium chloride to 1.8 litres of water. The pH was then adjusted, from approximately 6.5 to the pH required, by the addition of hydrochloric acid or sodium hydroxide. Once the pH reading had reached a constant value the solution then had 300 grams of reduced ilmenite added to it and was heated to a temperature of 70 to 80 degrees Celsius. An air flow rate of 1.0 litre per minute was then passed through the slurry for a period of 7.0 hours. Readings of pH and percentage metallic iron present in the reduced ilmenite were recorded hourly. These readings are represented graphically in Figure 3.6 and Figure 3.7.

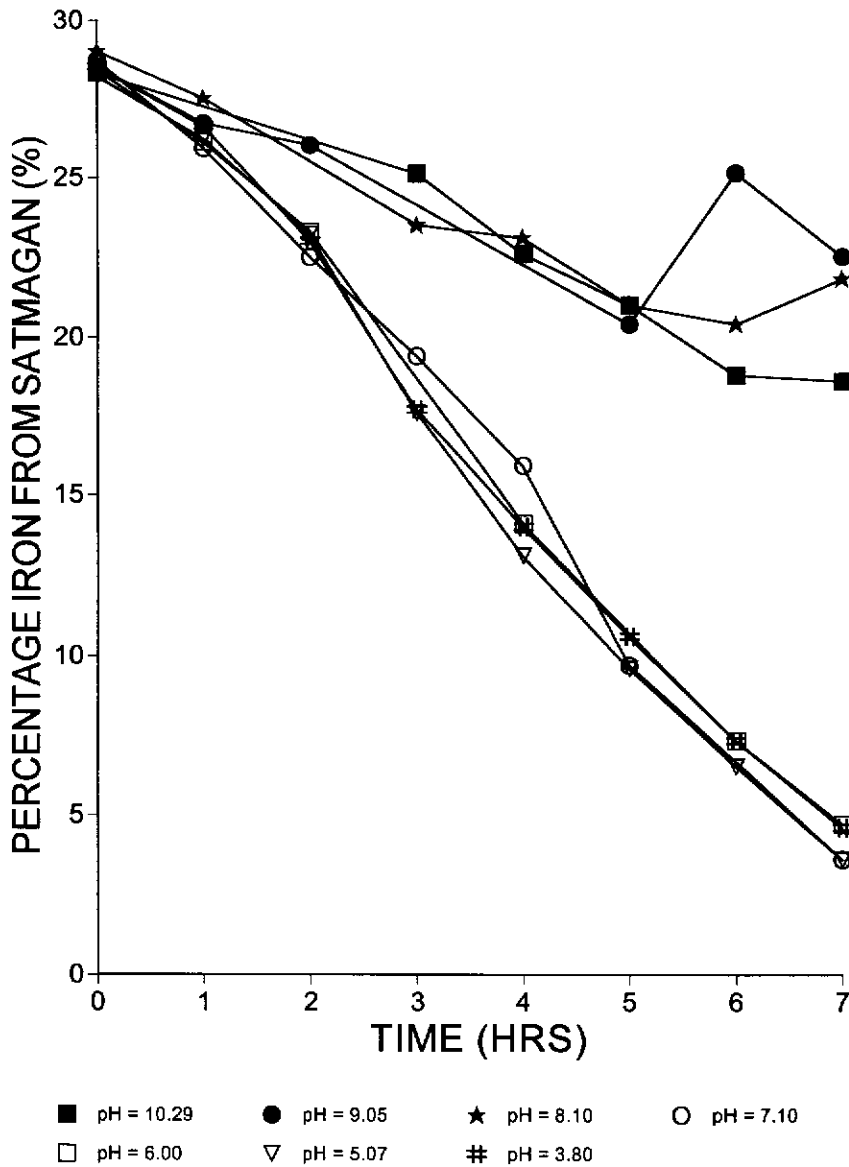


Figure 3.6: The effect of pH variations on the removal of metallic iron from the reduced ilmenite, as determined by SATAMAGAN.

From the results shown in Figure 3.6 two distinctive groups of tests appear; those in which complete aeration occurs in the 7.0 hour period and those that aerate poorly. There was a very distinct break between the two groups - the slurry with a starting pH of 8.10 reached a residual metallic iron level of 21.8 per cent in the 7.0 hour period. By contrast, the slurry with an initial pH of 7.10 completed the aeration, with a residual metallic iron content of 3.6 per cent, in the 7.0 hour period. Within the two groups themselves there was little variation in their path or final values. The group that completed the aeration in the 7.0 hours, those tests at pH 7.10 and lower, all followed a similar aeration path with little variation in the final metallic iron

values. The other group that was unable to complete the aeration also followed a similar path for the first 5.0 of the 7.0 hours with only some minor variations. There was a larger spread of final results in this grouping, ranging from 18.6 to 22.5 per cent metallic iron. An explanation for this behaviour may found in Figure 3.7 which shows the pH as a function of leaching time.

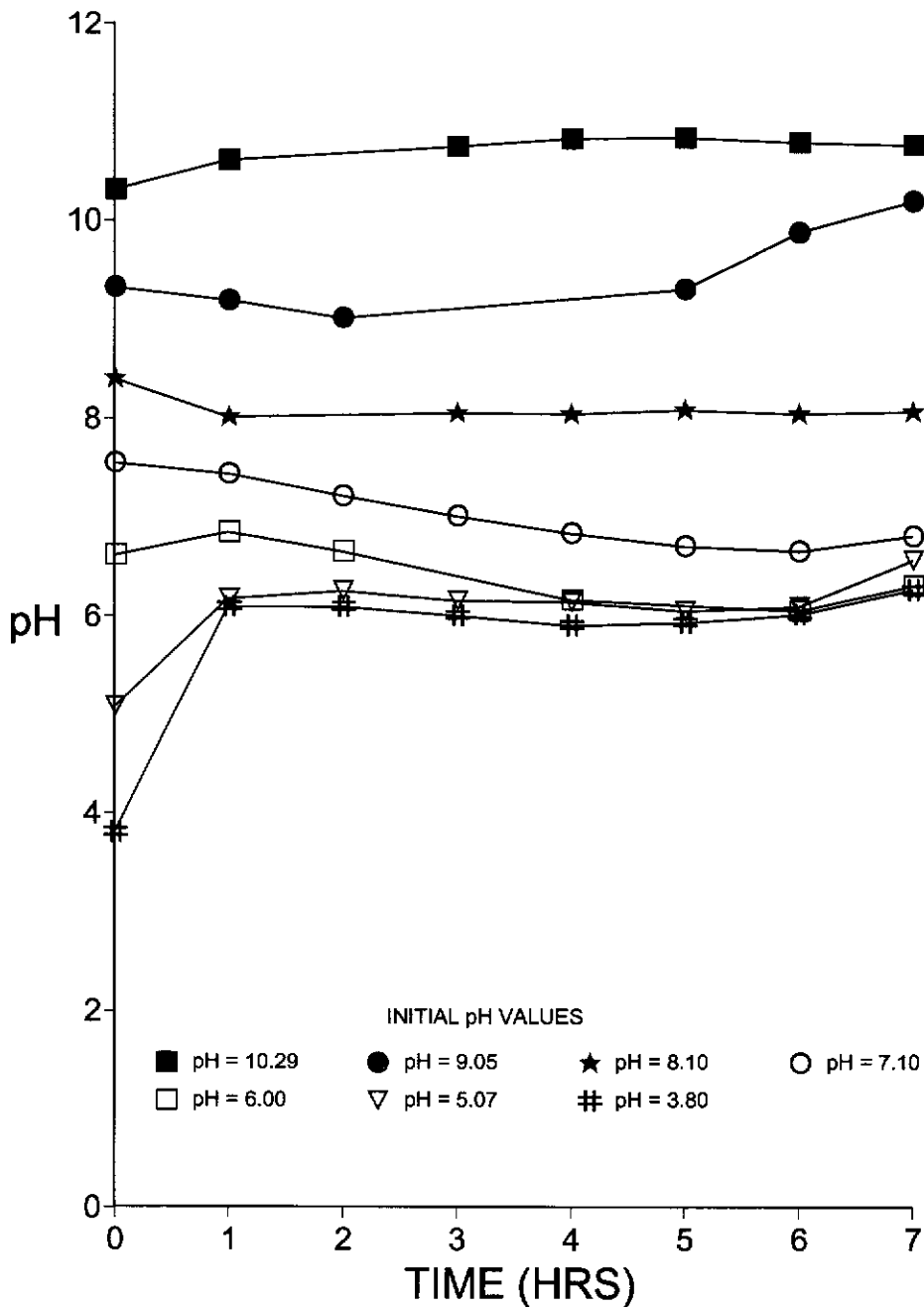


Figure 3.7: Changes in the pH of experimental slurries over the course of a 7.0 hour leaching trial

By observing the trends indicated in Figure 3.7 a possible explanation of the groupings seen in Figure 3.6 can be found. The two experiments that started with pH values below 7 can be seen to change their pH rapidly in the first hour of aeration. By the second hour of aeration the lower pH tests were converging on the pH pathway of the 7.10 pH test to follow it to the end of the 7.0 hour period. Those pH tests of higher than pH 7.10 all show independent trends, that is there was no deviation in pH in the first hour toward the pH 7.10 pathway. These higher pH solutions remained relatively unchanged and thereby hampered the buffering action of the ammonium chloride by shifting the equilibrium to the ammonia form. This was thought to have caused considerably more *in situ* rusting. To prove this hypothesis analyses of metallic iron and total iron were conducted on the final reduced ilmenite products - the results of these tests are shown in Table 3.4.

Table 3.4: Metallic iron and total iron contents for the final reduced ilmenite products of slurries leached with different initial solution pH

Initial pH of the Experiment	Percentage Metallic Iron	Percentage Total Iron
10.29	4.50	24.2
9.05	2.52	16.7
8.10	14.60	26.0
7.10	2.02	6.20
6.00	3.67	7.04
5.07	1.32	6.04
3.80	2.50	7.15

The results shown in Table 3.4 indicate that although the higher pH tests result in higher metallic contents, the bulk of the Satmagan analysis readings comes from the presence of iron oxides (eg haematite and magnetite) present within the reduced ilmenite grains, with exception of pH 8.10 (total iron - metallic iron = iron oxides). This indicates that while pH values above seven can oxidise the metallic iron, they are unable to promote the transportation of the iron(II) out of the grain to the same extent as the systems below pH 7.0.

3.6.2 Iron oxides produced

From the final products of the aeration trials in this section the oxides were separated from the reduced ilmenite to be analysed by XRD. While all the oxides looked to be a similar dark brown or black colour the XRD traces indicated the presence of different types of iron oxide present in different samples. In the case of the higher pH trials, for example pH 10.29, the resultant XRD pattern found the presence of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and haematite ($\alpha\text{-Fe}_2\text{O}_3$). As the pH of the trials decreased, for example pH 6.00, the XRD trace found a major amount of haematite and magnetite (Fe_3O_4) with a minor amount of goethite ($\alpha\text{-FeO(OH)}$). Finally, as the pH decreased to 3.80 it was noted that the same oxides were produced in both the pH 3.80 and the 6.00 trials in approximately the same quantities. This information indicates that pH can vary the amount of oxide produced and can even produce different types of oxides altogether.

3.7 Changes in aeration by altering the oxygen partial pressure

Under normal plant conditions the oxidising agent, oxygen, is introduced to the standard ammonium chloride slurry by means of compressed air pumped through blowers at the bottom of the leaching tanks. This feed of oxygen is approximately 20 per cent pure. An increase in the partial pressure of oxygen in the gas feed into the leach tank should therefore increase the rate of reaction. To test this principle oxygen and another gas were combined together and blown through the aeration reactor using the conventional ammonium chloride as the catalyst.

For these experiments a flow of oxygen was passed through a flow meter and, in most cases, air was passed through another, the exception being when nitrogen was used to achieve oxygen partial pressures less than 0.2 atmospheres. The 2 flows were merged and passed through the slurry. In all cases the mixture of gases used always had a total flow rate of 0.3 litres per minute. The partial pressure of oxygen was varied from 0 to 100 per cent of the atmospheric pressure through the series of these tests. The other parts of slurry mixture and conditions for these experiments can be

found in section 3.2.2. The results for a 7.0 hour leaching period are presented in Figure 3.8.

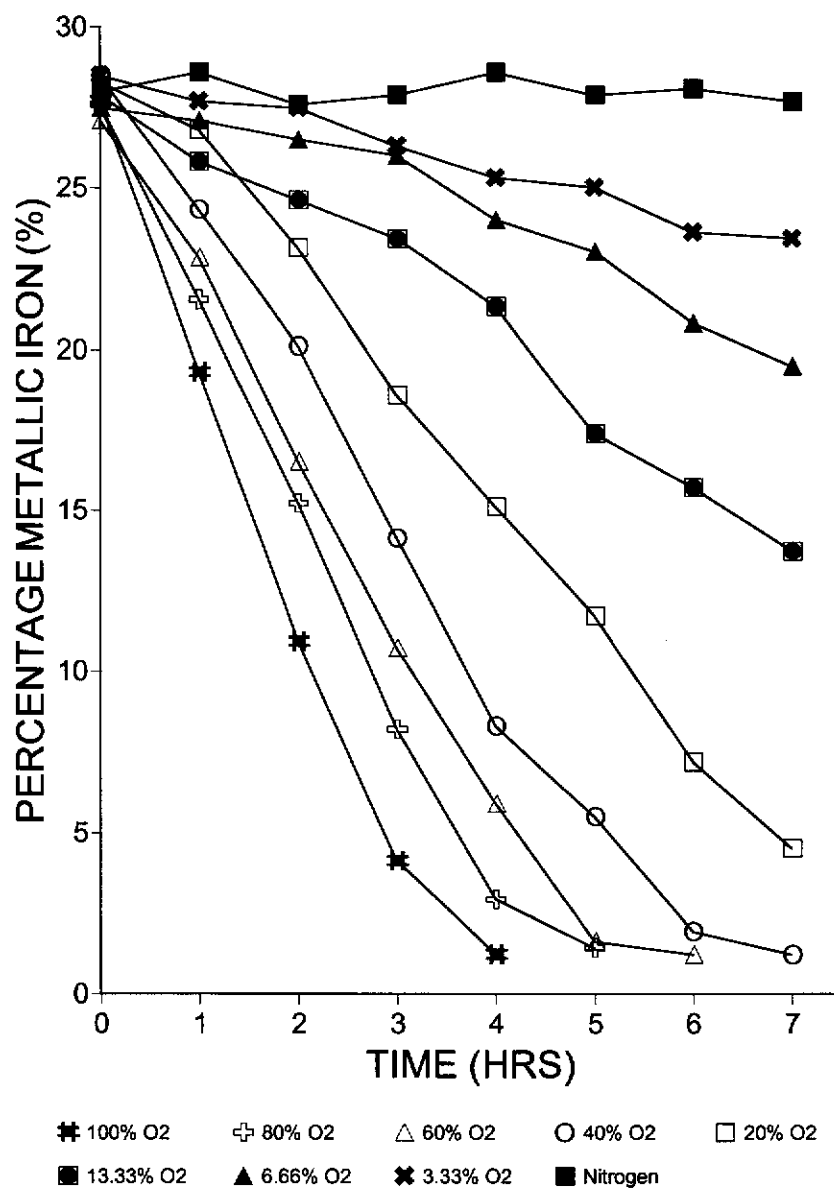


Figure 3.8: The effect of oxygen partial pressure on the leaching of metallic iron from reduced ilmenite using ammonium chloride as an aeration catalyst

The prominent trend apparent from Figure 3.8 is that an increase in the partial pressure of oxygen dramatically increases the rate of removal of the metallic iron from the reduced ilmenite matrix. A comparison between the gas mixture containing 100 per cent nitrogen (no reaction) and 100 per cent oxygen (4.0 hours to completion) shows that an increase in oxygen partial pressure dramatically increases

the rate of reaction. This increase was so well defined that it was also noted that no passivation effects were seen at higher oxygen partial pressures. From these the results Figure 3.9 was created from this series of experiments by measuring the gradient to determine the kinetics of aeration at each of the partial pressures and plotting it against the oxygen supplied, in millilitres per minute.

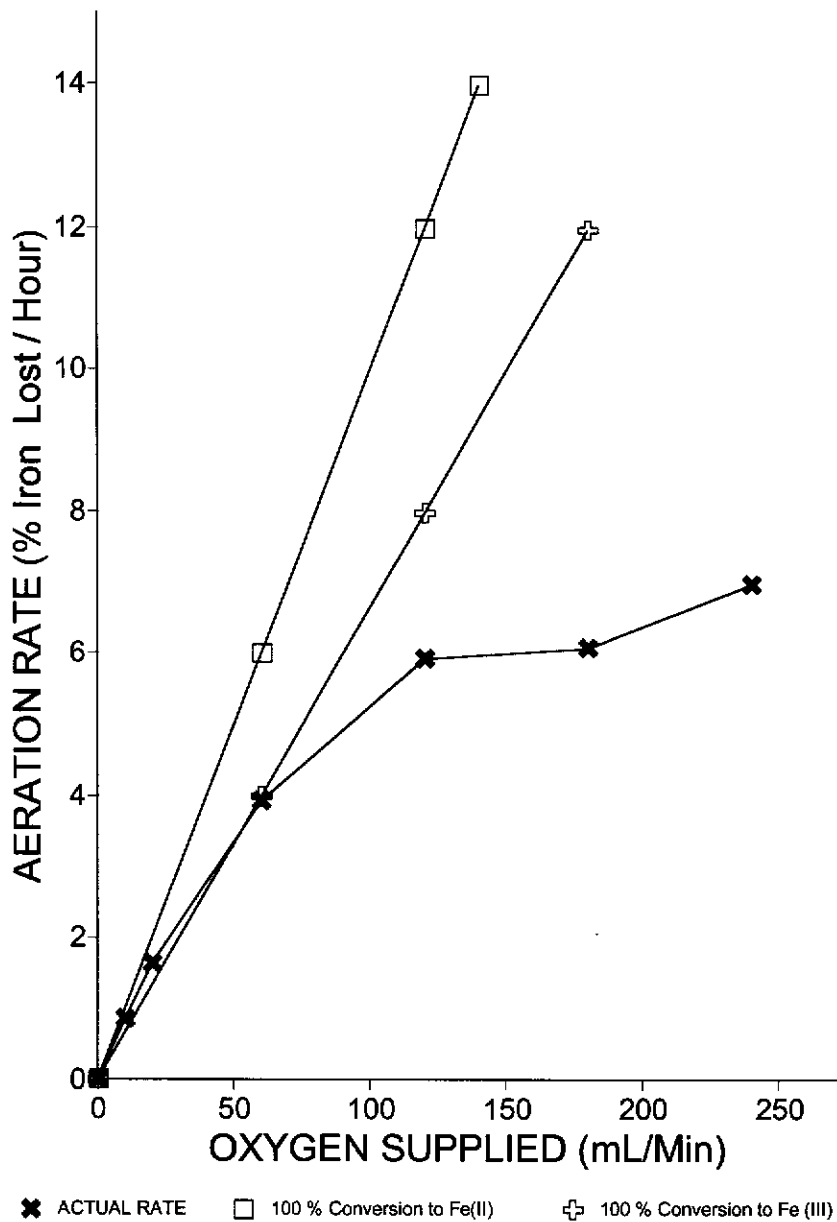


Figure 3.9: Rate of metallic iron removal as a function of the amount of oxygen supplied

The results shown in Figure 3.9 are compared with the 100 per cent efficiency of conversion of metallic iron to iron (II) and iron (III) oxides. From the comparison

of the actual rate against both the iron (II) and iron (III) conversions, the graph reveals that initially the actual rate was close to 100 per cent utilisation efficiency for the oxygen provided. After the amount of oxygen provided increased to above 50 millilitres per minute the actual rate began to decrease below the 100 per cent conversion limits and continued to decrease steadily.

The reasons for this decrease away from 100 per cent efficiency are likely to be due to the oxygen solubility in the solution together with poor mixing, which prevented the oxygen bubbles from breaking up on contact with the reduced ilmenite and then dissolving into the solution.

3.8 Mineralogy of the reduced ilmenite

In the past, Scanning Electron Microscope studies on ilmenites and reduced ilmenites have been conducted on samples before or after aeration (Bax and Ritchie, 1984). The purpose of this study was to examine the location of the metallic iron and other elements as a leach proceeds, while using ammonium chloride as the catalyst. Samples of the reduced ilmenite were taken from the aerator at hourly intervals. These samples were prepared and then studied to map the location of several key elements present within the reduced ilmenite grains. The elements that were analysed were iron, sulfur and manganese. The purpose of this investigation was to establish where the various elements were leached from in relation to the grain - solution boundary, as a function of leaching time.

The slurry mixture used for this series of results consisted of 300 grams of reduced ilmenite, 1.8 litres of water and 9 grams of ammonium chloride. This slurry had 1.0 litre per minute of air passed through it at a temperature between 70 to 80 degrees Celsius. Samples of reduced ilmenite were taken from the aeration regularly and washed with deionised water, and then oven dried. The samples were then prepared as polished sections and analysed under a Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray Analyser (EDXRA).

3.8.1 Metallic iron detected in the titanium dioxide matrix

Images of the polished sections under the SEM that highlighted the presence of metallic iron have been compared with a backscatter image to assist in finding the position of the metallic iron within the grain. The SEM images were recorded from samples taken an hour apart to follow the progressive leaching of the metallic iron over a seven hour period.

In the images showing the reduced ilmenite before leaching began, metallic iron was found spread evenly but not uniformly, throughout the grains. A comparison between the metallic iron distribution and the backscatter image, in Figure 3.10 B and A, was made as it was difficult to distinguish the grain edge in the metallic iron distribution. From this comparison it was evident that the metallic iron was located throughout the grain, including the boundary.

The SEM images, from samples removed after 1.0 hour of aeration, for the detection of metallic iron and backscatter, in Figure 3.11 B and A, were compared. At this stage the iron still appears to be evenly distributed throughout the reduced ilmenite grains although there was possibly a decrease in the amount of iron in the area immediately around the grain edges.

The comparison between the metallic iron and the backscatter images in Figure 3.12 B and A, after 2.0 hours of aeration, shows an evident decrease in the amount of metallic iron in the area around the edge of the grains. At the same time there appears to be no significant decrease in the concentration of the metallic iron in the central parts of the grains.

The metallic iron and backscatter images in Figure 3.13 B and A, after 3.0 hours of aeration, were compared and indicated a larger concentration gradient going through the reduced ilmenite grains. There was a much more obvious difference

between the lower concentrations of the iron in the boundary area and the higher concentration in the centres of the grains.

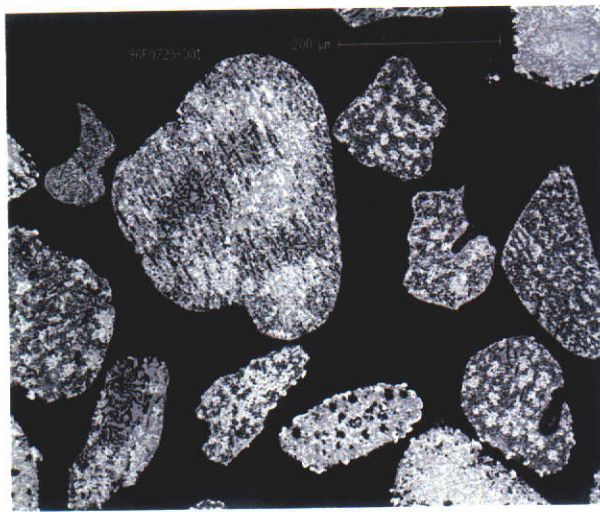
The comparison of the metallic iron SEM and the backscatter images in Figure 3.14 B and A, after 4.0 hours of aeration, show almost total removal of the metallic iron from the outer boundary area. The inner area of the grains still show a high concentration of metallic iron. Another characteristic shown between these images was the effect of grains that appear to be more porous. An example of what appears to be a more porous grain can be found in the bottom left hand corner of the backscatter image in comparison with some of the grains in the centre of the image. This porous grain has, by this stage, had all the metallic iron completely leached which can be observed in the iron distribution in Figure 3.14, while the less porous grains in the centre still contain considerable concentrations of metallic iron in the central area of the grains.

The comparison of the metallic iron and backscatter images, in Figure 3.15 B and A, of the sample taken after 5.0 hours of aeration show a further decrease in the amount of metallic iron in the outer boundary and that there was a decrease in the concentration further within the grains. This seems to indicate a trend of removing the outer layer of metallic iron first, followed by removal of the metallic iron further into the interior of the grains.

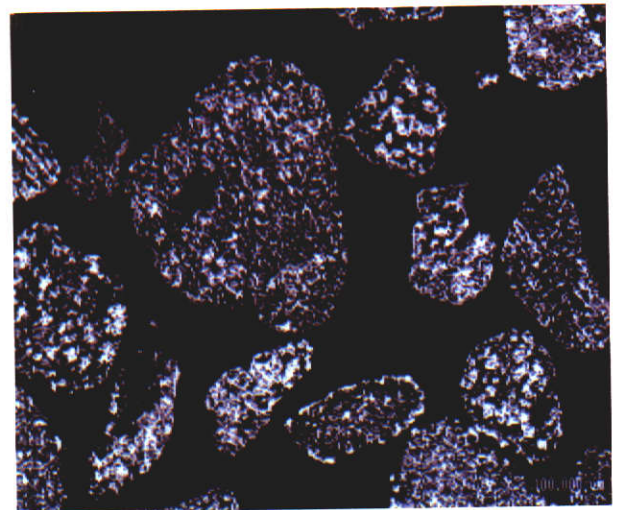
The comparison of the metallic iron and backscatter images in Figures 3.16 and 3.17 for 6.0 and 7.0 hours of aeration respectively show further evidence for a trend of the iron being consumed in an ordered progression from the boundary to the centre of the reduced ilmenite grain. This trend continued until at last the remaining iron was removed from the centre of the grain.

From all the observations from the SEM iron images, and comparison with backscatter images there was a trend toward the metallic iron being removed from the outer edges of the grain first, and then continuing until the metallic iron in the centre of the grain was reached and removed. This behaviour resembles that of the

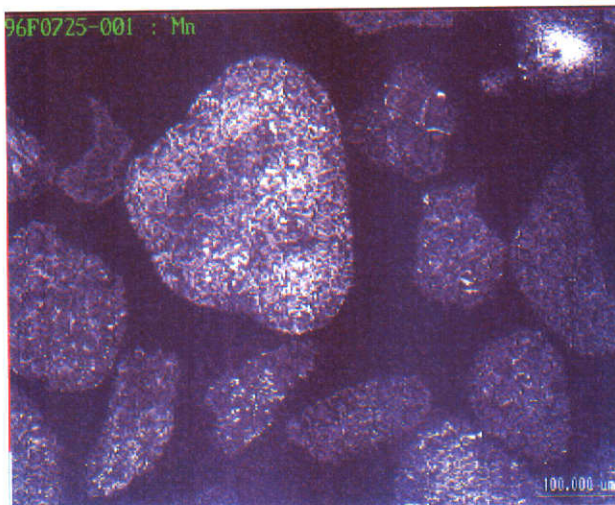
'shrinking core model'. From the same observations it was also apparent that the smaller grains were leached faster than that larger grains of reduced ilmenite. This was believed to have occurred as the centres of the smaller grains are less distance for the leaching boundary, and leaching may be presumed to proceed at approximately the same lineal rate. In the cases where the smaller particles appear to leach at the same rate, or slower, than larger particles, other factors, such as the heterogenous nature of the mineral material, porosity and composition, may be responsible for variations between particles. The other observation of note through this series of images was the greater speed at which the apparently more porous grains were leached compared to the less porous grains.



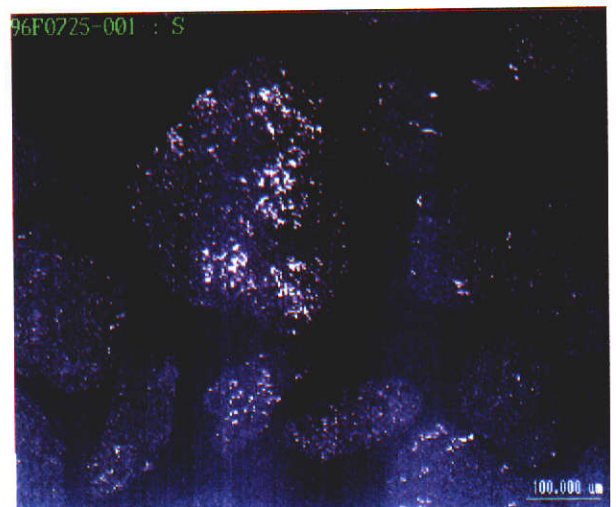
A: Backscatter



B: Iron

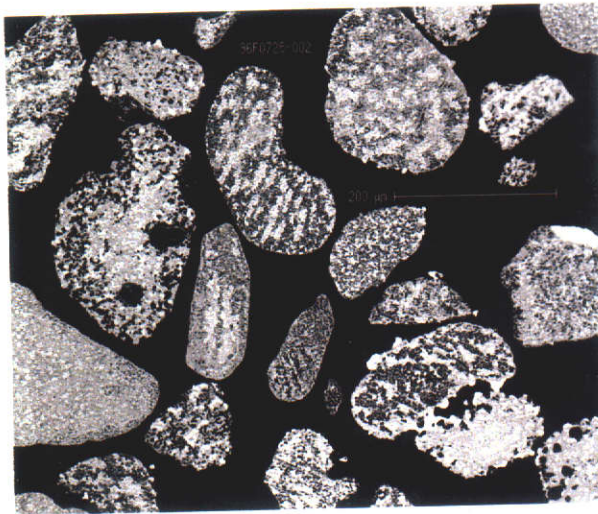


C: Manganese

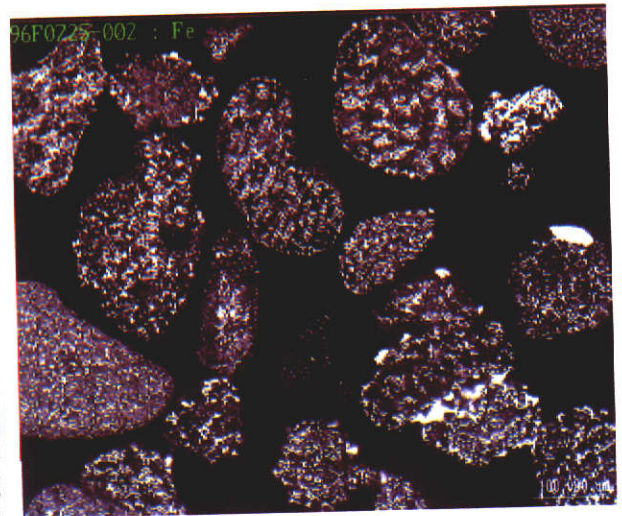


D: Sulfur

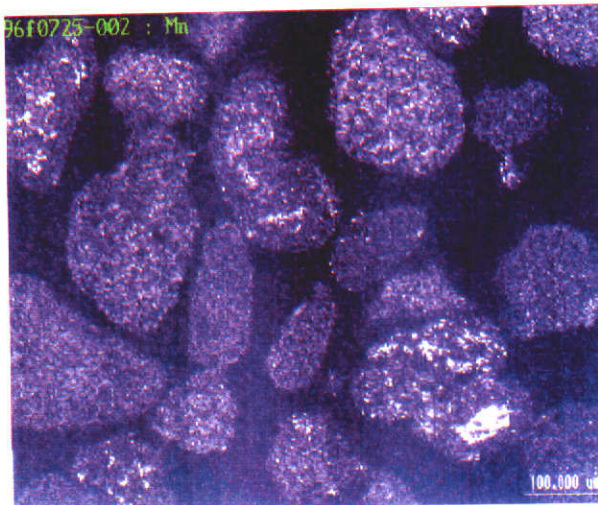
Figure 3.10: A Backscatter (A) and EDXRA SEM images of a reduced ilmenite sample prior to leaching showing the iron (B), manganese (C) and sulfur (D) distributions



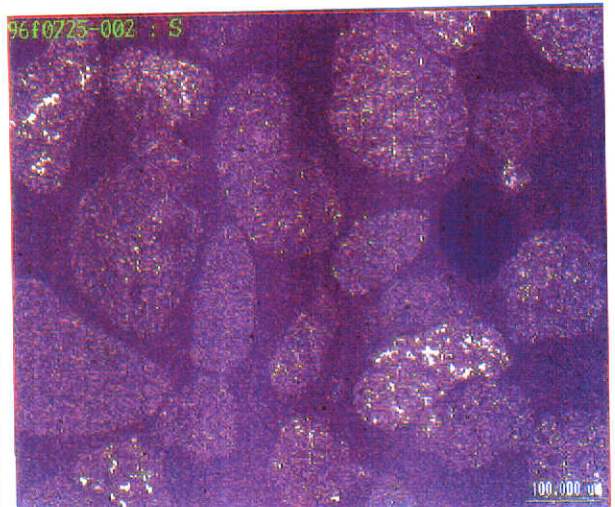
A: Backscatter



B: Iron

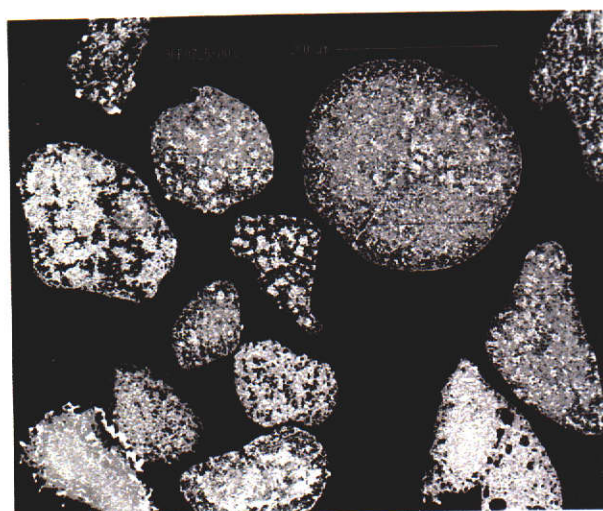


C: Manganese

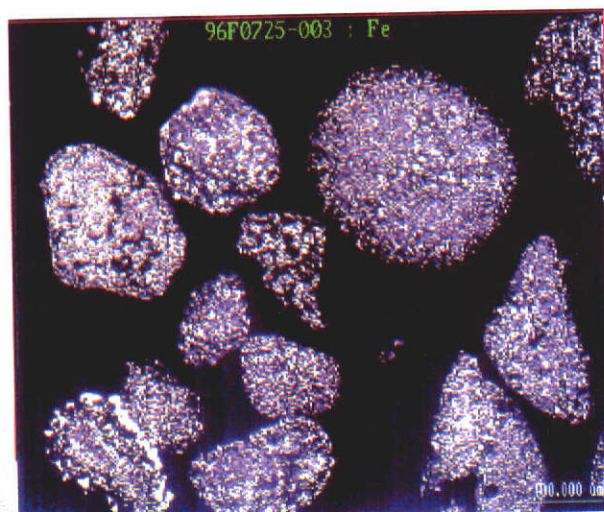


D: Sulfur

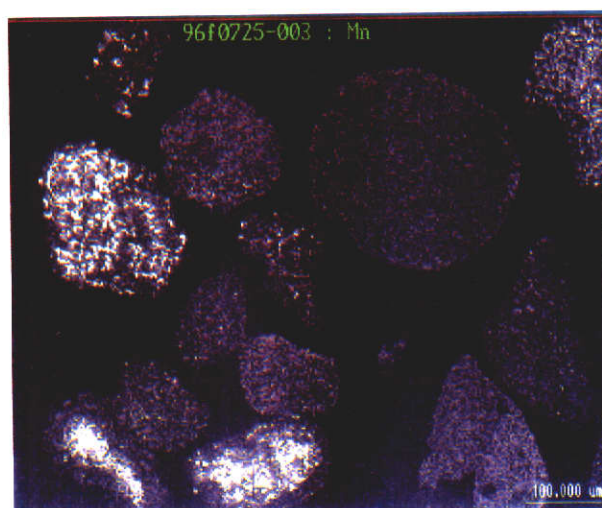
Figure 3.11: A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 1 hour of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions



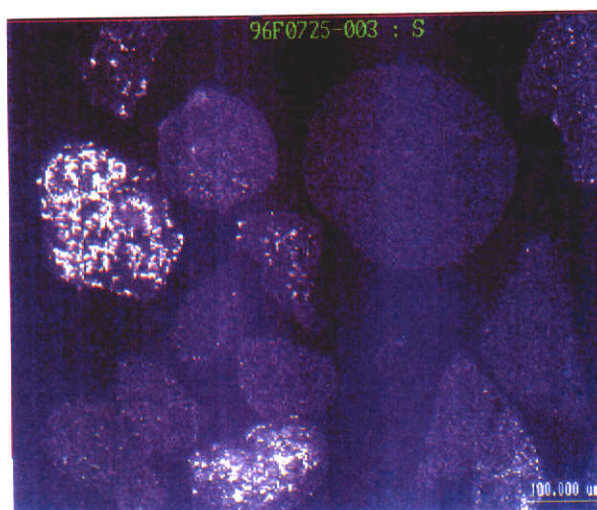
A: Backscatter



B: Iron

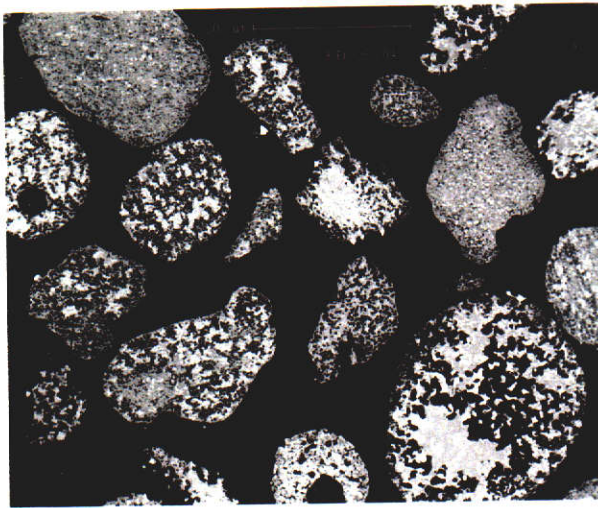


C: Manganese

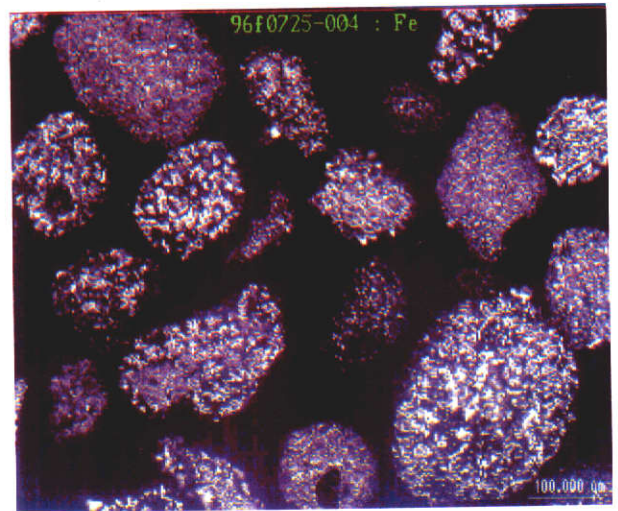


D: Sulfur

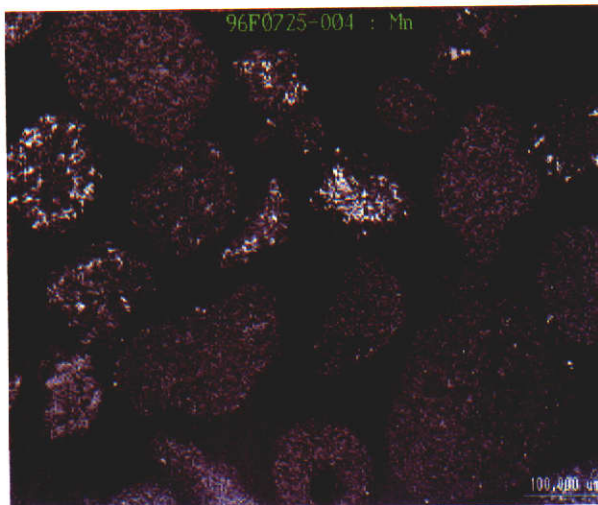
Figure 3.12: A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 2 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions



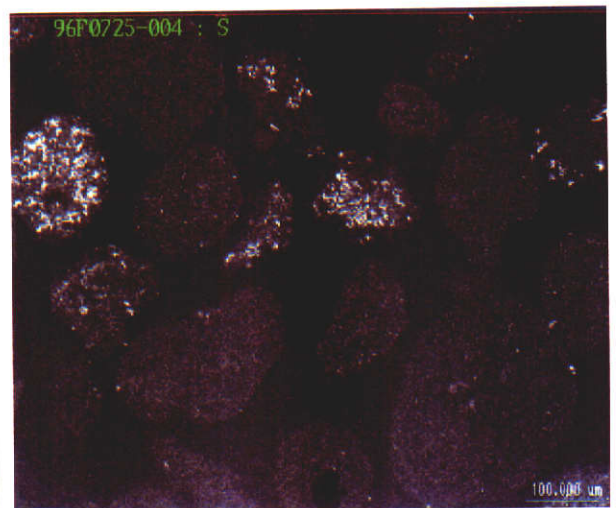
A: Backscatter



B: Iron

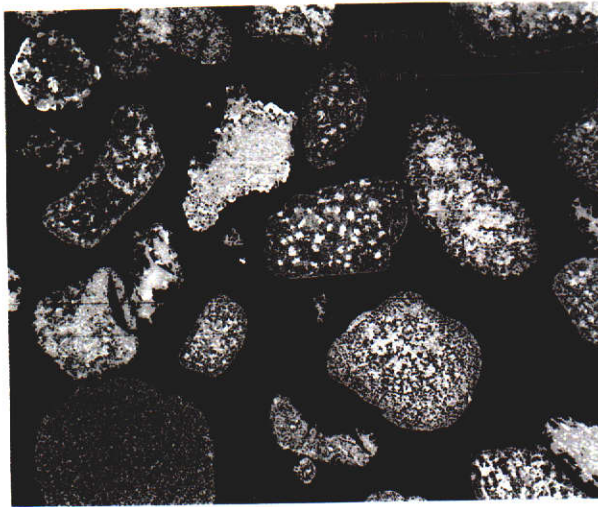


C: Manganese

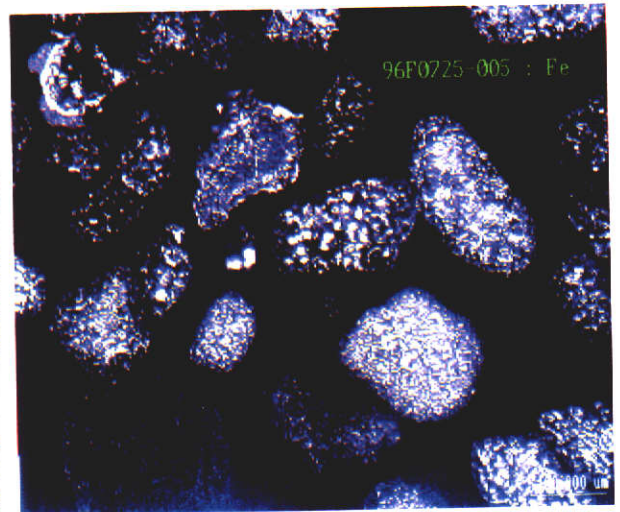


D: Sulfur

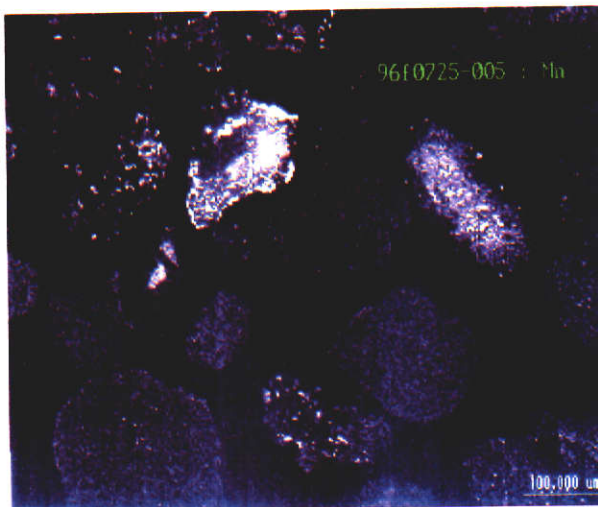
Figure 3.13: A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 3 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions



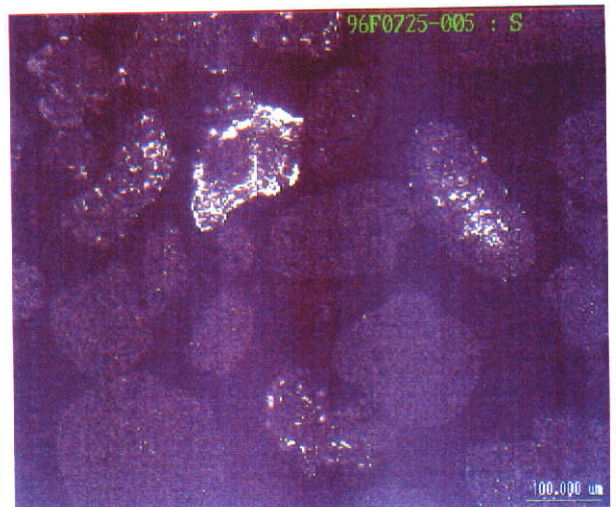
A: Backscatter



B: Iron

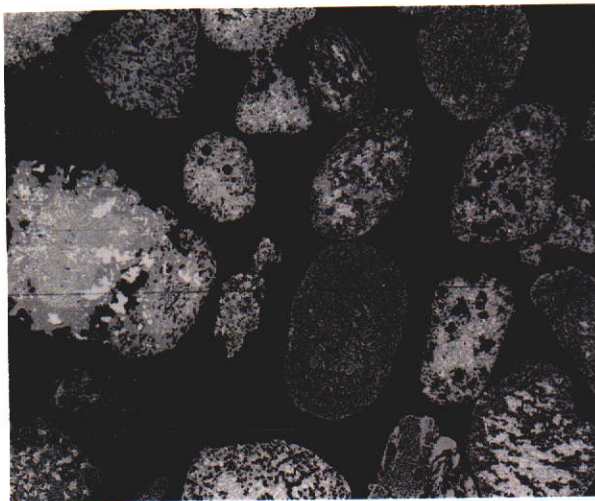


C: Manganese

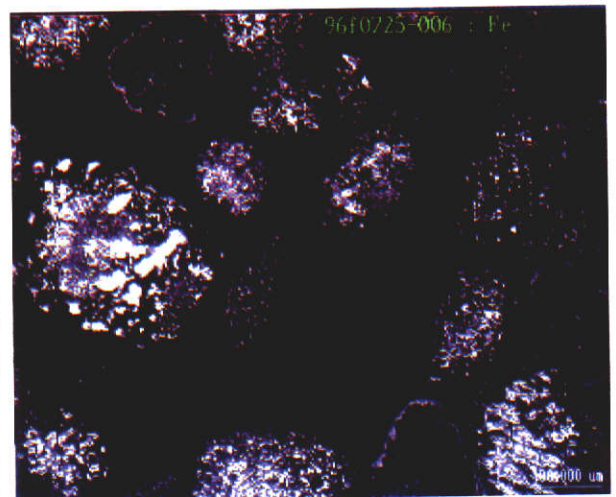


D: Sulfur

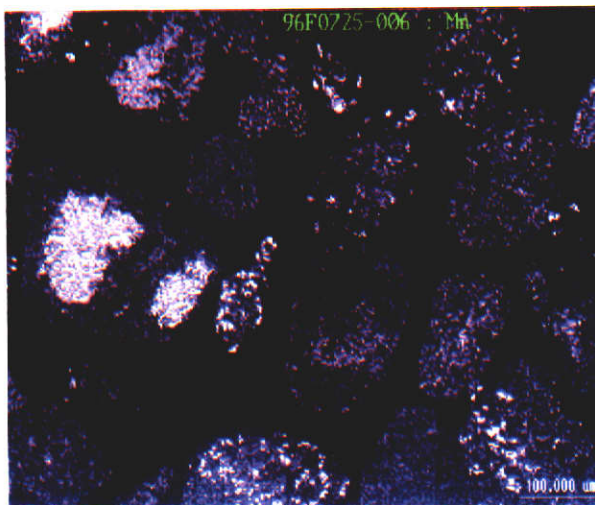
Figure 3.14: A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 4 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions



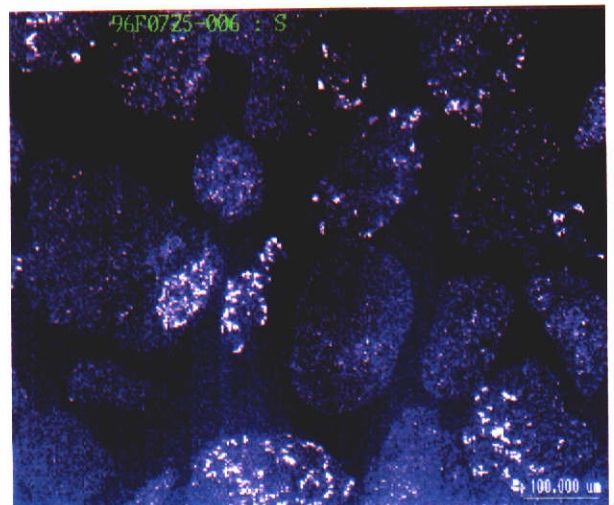
A: Backscatter



B: Iron

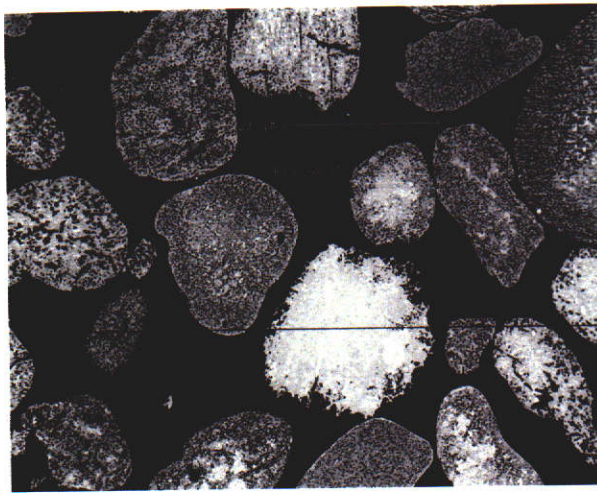


C: Manganese

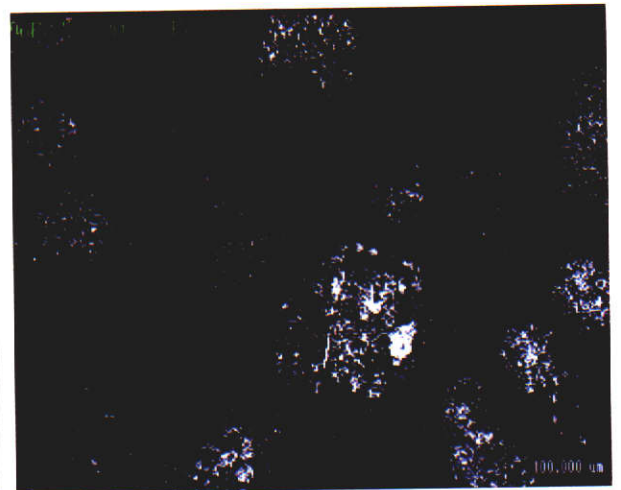


D: Sulfur

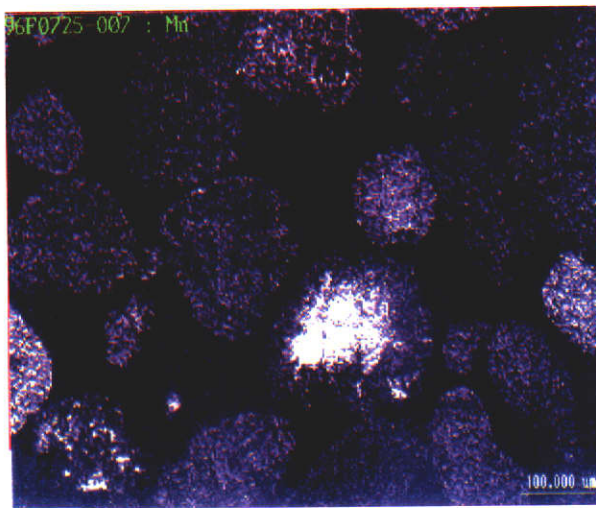
Figure 3.15: A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 5 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions



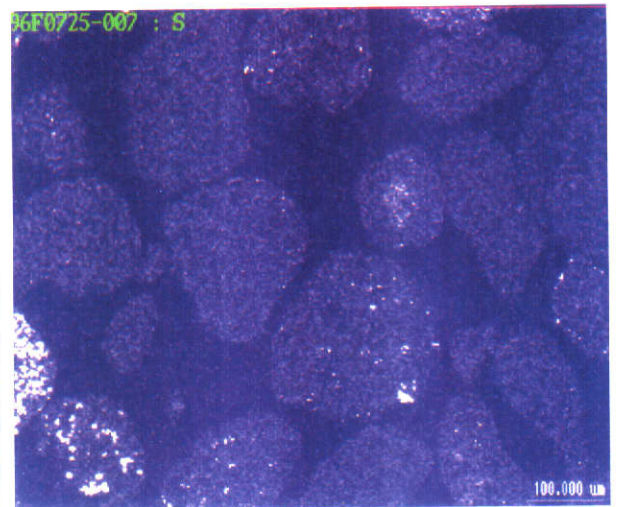
A: Backscatter



B: Iron

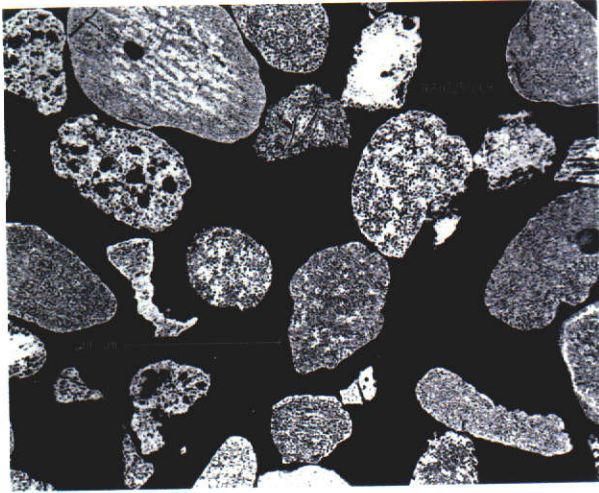


C: Manganese



D: Sulfur

Figure 3.16: A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 6 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions



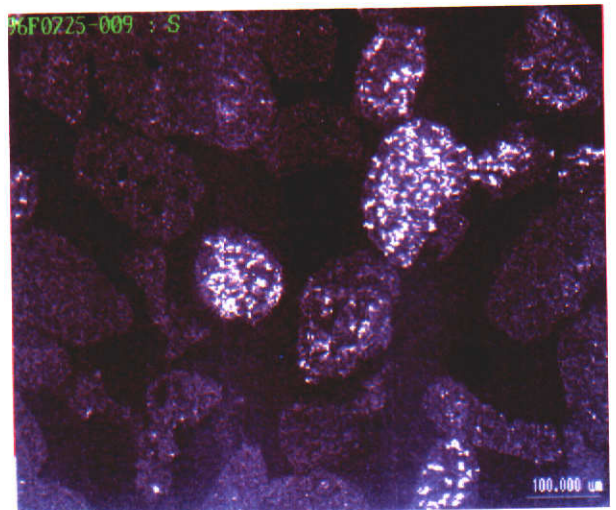
A: Backscatter



B: Iron



C: Manganese



D: Sulfur

Figure 3.17: A Backscatter (A) and EDXRA SEM image of a reduced ilmenite sample, after 7 hours of leaching in an ammonium chloride slurry, showing the position of iron (B), manganese (C) and sulfur (D) distributions

3.8.2 Sulfur and manganese detected in the titanium dioxide matrix

Images of the polished sections under the SEM that highlighted the presence of manganese and sulfur have been compared with a backscatter to assist in finding the position of the sulfur and manganese within the grain. The images of sulfur and manganese distribution in Figure 3.10 to Figure 3.17 were recorded from samples taken usually an hour apart to follow the progressive leaching of these elements over a 7.0 hour period.

By looking through this series of SEM images showing the distribution of sulfur it was evident that the sulfur was unevenly scattered throughout the reduced ilmenite matrix. By further examination of the location of manganese in the grains it was evident that the manganese and sulfur generally occurred together in the grain. This suggests that the manganese and sulfur exist as a manganese sulfide phase.

As the aeration proceeds there was no significant evidence of the manganese and sulfur decreasing in concentration; that is the ammonium chloride failed to significantly leach the manganese or sulfur impurities within the 7.0 hour period. Manganese sulphide is usually removed in the post aeration acid leach.

3.9 Reproduction of results for ammonium chloride aerations

In all of the work so far ammonium chloride has been used as a catalyst in standardisation experiments. What now needs to be investigated is the reproducibility of these aeration results using one source of reduced ilmenite. The purpose of the repeat experiments in this section is to establish whether an ammonium chloride catalyst gives reproducible results.

The four slurries tested with ammonium chloride were all operating under optimum conditions for the this catalyst; that is, 0.093 M (9 grams) ammonium

chloride in 1.8 litres of water at 70 to 80 degrees Celsius. The results of the aerations are illustrated in Figure 3.18.

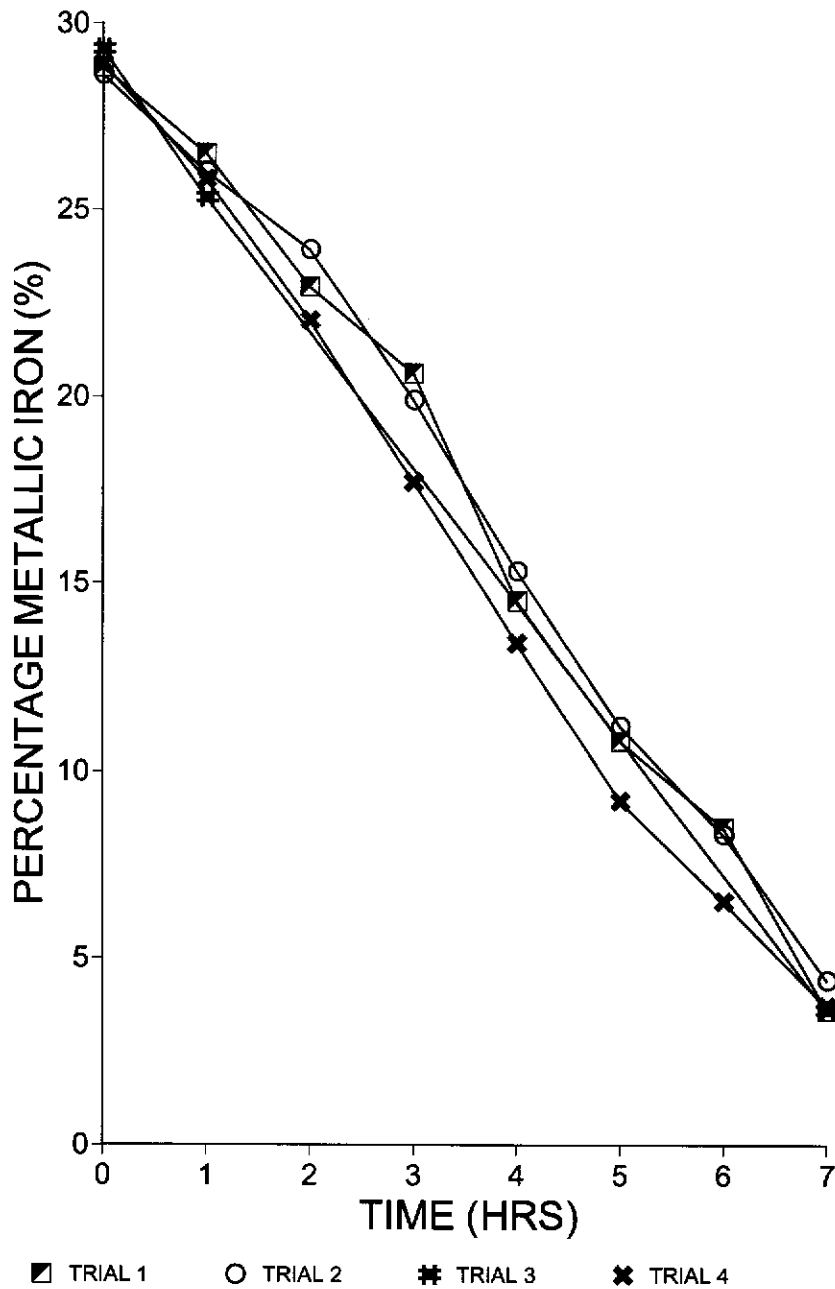


Figure 3.18: The ammonium chloride experiment under optimum conditions repeated four times to assess the reproducibility of the experiment.

The repetition of the ammonium chloride experiment has shown that the results of the experimental procedure were reasonably consistent. All four slurries, after 7.0 hours of aeration attained residual metallic iron values within 0.8 per cent of one another. Each of the experiments also followed a similar pathway throughout the

entire aeration. These experiments yielded results with a mean of 2.9 per cent metallic iron with a standard deviation of 1.7 per cent. Further calculations yielded an error of +/- 1.9 per cent from a 95 per cent confidence level.

These results show that while using the same reduced ilmenite batch, test trials can be repeated and produce the same aeration times and rates while using ammonium chloride as the catalytic reagent. Further trials will be shown in Chapter Five for the reproducibility of other catalysts in reduced ilmenite slurries.

3.10 Conclusions

Removal of metallic iron from reduced ilmenite is a complex reaction that relies on many factors that not only determine the extent of reaction, but also the speed at which the process occurs. The process variables examined in these tests were air flow rate, pulp density, ammonium chloride concentration, temperature and oxygen partial pressure.

The tests made on air flow rates indicated a minimum flow rate of 0.3 litres per minute of air, in the case of the 100 gram reduced ilmenite slurry, will extract the accessible metallic iron in five hours of aeration. In the case of the higher pulp density, (ie 300 grams of reduced ilmenite), the results indicated that an air flow rate of 0.5 litres per minute or above would assure that the minimum percentage of residual metallic iron was reached in 7.0 hours of aeration. An air flow of 1.0 litre of air per minute managed to achieve slightly lower residual iron level in the same period.

The 100 gram reduced ilmenite pulp required a minimum of 0.30 litres of air per minute over 5.0 hours to completely leach the pulp of metallic iron, compared with the 300 gram reduced ilmenite pulp that required a minimum of 1.0 litre per minute of air over 7.0 hours to completely leach the pulp of metallic iron. This was again shown when the highest pulp density of 600 grams of reduced ilmenite took

only 10.0 hours to aerate at the same air flow rate. This indicates the higher pulp densities utilise the oxygen provided more efficiently than the lower density pulp.

The effect of varying the ammonium chloride concentration demonstrated that concentrations under 0.093 M (0.5 per cent w/v) do not catalyse the reaction to the same extent as those that are above 0.093 M (0.5 per cent w/v). Increasing the concentration above 0.093 M of ammonium chloride made little difference to the rate or extent of iron removal.

The effect of varying temperature showed that an ammonium chloride catalysed aeration produced the fastest (shortest) leaching times when the temperature was held at the 70 to 80 degrees Celsius range. At higher and lower temperatures more *in situ* rusting was found to occur. This resulted in a slowing of the oxidation of the metallic iron due to the deposition of iron oxides within the grains.

The effect of varying the pH of the ammonium chloride slurry showed at pH higher than 7 the ammonium chloride catalyst does not work as well because the equilibrium was altered to produce more ammonia, this was evident from the subsequent odour. At lower pH values aeration proceeds at approximately the same rate as pH 7.1. Any small increase in aeration rate at the lower pH values was attributed to acid leaching of the iron.

By changing the oxygen partial pressure of the aeration gas the aeration times of an ammonium chloride slurry were dramatically decreased. There appeared to be an inverse relationship between the oxygen partial pressure and the aeration times of the slurries.

The SEM studies showed that the leaching of metallic iron from the reduced ilmenite matrix occurs at the outer boundary first. As the aeration continues the iron

is removed preferentially from the outer edge of the grain moving slowly toward the centre of the grain.

Chapter Four

Substitution of ammonium chloride with other electrolytes in the Becher process

4.1 Introduction

The aim of this section was to compare the performance of ammonium chloride against other compounds that have various similarities to ammonium chloride. From this comparison a greater understanding of the mechanism of the Becher process could be obtained and therefore predictions of superior catalysts could be made. Previous investigations in this area include Farrow and Ritchies (1985) work with sodium chloride, magnesium chloride and zinc chloride. These results were used to formulate their mechanism for the action of ammonium chloride in the system. Other papers suggest that sea water would work as a catalyst as effectively as ammonium chloride (Ramakrishna *et al*, 1988). Various other compounds similar in reactivity and structure have been investigated in this chapter: sodium chloride, sodium acetate, sodium sulfate, sodium perchlorate, sodium nitrate, ammonium perchlorate, ammonium nitrate and ammonium sulfate.

4.2 The use of sodium salts as catalysts for aeration reactions

4.2.1 Sodium chloride as an aeration catalyst

Sodium chloride was the initial choice as the replacement catalyst for ammonium chloride, because of its similarities to ammonium chloride. The action of the chloride constituent of the catalyst of sodium chloride was expected to be the same as in the ammonium chloride compound. Any differences in the action of the

two salts could be attributed to the cation, sodium or ammonium.

The slurry mixture that was used to compare the sodium chloride to ammonium chloride consisted of 300 grams of reduced ilmenite, 1.8 litres of water and 9.8 grams (0.1 M) sodium chloride. This slurry was kept at a temperature between 70 and 80 degrees Celsius. The slurry was aerated with a constant air flow rate of 1.0 litre per minute for a 7.0 hour period. The data from this experiment was compared to the results for ammonium chloride used under the same conditions by the use of the graph presented in Figure 4.1.

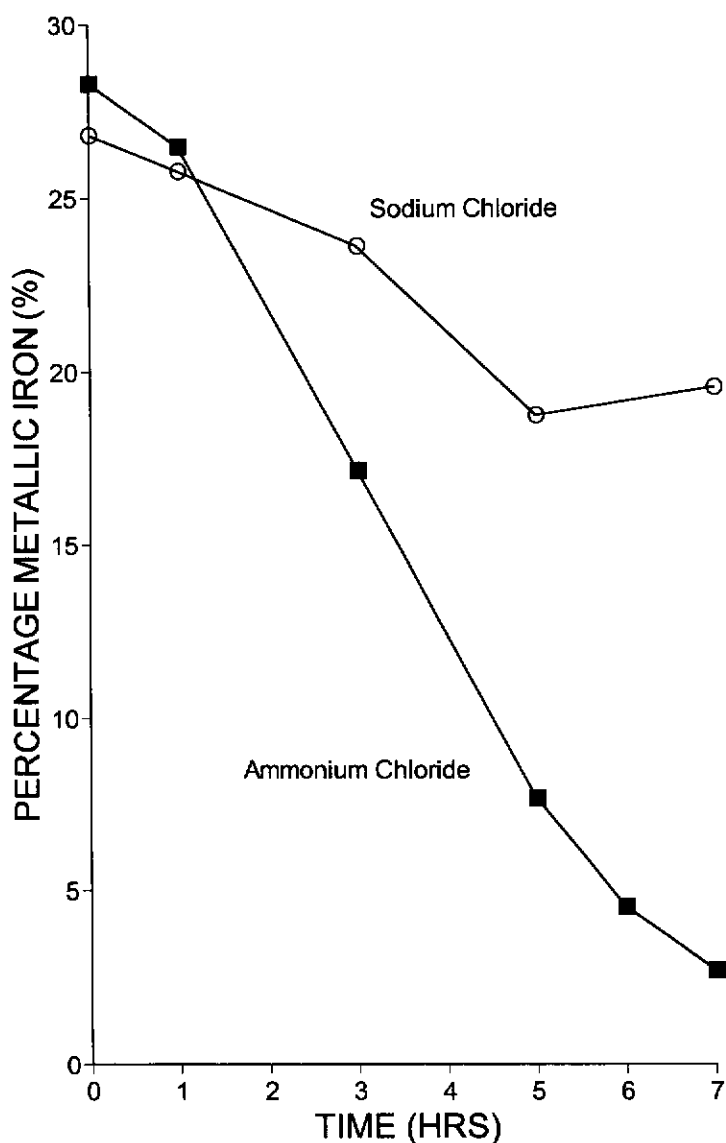


Figure 4.1: Sodium chloride (0.1 M) and ammonium chloride (0.1 M) used as aeration catalysts to remove metallic iron from reduced ilmenite.

From the graph in Figure 4.1 it is obvious that the ammonium chloride acted as the better catalyst when compared to the sodium chloride. The sodium chloride catalysed aeration reduced the metallic iron content of the reduced ilmenite from 27 per cent to 19.5 per cent after 7.0 hours of aeration. In the case of ammonium chloride, after the same 7.0 hour aeration period, the metallic iron level was at 2.3 per cent. The difference in the rate of reaction between the two catalysts was approximately 2.5 per cent metallic iron per hour. The difference in the leaching behaviour must be related to the replacement of the ammonium ion with the sodium ion. The aeration reaction in the sodium chloride system occurs at a much slower rate and appears to stop in the seventh hour of aeration after approximately 30 per cent of the metallic iron has been dissolved. Partial oxidation of some of the metallic iron to the iron (II) has occurred, but these iron (II) species were not all transported out of reduced ilmenite grain before reacting with hydroxide or oxygen present to form solid iron hydroxides or oxides (*in situ* rusting). These oxides were then able to retard the oxidation of further iron by blocking the pores of the grains, until the remaining metallic iron became inaccessible to the leach solution. These findings are consistent with work done by Farrow and Ritchie (1985), which used a much smaller amount of sample.

4.2.2 Sea water as an aeration catalyst

Other reports on the removal of metallic iron from reduced ilmenite have indicated that sea water was a possible electrolyte to use in the place of ammonium chloride (Ramakrishna *et al*, 1988). The results shown by Ramakrishna *et al* indicate that sea water, with acid added to create a low pH of 2.5, was a good leaching reagent for reduced ilmenites with high titanium dioxide contents (in excess of 90 per cent) (Ramakrishna *et al*, 1988). As the main constituent of the soluble component of sea water is sodium chloride it was decided to investigate if the use of sea water resulted in any major difference to pure sodium chloride as a catalyst in the removal of metallic iron from reduced ilmenite. The major difference between the solution used in section 4.2.1 and this sea water is the chloride ion concentration and the addition

of other trace elements. In the case of sea water the chloride ion concentration is reported to be approximately 0.54 M (Parker, 1980) compared with the chloride concentration of 0.1 M used in section 4.2.1.

To achieve this a slurry consisting of 300 grams of reduced ilmenite and 1.8 litres of sea water was prepared. The sea water was obtained off the Western Australia coast and had a pH of 7.9. This slurry was heated to a temperature of 70 degrees and held at a temperature between 70 and 80 degrees over a 7.0 hour period. During this 7.0 hour period the slurry was aerated with air passed though the slurry at 1.0 litre per minute. Hourly samples were taken and analysed for the metallic iron content in the reduced ilmenite. The results of these tests are represented in Figure 4.2.

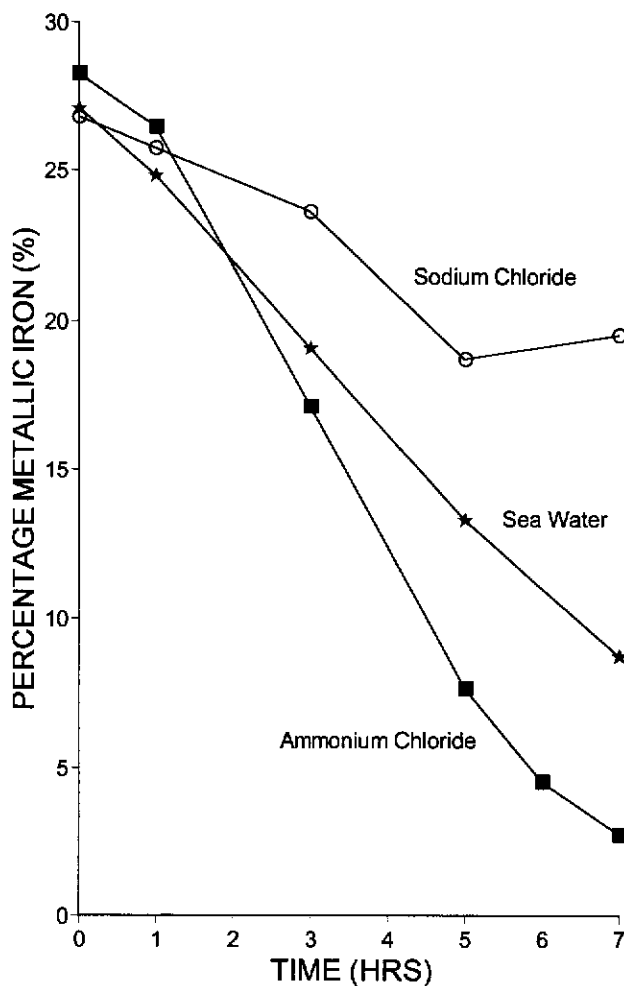


Figure 4.2: Sea water, sodium chloride (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the leaching of metallic iron from reduced ilmenite.

The data in Figure 4.2 shows that the sea water was a better aeration catalyst than pure 0.1 M sodium chloride, but not quite as good ammonium chloride. The sea water achieved a residual metallic iron level of 8.7 per cent, compared to the residual level in sodium chloride of 19.5 per cent and ammonium chloride at a level of 2.3 per cent after 7.0 hours. The reason for the exceptional performance of sea water as a catalyst, when compared to the performance of sodium chloride, could be due to the much higher concentration of chloride ion (0.54 M) or due to the presence of some other species in sea water. It was impossible to precisely attribute the exceptional performance as there are over 45 different elements present (Parker, 1980) in many different forms in sea water. The analysis of sea water shows several inorganic cations and anions other than sodium and chloride were present in large quantities. The cations were magnesium, potassium and calcium along with the sulfate anion (Parker, 1980). The concentrations of these cations in sea water were reported as 0.456 M sodium ion, 0.056 M magnesium ion, 0.01 M potassium ion and 0.01 M calcium ion while the sulfate ion was present in an approximate concentration of 0.025 M. Previous work completed by Farrow and Ritchie (1985) used a combination of 0.1 M sodium chloride and 0.1 M magnesium chloride as an aeration catalyst to leach a reduced ilmenite sample. It was found that while aeration of the mixture was significantly better than with sodium chloride alone, the ammonium chloride aeration was still significantly faster. The reason given for the difference in the aeration with ammonium chloride and the sodium and / or magnesium chloride was due to a small amount of *in situ* rusting occurring in the reduced ilmenite. In this case where sea water was used, there appeared to be no slowing of the rate of removal of the metallic iron from the reduced ilmenite after 7.0 hours, only that the rate throughout was lower than that for the ammonium chloride aeration.

Although it was reported that sea water is a better leaching catalyst than ammonium chloride (Ramakrishna *et al*, 1988) it was important to understand that the sea water used in their experiments had an initial pH of 2.5. The measured pH of the sea water used in the present work was 7.93. This information leads to the conclusion that direct acid leaching occurs at low pH values which enhances the total

rate. The catalytic action of sodium chloride and magnesium chloride begins to take effect at higher pH values. The point at which the acid leaching finished and the catalytic action became prominent was indeterminable. As a result, the leaching rate obtained from the use of sea water at a low initial pH must take in account the effect of direct acid leaching as well as the catalytic effect of sodium chloride.

4.2.3 Sodium acetate as an aeration catalyst

The acetate ion is known to have buffering properties similar to those of the ammonium buffer used in the Becher process. The acetate ion also has some ability to act as a ligand with iron. Due to these properties sodium acetate was thought to be a possible leaching catalyst for metallic iron in reduced ilmenite.

The aeration involving the use of sodium acetate used the same conditions as for sodium chloride in section 4.2.1 with 14.76 grams (0.1 M) of sodium acetate in the place of the sodium chloride. The results of these analyses are shown in Figure 4.3.

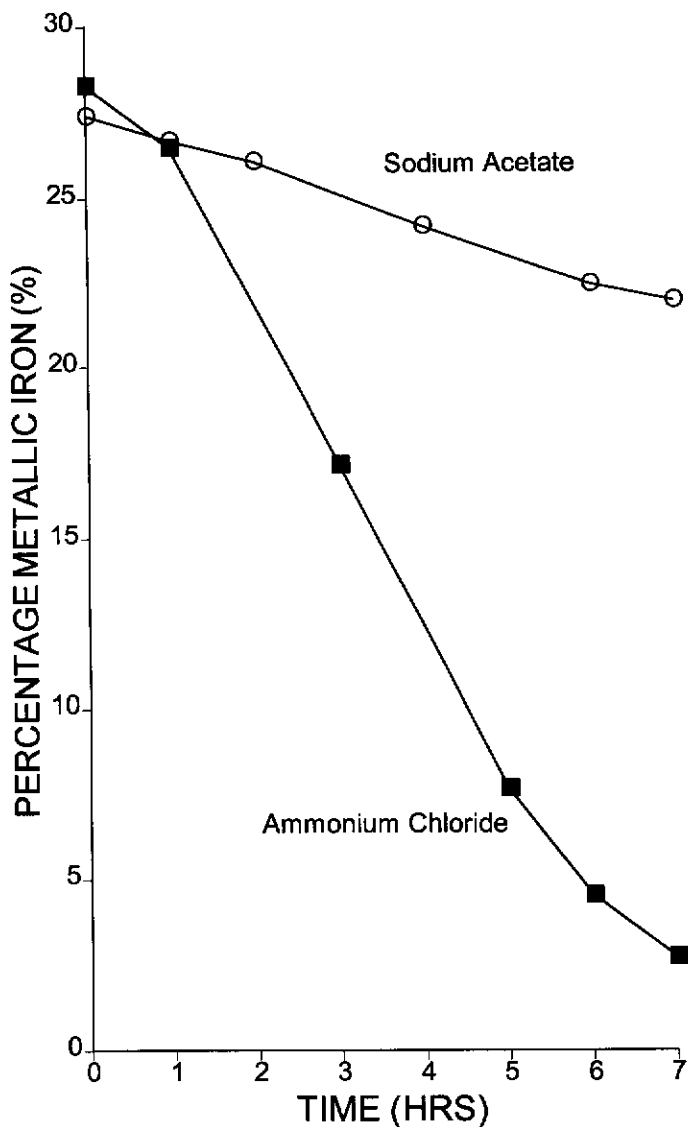


Figure 4.3: Sodium acetate (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron.

The results shown in graphical form in Figure 4.3 clearly revealed that sodium acetate does not act very well as a leaching catalyst when compared to ammonium chloride. After the 7.0 hours of aeration the slurry using sodium acetate reached a residual metallic iron level of 21.9 per cent, that is approximately 19 per cent of the metallic iron has been removed. This was consistent with previous work completed where no catalytic reagent was added to the slurry. This means that the sodium acetate contributed no catalytic or any other action by being present.

4.2.4 Sodium sulfate as an aeration catalyst

From the work completed by Denholm (1962) both the chloride anion and the sulfate anion can increase the rate of metallic iron dissolution by their presence in the aeration mixture. These two anions act in slightly different manners to prevent the surface of the metallic iron from forming a passive iron oxide film. Due to these differences sodium sulfate was chosen as an aeration catalyst to compare to the performance of the chloride ion in sodium chloride.

The slurry used for the sodium sulfate experiment used the same conditions as for sodium chloride in section 4.2.1, with 25.56 grams (0.1 M) sodium sulfate in place of the sodium chloride. The results of these analyses were constructed into a graph which is shown in Figure 4.4.

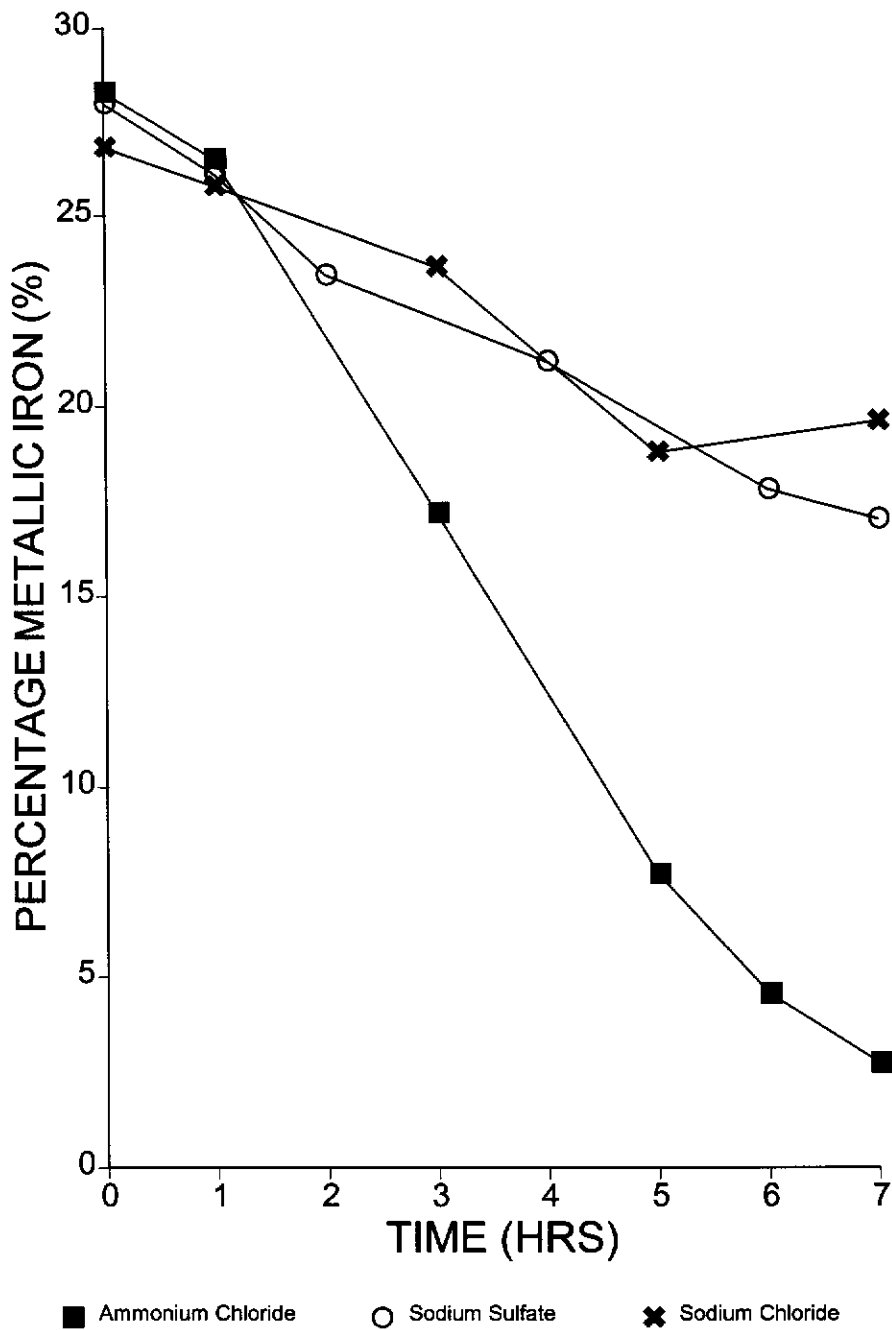


Figure 4.4: Sodium sulfate (0.1 M), sodium chloride (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron.

The sodium sulfate was observed to take almost the same path as the sodium chloride in the first 6.0 hours of aeration. The apparent deviation from the sodium chloride in the last hour of aeration shown in Figure 4.4 can be attributed to a combination of the sodium chloride slurry allowing some *in situ* rusting to occur and experimental error. The sodium sulfate aeration reached a residual metallic iron level

of 16.9 per cent after the 7.0 hours compared to 2.3 per cent for the ammonium chloride aeration. This experiment has shown the sulfate ion to have very similar reaction characteristics to the chloride ion when they are both used in conjunction with the sodium ion. Overall the performance of the sodium sulfate as a catalyst was approximately the same as sodium chloride but both were substantially poorer than ammonium chloride.

4.2.5 Sodium perchlorate as an aeration catalyst

For the purpose of comparison the perchlorate ion has been chosen because of its relative unreactive non-coordinating properties when compared to chloride and sulfate. In terms of acting in a catalytic capacity it will not buffer the solution, it will not stop passive films forming on the iron surface and it will not complex in any way with the iron. By using the perchlorate ion with the sodium ion the ability of the sodium ion to extract the metallic iron was highlighted.

The slurry prepared for this experiment used the same conditions as for sodium chloride in section 4.2.1, with 25.3 grams (0.1 M) sodium perchlorate monohydrate in place of the sodium chloride. The results of these samples are shown graphically in Figure 4.5.

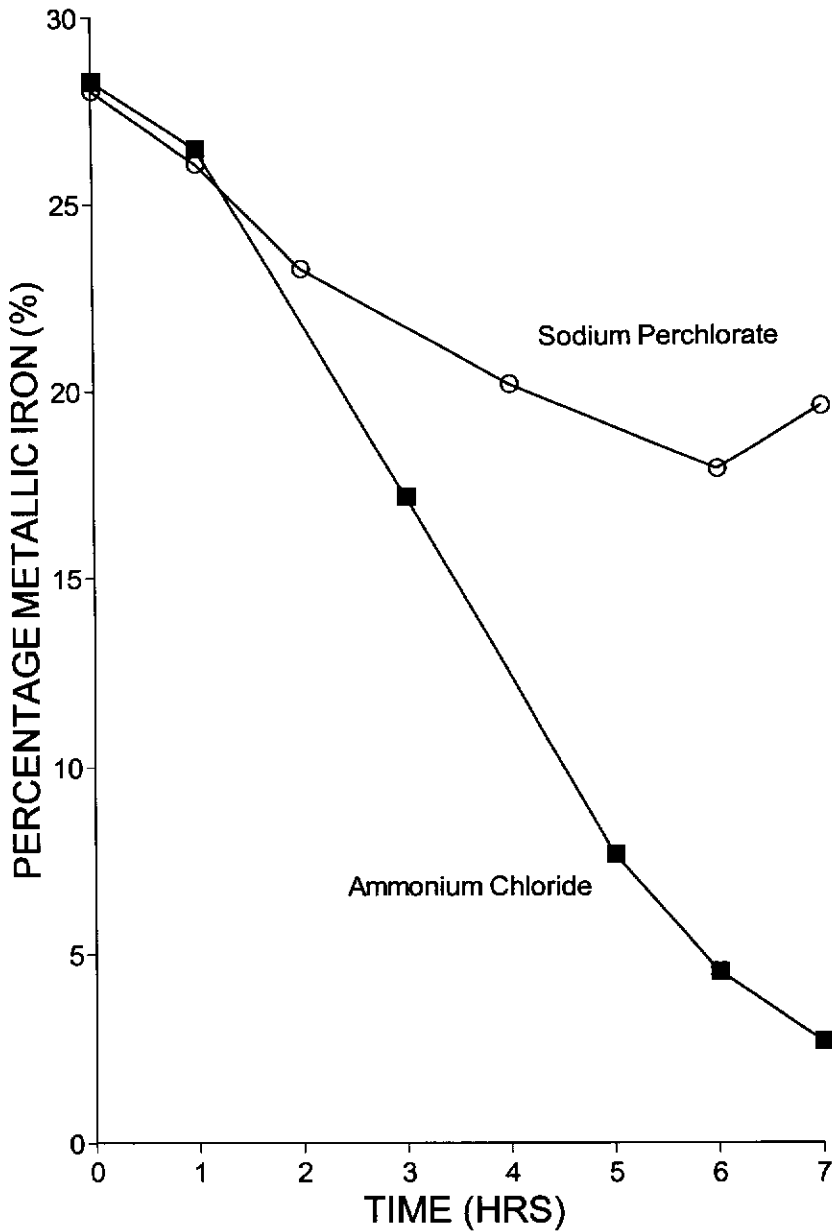


Figure 4.5: Sodium perchlorate (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron.

The results shown in Figure 4.5 indicate that the sodium perchlorate was not an effective catalyst for the leaching of metallic iron from reduced ilmenite. After the first hour of aeration the sample taken showed brown solid attached to the grains. This would indicate the presence of *in situ* rusting occurring on and within the grains. After the 7.0 hour period the progression of rate of metallic iron removal was found to be similar to the slurry that used sodium chloride.

This observation that the sodium perchlorate behaved very similarly to

sodium chloride indicated that chloride and sulfate ions when used in conjunction with the sodium ion have little or no effect on the rate of metallic iron dissolution.

4.2.6 Sodium nitrate as an aeration catalyst

To complete the series of catalysts containing the sodium cation, sodium nitrate was chosen as it is known to have a neutral anion that will not promote the dissolution of metallic iron. This experiment was conducted as a comparison to the perchlorate ion experiment to ensure that a rate of metallic iron removal due to the presence of sodium ion alone was determined.

The slurry for this experiment used the same conditions as for sodium chloride in section 4.2.1, with 15.3 grams (0.1 M) of sodium nitrate in place of the sodium chloride. The data were converted into a graph which is featured in Figure 4.6.

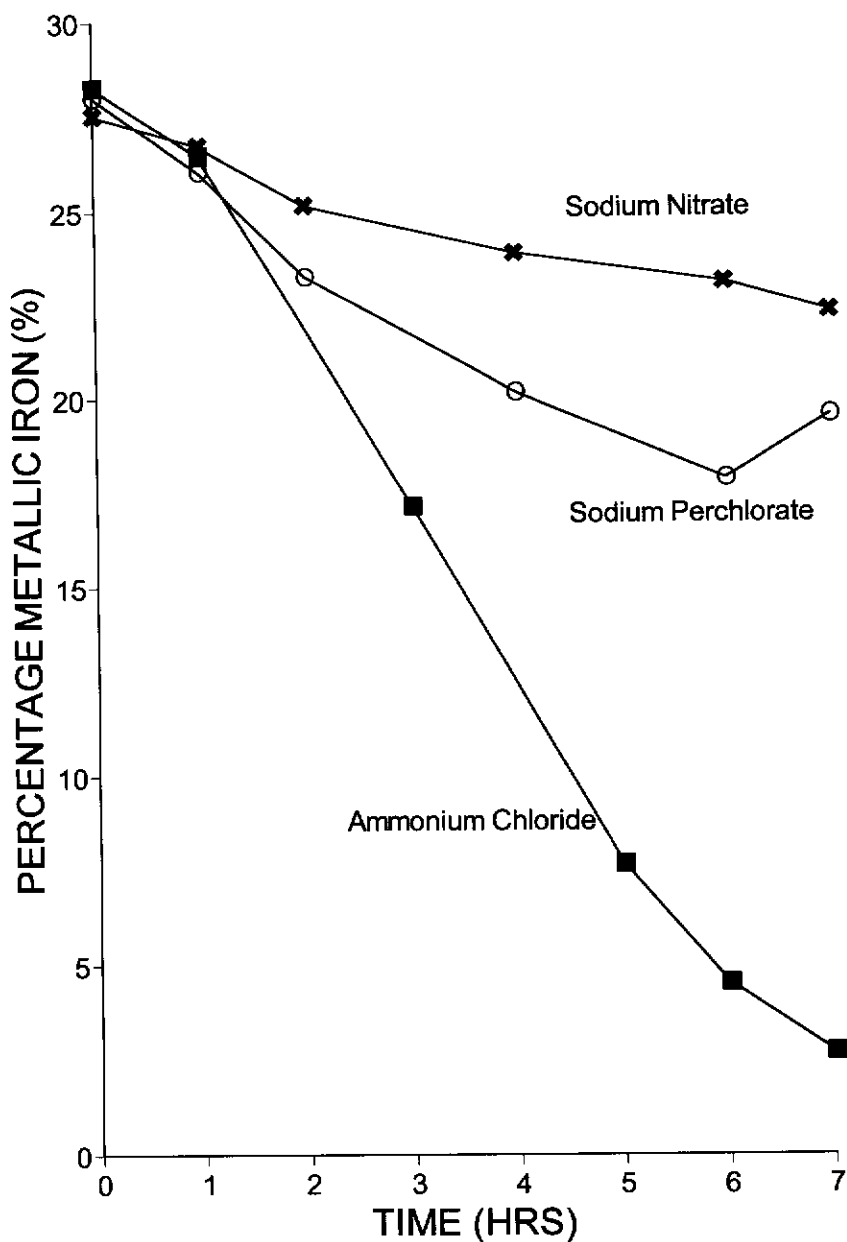


Figure 4.6: Sodium nitrate (0.1 M), sodium perchlorate (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron.

As the graph, in Figure 4.6 shows, sodium nitrate provides a very slow rate of metallic iron dissolution over the 7.0 hour period. When compared to all the other sodium compounds used in this chapter it was found to have the slowest rate overall. The closest rate of dissolution was found with the sodium acetate. There was a significant difference between the sodium perchlorate and the sodium nitrate experiments. As the perchlorate and the nitrate ions were expected to have no effect on the leaching rate they should have had very similar rates of reaction. This

indicated that either the perchlorate ion does cause a minor disturbance on the oxide layer on the surface of the metallic iron, or the nitrate ion interferes with the aeration in some unknown way to decrease the rate of reaction. This may involve some promotion of a passive layer on the iron surface.

4.3 The use of ammonium salts as catalysts in aerations

4.3.1 Ammonium perchlorate as an aeration catalyst

To compare the performance of the sodium cation to the ammonium cation the perchlorate anion was used in both cases. The perchlorate ion was expected to have little or no effect on the leaching rate because it was presumed not to have any interaction with the metallic iron, the iron oxide layer on the surface of the metallic iron or in the transportation of the ionic iron to the bulk solution. Any effect of perchlorate on the aeration rate will be discussed later, when it is compared with the effect of ammonium nitrate. What was important was that the perchlorate ion was known to have little or no effect on aeration rates so when combined with sodium and then ammonium the net effects of the cations can be seen.

The slurry used to conduct the aeration in which ammonium perchlorate was used, consisted of 300 grams of reduced ilmenite, 1.8 litres of water and 21.15 grams (0.1 M) ammonium perchlorate. This slurry was raised to and held at a temperature between 70 and 80 degrees Celsius while a 1.0 litre per minute air flow was passed through the slurry. The slurry was aerated for 7.0 hours during which periodic samples of the reduced ilmenite were taken for metallic iron content analysis. The results of these analyses are expressed in graphical form in Figure 4.7.

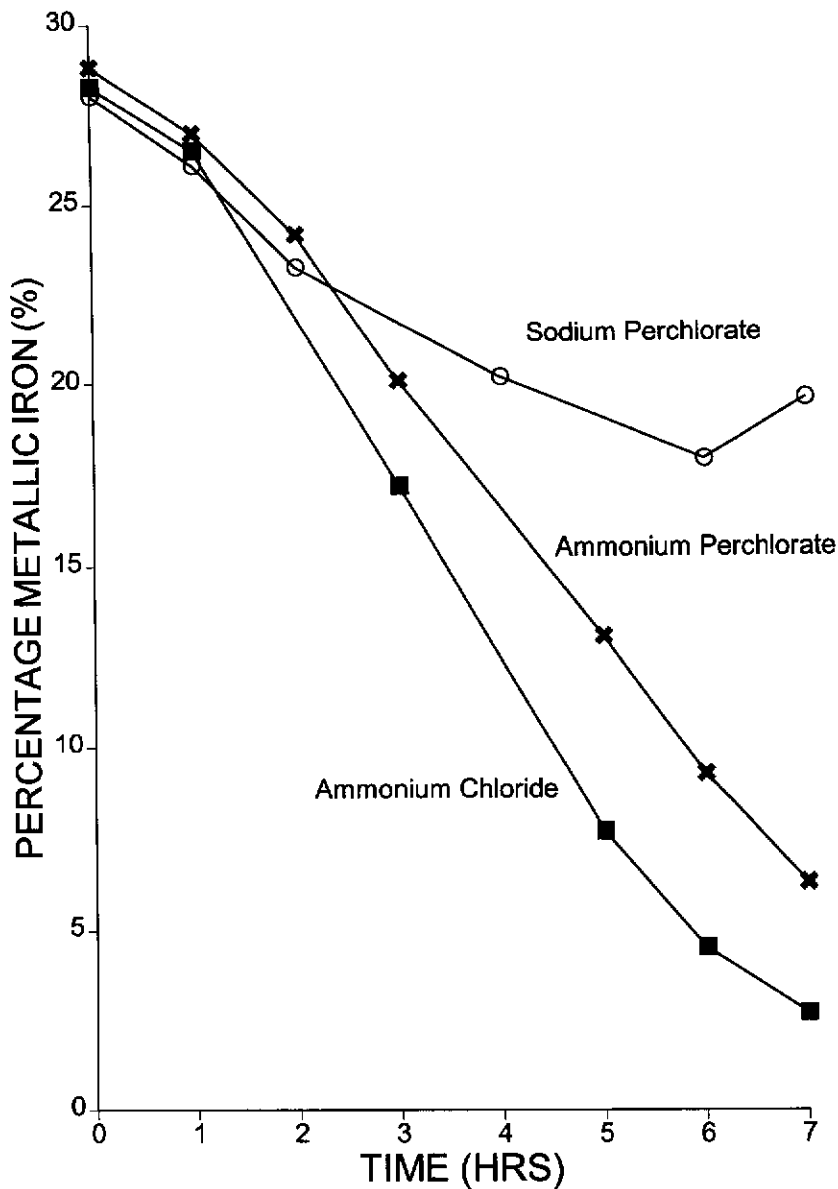


Figure 4.7: Ammonium perchlorate (0.1 M), sodium perchlorate (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron.

The graph featured in Figure 4.7 shows the extremely strong influence of the ammonium ion in the removal of metallic iron from the reduced ilmenite grains. When compared to the rate of reaction shown by sodium perchlorate, which reached a metallic iron level of 19.5 per cent after 7.0 hours, the ammonium perchlorate worked better as a catalyst by reaching a metallic iron level of 6.3 per cent. As the perchlorate ion was present in both compounds the increase in the rate of reaction can be attributed to the presence of the ammonium ion. The reason believed to be behind the catalytic behaviour of the ammonium ion comes from its ability to buffer the

solution and its ability to complex with iron (II) (Lewis, 1994).

4.3.2 Ammonium nitrate as an aeration catalyst

Again the nitrate ion was chosen as a comparison to the perchlorate ion to establish if the perchlorate ion was actually participating in the catalytic aeration. The nitrate was also supposed to have the effect of a spectator ion in the catalytic reaction of ammonium nitrate. To establish which of the two anions was interacting, constructively or destructively, in the aeration a comparison to a slurry with no catalyst present was made.

The slurry containing the ammonium nitrate used the same conditions as for ammonium perchlorate in section 4.3.2, with 14.4 grams (0.1 M) of ammonium nitrate in place of the ammonium perchlorate. The results of these analyses are represented with those for ammonium perchlorate, ammonium chloride and a slurry with no catalyst in Figure 4.8.

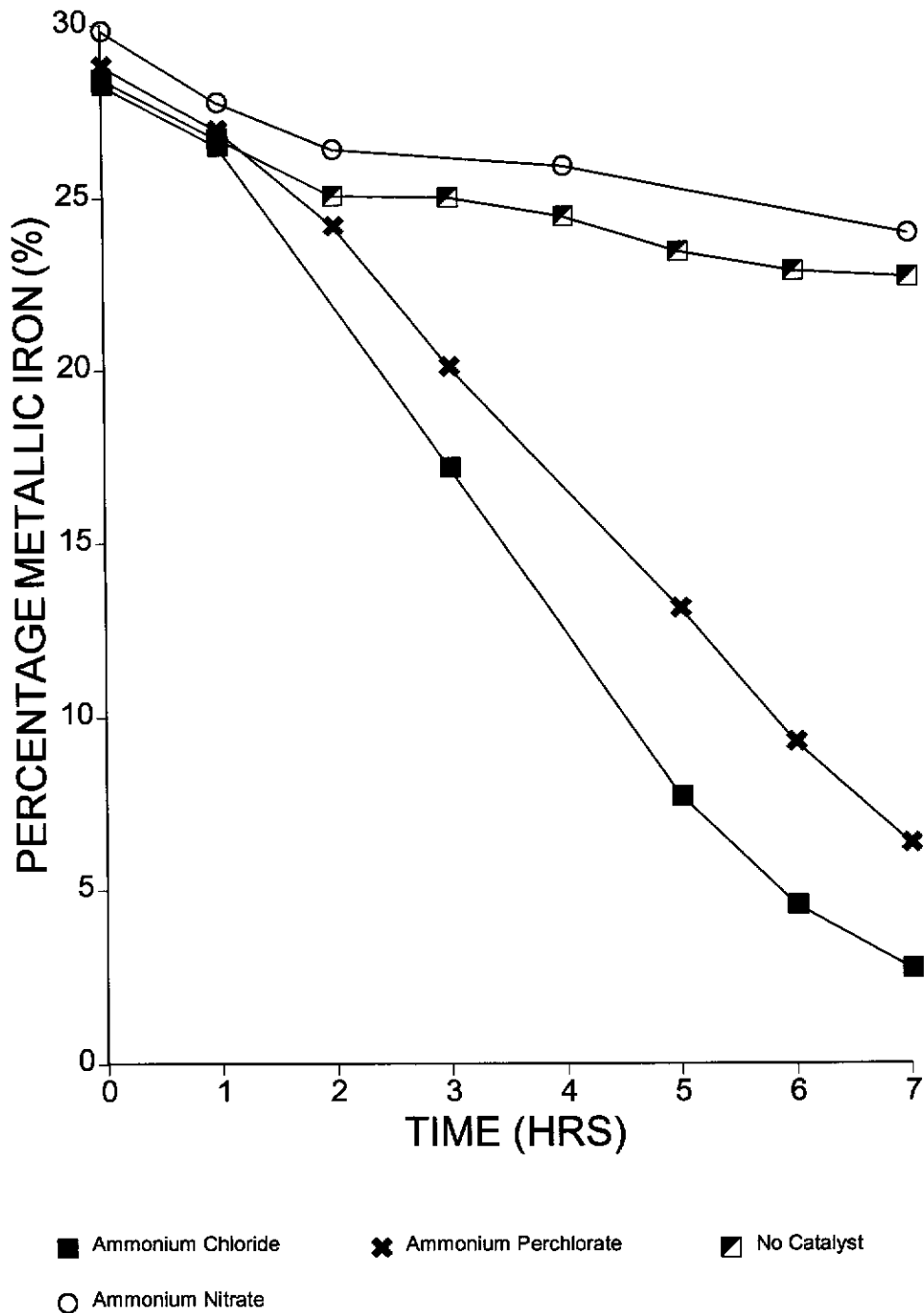
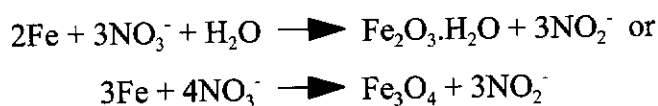


Figure 4.8: Ammonium nitrate (0.1 M), ammonium perchlorate (0.1 M), ammonium chloride (0.1 M) used as catalysts to remove metallic iron, and a non catalysed aeration of reduced ilmenite.

The graph shown in Figure 4.8 shows a large difference between the ammonium perchlorate and the ammonium nitrate. These two slurries were expected to show similar reaction rates if the anions did not react in any way. The graph also shows how close the ammonium nitrate slurry was in reaction rate to the slurry

containing no catalyst. This observation would seem to indicate that the presence of the nitrate ion counteracts any effect produced by the ammonium ion. The actual reaction progress of the ammonium nitrate, which finishes with a metallic iron level of 23.8 per cent, indicated that almost none of the metallic iron had been leached. This in comparison to the ammonium chloride, with essentially all the iron removed and ammonium perchlorate, with only 6.3 per cent iron remaining, seems to indicate that the nitrate ion was disturbing the function of the ammonium ion. This information further suggests that the perchlorate ion was the ion that actually took no part in the reaction whereas the nitrate ion actually helped prevent the metallic iron from being oxidised. To explain this phenomenon it is possible that the nitrate ion underwent further reactions to form passivating iron oxides on the surface of the reduced ilmenite.



The thermodynamic data for these equations suggest that iron oxides may be formed in this way, but the kinetics may well prevent this reaction pathway from contributing at a significant rate.

4.3.3 Ammonium sulfate as an aeration catalyst

The previous experiments involving the use of sodium sulfate and sodium chloride have shown that the sulfate and chloride anions act in much the same manner, and as a result produced similar results. This information, plus the work of Denholm (1962) on the destruction of passive films, indicated that ammonium sulfate may be a catalyst that can perform as well as, or better than, ammonium chloride.

The slurry used for this experiment used the same conditions as for ammonium perchlorate in section 4.3.2, with 23.8 grams (0.1M) ammonium sulfate in place of the ammonium perchlorate. The results of these analyses were plotted in graphical form and presented in Figure 4.9.

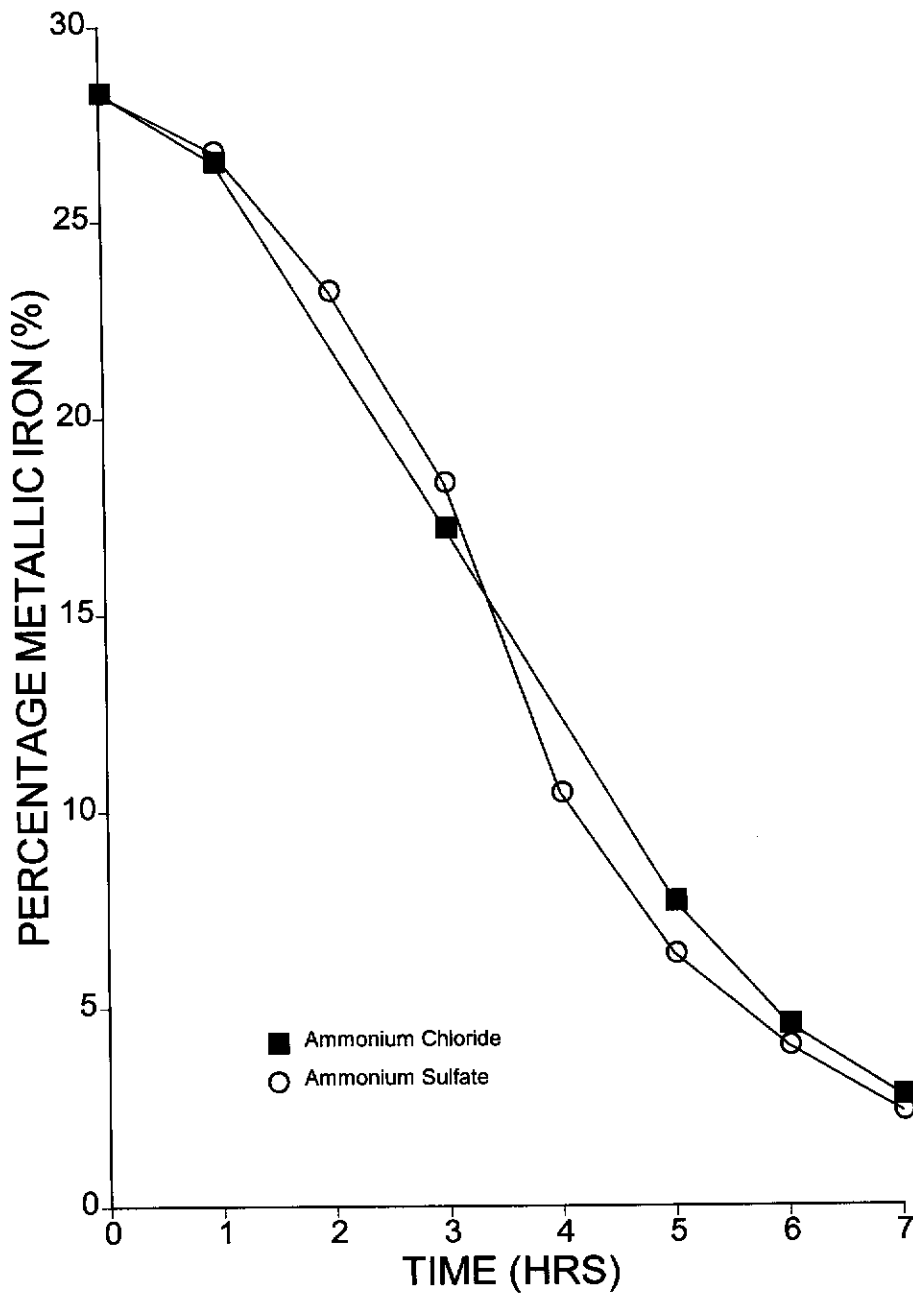


Figure 4.9: Ammonium sulfate (0.1 M) and ammonium chloride (0.1 M) used as catalysts in the aeration of reduced ilmenite to remove metallic iron.

The results of the graph in Figure 4.9 show that using ammonium sulfate as a catalyst could remove all of the available metallic iron present in the reduced ilmenite in the 7.0 hour period. When compared to an ammonium chloride slurry, also in Figure 4.9, the ammonium sulfate leach follows an almost identical reaction pathway throughout the 7.0 hour aeration but maybe fractionally superior during the second half of the aeration period. The final residual metallic iron levels of the ammonium sulfate slurry are actually slightly lower, with a value of 2.3 per cent,

compared with the ammonium chloride slurry 2.7 per cent. These final values indicate that the ammonium sulfate works as well as the ammonium chloride as a catalyst.

4.4 Conclusions

Using the sodium cation in conjunction with various anions as catalyst in the aeration of porous reduced ilmenite has shown a wide range of results. The reason for the wide range of reaction rates was related to the anions used in conjunction with the sodium. In the case of the sulfate ion the reaction rate was the highest of the single anion mixtures, this fast reaction rate was attributed to the disruptive influence the sulfate ion has on the formation of iron oxide layers which would stop the oxidation of the metallic iron. The chloride anion was expected to yield much the same results as the sulfate anion because the chloride also disrupts iron oxide layers. As the data have shown the chloride and sulfate experiments follow almost the same pathway over the aeration period.

The acetate and nitrate anion experiments also follow a similar path over the aeration period. These two anion experiments gave results that were consistent with previous experiments carried out without any catalyst added. This would seem to indicate that the acetate and nitrate have a negative effect on the rate of reaction.

The perchlorate anion also yielded a slow reaction rate when compared to an ammonium chloride experiment but it was faster than the nitrate and acetate experiments.

The final experiment using the sodium cation was a multicomponent system using sea water. Although sea water is predominantly sodium chloride it was the additional species that managed to significantly increase the reaction rate when compared to an experiment using sodium chloride alone. The use of sea water was the best leaching reagent employed for this series of tests but still fell short of the

performance of ammonium chloride.

Looking at the overall performance of the sodium compounds, the best results still did not manage to compete with the performance of ammonium chloride. But the various anions did have differing effects on the aeration rate. The experiments involving the ammonium ion were carried out to observe the behaviour of these various anions to observe if any higher rates of reaction could be obtained.

The initial use of ammonium sulfate again followed a very similar path to the ammonium chloride standard. The ammonium sulfate showed a slightly lower metallic iron level after 7.0 hours but this value was within the experimental error of the ammonium chloride value so the two experiments can be said to have essentially the same rate of aeration.

The ammonium perchlorate managed to remove most of the metallic iron in the 7.0 hours that made it less effective than ammonium chloride. The ammonium nitrate managed to remove only a small amount of metallic iron that was consistent with aerial rusting. This indicated that the nitrate ion was inhibiting the oxidation / removal of the metallic iron. With this information it was assumed that the performance of ammonium perchlorate was due only to the presence of ammonium ion and not the perchlorate ion.

The comparison between the ammonium perchlorate and sodium perchlorate experiments has shown the difference between the use of the sodium ion and the ammonium ion. Although chloride ion may participate to a certain degree, the greater rate of iron leaching in ammonium chloride compared to sodium chloride reinforces the conclusion that the ammonium ion is the primary key component for effective leaching.

Chapter Five

Other amine compounds as catalysts in the Becher process

5.1 Introduction

The Becher process became a viable option to produce synthetic rutile through the catalytic actions of ammonium chloride. Without the ammonium chloride this process would be extremely slow with significant *in situ* rusting occurring. The reasons given for ammonium chloride's ability to catalyse the aeration of the metallic iron were its buffering ability, its ability to disrupt passive iron oxide layers and its complexing ability. It is this complexing ability with the ionic iron (II) that has still eluded complete understanding.

From the work of Farrow and Ritchie (1985) and Lewis (1994) it is known that the iron (II) species does complex with aqueous ammonia, but the nature of the bonding in the complex and why similar compounds are not formed with other ligands is still unknown. The purpose of the experiments in this chapter is to search for some reasons for the success of ammonium chloride over other catalytic reagents by testing compounds which are similar to ammonium chloride.

5.2 Methyl substituted ammonium chlorides

This first series of experiments was designed to observe the change in the rate of reaction, if any, as the ammonium ion has its hydrogen atoms replaced with methyl groups, one at a time. The simple methyl group was used in these experiments because it does not have many reactive tendencies, that is, it does not form hydrogen bonds or other specific intramolecular or intermolecular interactions.

In each of the following experiments a slurry mixture of 300 grams of reduced ilmenite, 1.8 litres of water and 0.093 M of the substituted ammonium chloride compounds was used. The substituted ammonium chloride compounds tested were methylamine hydrochloride ($\text{CH}_3\text{NH}_2\text{Cl}$), dimethylamine hydrochloride ($[\text{CH}_3]_2\text{NH}_2\text{Cl}$), trimethylamine hydrochloride ($[\text{CH}_3]_3\text{NHCl}$) and tetramethylammonium chloride ($[\text{CH}_3]_4\text{NCl}$). All these experiments were carried out at a temperature between 70 and 80 degrees Celsius while having an air flow of 1.0 litre per minute passed through the slurry. Samples were periodically taken as the aeration progressed. These samples were then analysed for the metallic iron content. The results of the analyses are presented in Figure 5.1.

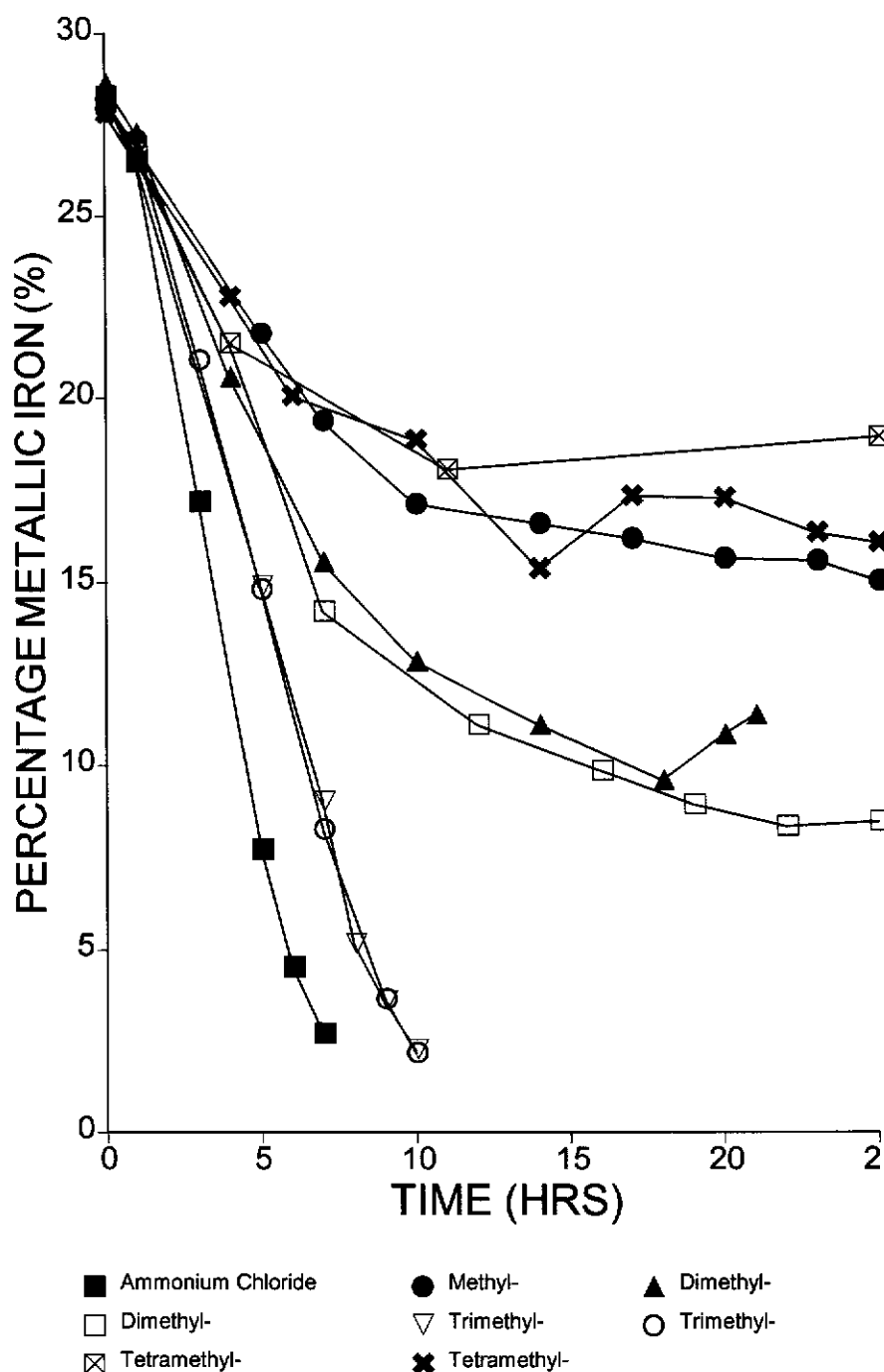


Figure 5.1: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using ammonium chloride, methylamine hydrochloride, dimethylamine hydrochloride (in duplicate), trimethylamine hydrochloride (in duplicate) and tetramethylammonium chloride (in duplicate) as catalytic reagents.

The data presented in Figure 5.1 shows no obvious trend between the reaction rate and the degree of substitution. The numerical comparison of the rates of reaction for these catalysts can be found in Table 5.1.

Table 5.1: Table to compare the rates of removal of metallic iron from reduced ilmenite by a series of substituted amine compounds.

Rank of Reaction Rate	Compound	Rate (%/Hr)
Fastest	ammonium chloride	3.65
Second	trimethylamine hydrochloride	2.57
Third	dimethylamine hydrochloride	0.795
Fourth	methylamine hydrochloride	0.529
Fifth	tetramethylammonium chloride	0.424

Table 5.1 shows that once substitution of the hydrogen atoms with methyl groups begins the rate of reaction decreases. All the amine compounds, with the exception of tetramethylammonium chloride, were still able to buffer the slurry at a pH range from 7.9 to 6.0. This proves that the amine compounds still have the ability to buffer the solution and the presence of the chloride ion will still assist in the breaking down of the passivating iron oxide layers. So any changes to the reaction rates of the amine compounds could only be due to the inability of the respective amine compounds to complex with ionic iron (II) and transport it out of the reduced ilmenite grain. The first possible explanation for the behaviour seen in Table 5.1 was that the addition of methyl groups to replace hydrogen atoms began to cause a steric hindrance in the amine group. The predicted steric hindrance would then make the process of forming a complex compound between iron (II) and the methyl-substituted nitrogen of the amine compounds harder to achieve. This steric effect has been noted by Martell and Handcock (1996) when it caused a curvature in the relationship between the free energy and the number of methyl groups on the donor atom for the R_3N series with increased methylation of the cation. If this were the only process occurring it would be expected for the reaction rate to decrease in the order mono-methyl, di-methyl, tri-methyl and finally tetra-methyl. However, this was not the pattern observed so other additional relationships were looked at, such as the exact pH range and the acid dissociation constants (K_a).

The pH ranges were found to vary little for most of these compounds and the ranges failed to follow the trend shown in Table 5.1. The pK_a values for the series of amines do follow the aeration rate trend to some extent. The pK_a values for the conjugate acids of the particular amines are listed in Table 5.2.

Table 5.2: Table of ammonium ions used for aeration and their pK_a values at 348 K (Stark and Wallace, 1976)(J. Phys. and Chem Ref, 1982)

Ion	pK_a
NH_4^+	7.90
$(CH_3)_3NH^+$	8.42
$(CH_3)_2NH_2^+$	9.47
$CH_3NH_3^+$	9.70

The pK_a values follow the aeration rate trend quite well for the all four ammonium ions. Although there is a significant difference in the last two pK_a values they are close together and still substantially greater than the previous values. Furthermore the differences between the aeration rates for these two amines are quite small. To further test the theory that the aeration rate was related to the acid dissociation constants (Hammett, 1970) (Jaffe, 1953), other amines with similar and different dissociation constants were tested, as described in the following sections.

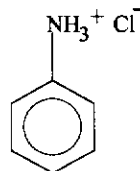
The exception to all the above discussion is the tetramethylammonium chloride because it lacks a hydrogen group in its structure that could deprotonate to form the unprotonated amine, and so it is unable to buffer a solution, unlike the other amines and their hydrochlorides. Another result of the lack of a proton is that there is no pK_a value as acid dissociation is not possible. With this in mind the differing aeration rate between the tetramethylammonium chloride slurry and the ammonium chloride slurry could have been caused by other influences in addition to its inability to form a complex with ionic iron (II).

5.3 Aniline hydrochloride as an aeration catalyst

The choice of aniline hydrochloride as aeration catalyst was decided by its pK_a value and its similarities to ammonium chloride, that is the presence of a positively charged quaternary ammonium ion and chloride ion in both compounds. As previously discussed in section 5.2 the best leaching catalyst had the lowest pK_a value. Aniline hydrochloride was chosen because of its low pK_a value of 4.62 (Stark and Wallace, 1976) which was a much lower value than those considered in section

5.2. The reason for the choice of a low pK_a value was to examine the effect of the change in value against any change in the aeration rate.

The slurries used in these experiments were the same as those used in section 5.2 except that 23.31 grams (0.1 M) of aniline hydrochloride was used as the catalyst in place of the methyl substituted amines. The metallic iron values obtained from this experiment are illustrated in Figure 5.2.



Aniline Hydrochloride

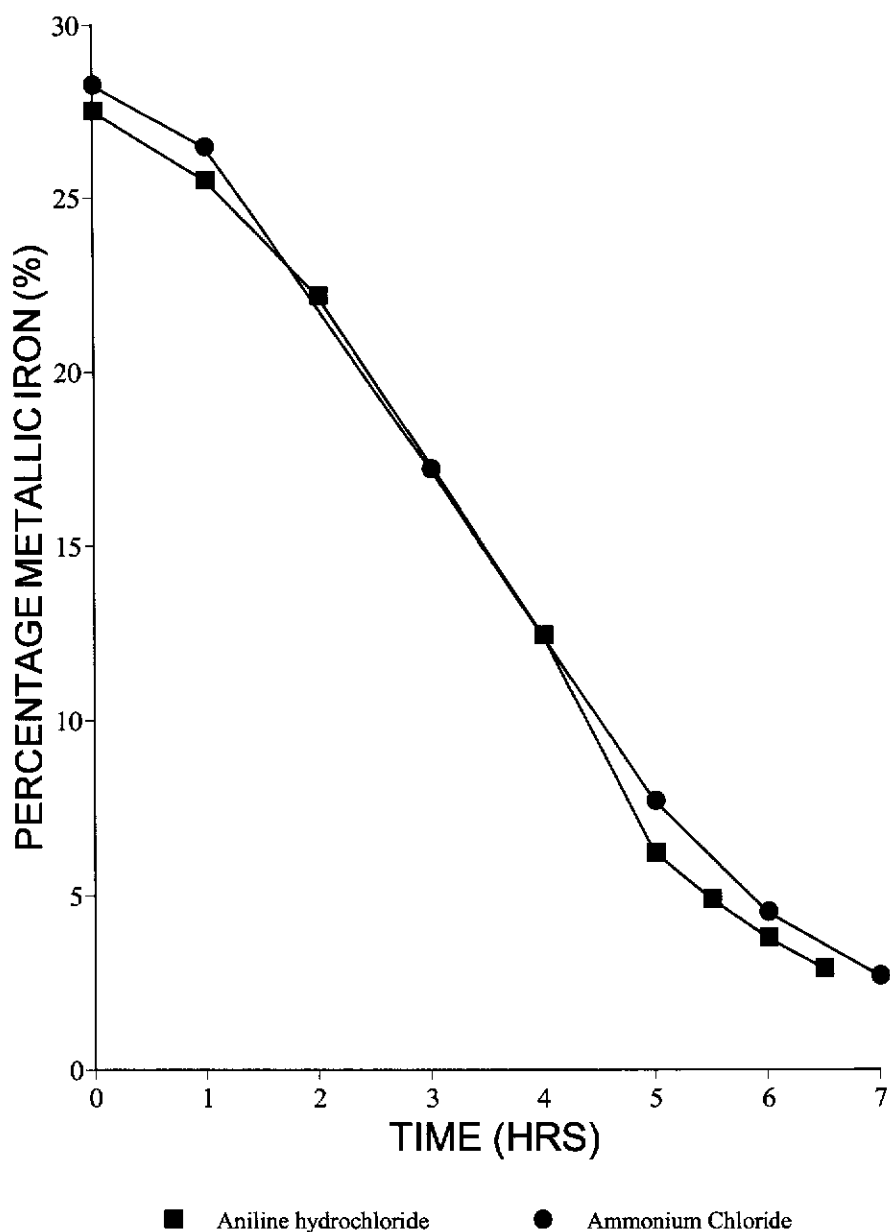


Figure 5.2: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using ammonium chloride (0.1 M) and aniline hydrochloride as catalytic reagents.

The results shown in Figure 5.2 did suggest that the aniline hydrochloride slurry appears to be capable of a slightly faster aeration rate than the standard ammonium chloride slurry although the difference is close to the experimental uncertainty.

This result is partially consistent with the postulation that the rates of aeration were related to the pK_a values. The pK_a for ammonium chloride is given as 9.25

while the value for aniline hydrochloride was 4.62 (Stark and Wallace, 1976). This value agrees with the trend of the pK_a influencing the rate of aeration, that is the higher pK_a value (ammonium chloride) caused the slower aeration rate and the higher pK_a (aniline hydrochloride) caused the faster rate of aeration.

The result of this experiment seems to show a relationship between the pK_a value of an aeration catalyst and the rate at which it will remove the metallic iron from the reduced ilmenite. This relationship has been found not to be a direct proportionality, and relies on the structures being of the same type so that steric interferences can be discounted. As a result of these experiments a faster aeration catalyst than the standard ammonium chloride has been found, this being the aniline hydrochloride. Due to this finding more tests were designed for compounds containing similar features to aniline hydrochloride and ammonium chloride.

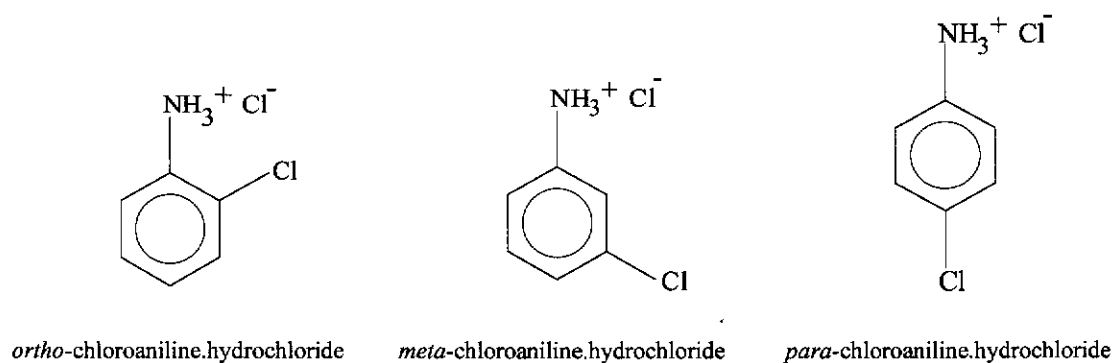
5.4 Aniline hydrochloride derivatives as aeration catalysts

As discussed in the previous sections, there is very little known about the mechanism of the complexation of the ionic iron (II) inside a reduced ilmenite grain. In this section aniline hydrochloride derivatives have been chosen for use as the aeration catalysts. This is because of the promising result yielded by aniline hydrochloride as described in the preceding section, and in order to continue to monitor the effect of a large group bound to the functional amine group. The first of these experiments involved the substituting of a chloro group on the benzene ring of aniline hydrochloride in the *ortho*-, *meta*- and *para*- positions. The series of experiments described in the following section used the nitro group also in the *ortho*-, *meta*- and *para*- positions. The final experiments in this section also substituted a methyl group for the same sequence of comparisons.

5.4.1. Chloro - substituted aniline hydrochloride

The substitution of chlorine on to the aniline hydrochloride compound was chosen as a means of varying the electronic inductive effect through the benzene ring to the nitrogen in the amine group. This will have the effect of varying the pK_a , and presumably the complexing tendencies. The chlorine atom was substituted at the *ortho*-, *meta*- and *para*- positions to observe the influence of the electronic effect, and any possible steric interference occurring.

The experimental slurries and conditions were the same as those employed for aniline hydrochloride in section 5.3 with the exception of using 29.52 grams (0.1 M) of 2-chloroaniline hydrochloride, 3-chloroaniline hydrochloride and 4-chloroaniline hydrochloride respectively in the place of aniline hydrochloride. These results are graphically depicted in Figure 5.3.



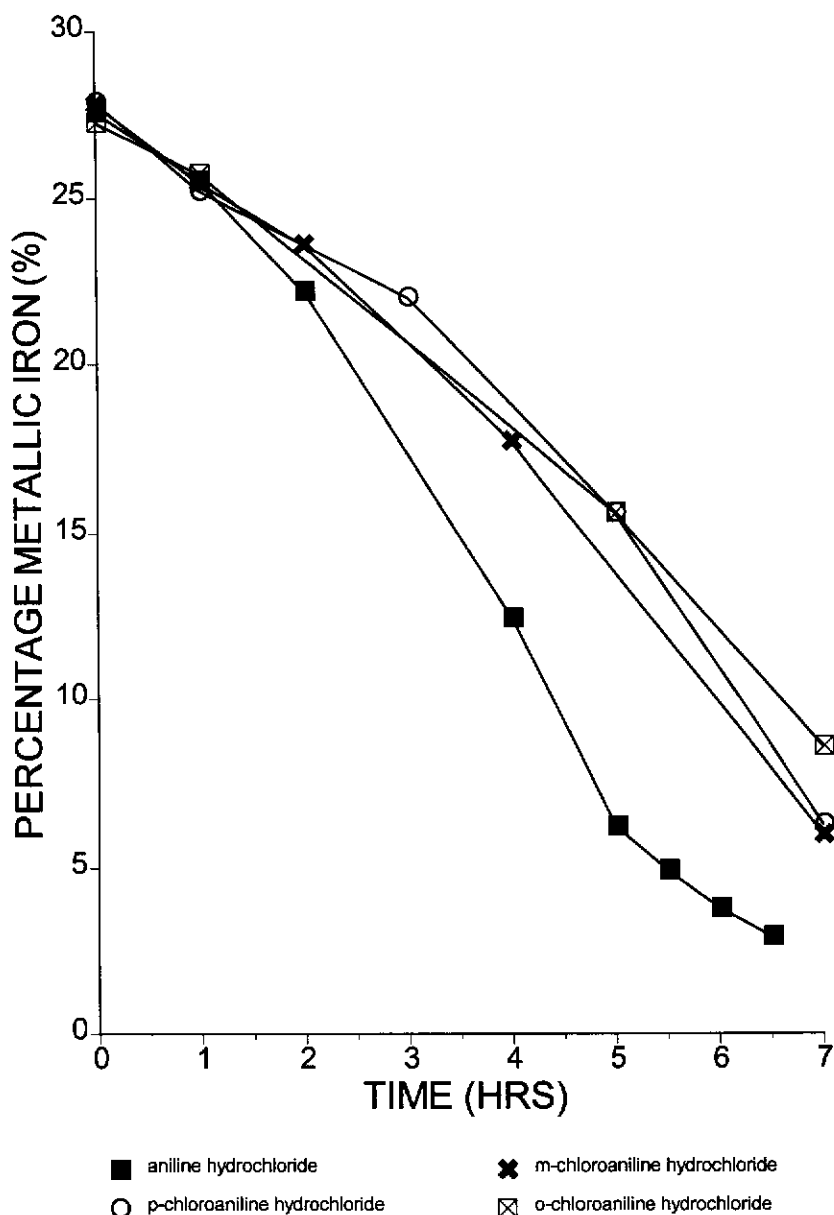


Figure 5.3: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using aniline hydrochloride, *para*-chloroaniline hydrochloride, *meta*-chloroaniline hydrochloride and *ortho*-chloroaniline hydrochloride as catalytic reagents.

From the graph in Figure 5.3 it was evident that the *ortho*-substituted aniline hydrochloride has a slightly slower aeration rate than the other two substituted compounds. The final residual metallic iron level in the *ortho*-substituted compound was found to be 8.54 per cent whereas the *meta*- and *para*-substituted compounds had residual levels of 5.9 and 6.3 per cent respectively. The close correspondence of the plots for the *meta*- and *para*-chloroaniline hydrochloride, that are within the normal variation of replicate results, show that the positioning of the chloro group in

either position has little effect on the aeration rate. The difference between the aeration rate of *ortho*-chloroaniline hydrochloride and the *meta*- and *para*-chloroaniline hydrochlorides, which is outside the normal variation in replicates, appears to come from steric hindrance at the nitrogen and hydrogen groups that make the functional amine group, by the close proximity of the chloro group.

In comparison to aniline hydrochloride all these substituted derivatives result in significantly slower aeration rates, which can not be explained by their pK_a values as the *ortho*-, *meta*- and *para*- derivatives have values of 2.65, 3.46 and 4.15 respectively while aniline hydrochloride has a value of 4.62. If the pK_a were the sole controlling factor the substituted derivatives were expected to have a faster rate of aeration than aniline hydrochloride. In this instance the steric effect of the large chlorine group must have been significantly greater than the pK_a .

5.4.2. Nitro - substituted aniline hydrochloride

The use of the nitro group that was substituted on to the benzene ring of aniline hydrochloride was chosen because it displays a similar inductive effect to the effect shown by a chloro group and can, therefore, be used as a comparison. The nitro group also contains a nitrogen atom, but this is thought to be unreactive itself under the aeration conditions. In this series of experiments the *ortho*-, *meta*-, and *para*-nitroaniline hydrochlorides were used for a comparison to examine the effect of positioning of the nitro group.

The slurry compositions for these three experiments were the same as those for aniline hydrochloride in section 5.3, with the exception of using 31.43 grams (0.1 M) of the respective *ortho*-nitroaniline hydrochloride, *meta*- nitroaniline hydrochloride and *para*- nitroaniline hydrochloride respectively in place of the aniline hydrochloride. These analyses gave a metallic iron content at a given time which is shown graphically in Figure 5.4.

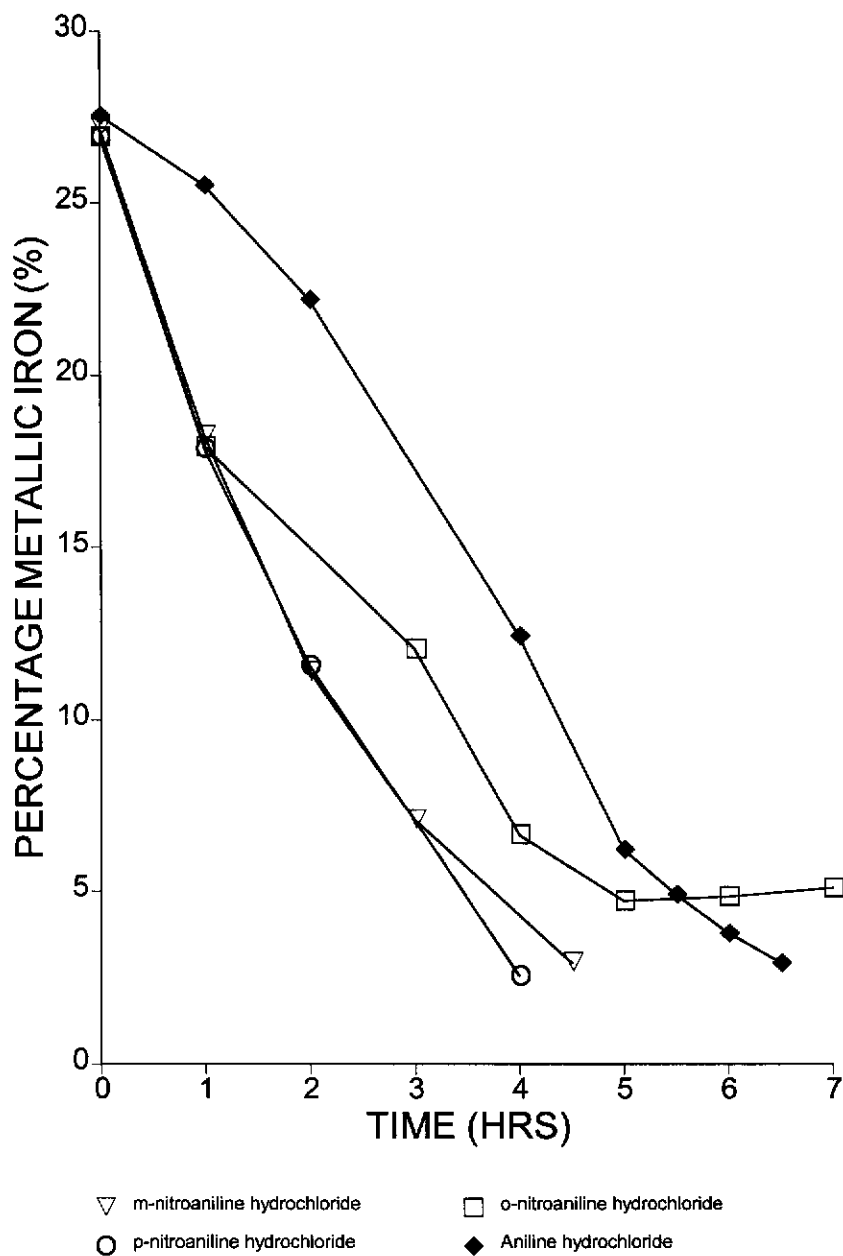
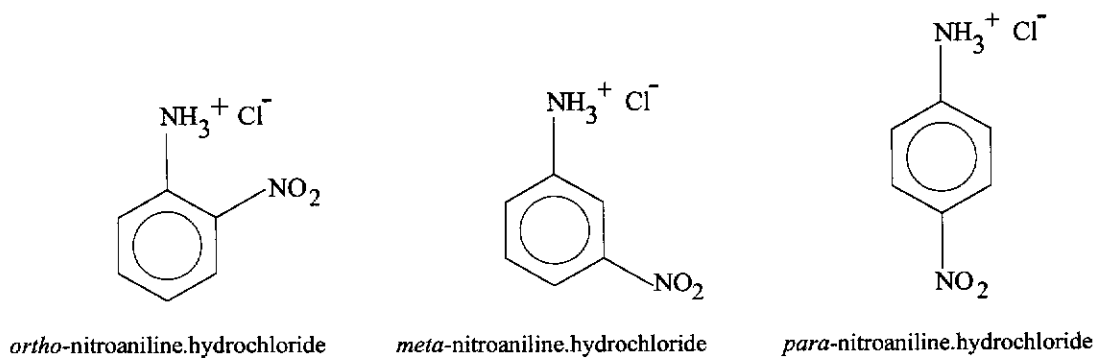


Figure 5.4: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using *para*-nitroaniline hydrochloride, *meta*-nitroaniline hydrochloride, *ortho*-nitroaniline hydrochloride and aniline hydrochloride as catalytic reagents.

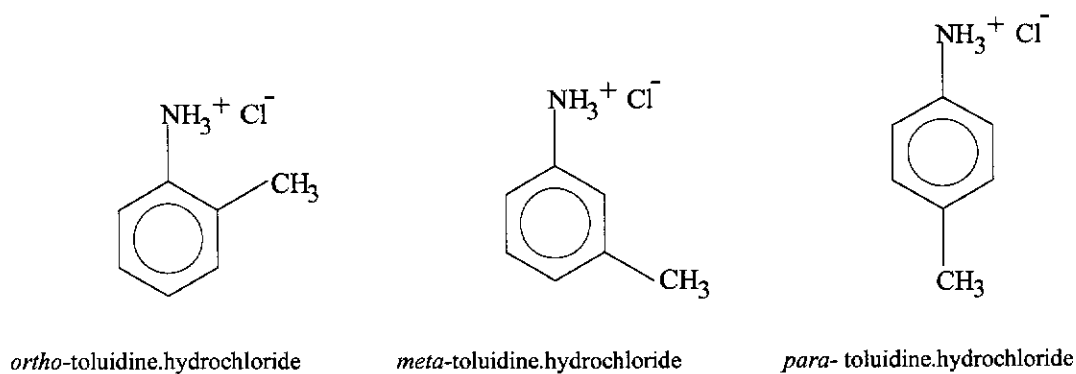
The trend seen in Figure 5.4 was that the *ortho*- compound was slower than the *meta*- compound which was slightly slower than the *para*- compound. The *ortho*- compound at the end of its 7.0 hour aeration time still had a metallic iron content of 5.1 per cent. In the case of the *meta*- and *para*- compounds both managed to completely remove all their leachable metallic iron in 4.5 and 4.0 hours respectively. The great difference between the *ortho*- compound's aeration rate would appear to be partially if not wholly due to the steric hindrance of the nitro group so close to the amine group. This trend was consistent with the results found in section 5.4.1 where the chloro group was used and explains why the trend is not reversed with the *ortho*-, *meta*- and *para*- pK_a values of -0.26, 2.466 and 1.0 respectively (Lide, 1996). What was remarkably different about this series was the comparison of the overall aeration rates. The *ortho*-nitroaniline hydrochloride compound, although the slowest in its series, was still faster than the *para*-chloroaniline hydrochloride. The comparison of the two *para*- compounds highlights the difference. The *para*-nitro compound completed the leaching of the reduced ilmenite in 4.0 hours while the *para*-chloro compound still had not come close to completing the leaching at the end of the 7.0 hour period. The likely reason for the difference in aeration rates when the chloro group was exchanged with the nitro group is due to the inductive effect exerted on the amine group by either the nitro or chloro group. This effect on the benzene ring and the amine group is reflected in the pK_a . The pK_a values for the *para*-chloroaniline hydrochloride compound and the *para*-nitroaniline hydrochloride compound were found to be 4.15 and 1.0 respectively (Lide, 1996). These results also support the theory that the lowest pK_a value for compounds with similar structures will have the fastest aeration rate.

5.4.3. Methyl - substituted aniline hydrochloride

The use of a substituent that has a positive inductive effect on the aniline hydrochloride was chosen because it displays a positive inductive effect in contrast to the negative inductive effect shown by a chloro and nitro group to complete the study of the apparent effects of the pK_a of an ammonium compound on the aeration rate of

metallic iron in reduced ilmenite. The substituent chosen was the methyl group, resulting in the compound toluidine hydrochloride. The three isomers of toluidine hydrochloride, *ortho*-, *meta*- and *para*-, were used in these experiments.

The slurry compositions for these three experiments were the same as those for aniline hydrochloride in section 5.3 with the exception of using and 25.85 grams (0.1 M) of toluidine hydrochloride in the *ortho*-, *meta*- and *para*- forms respectively in place of the aniline hydrochloride. Over the course of the 7 to 12 hour operating period, samples of reduced ilmenite were taken to have their metallic iron contents analysed. These results are illustrated in Figure 5.5.



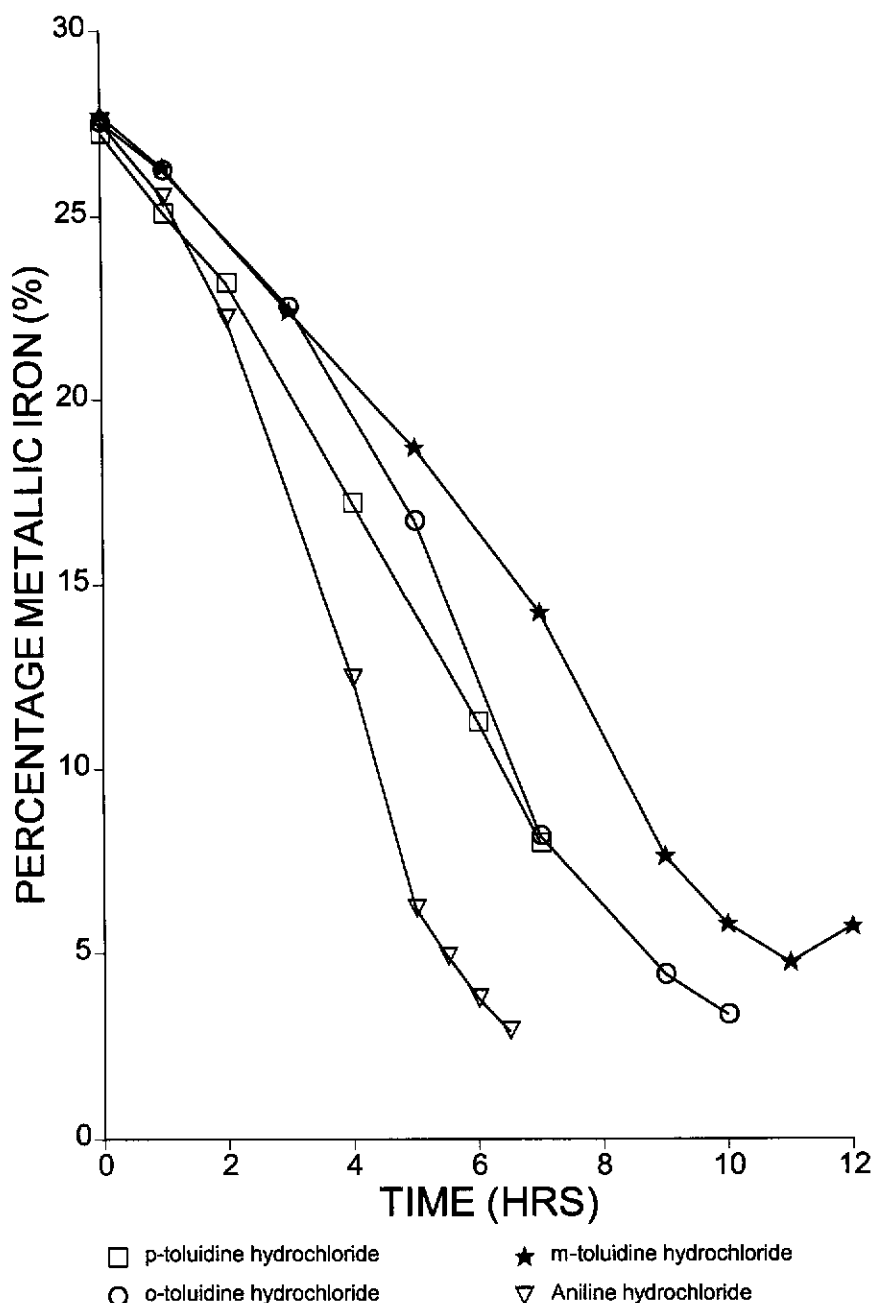


Figure 5.5: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using *para*-toluidine hydrochloride, *meta*-toluidine hydrochloride and *ortho*-toluidine hydrochloride as catalytic reagents.

The graph featured in Figure 5.5 indicates that the *para*-toluidine hydrochloride slurry had the fastest rate initially. After 5.0 hours of the experiment had elapsed the *ortho*-toluidine hydrochloride slurry began to increase its rate of reaction to match that of the *para*- compound's slurry. The *meta*- compound's slurry was found to be the slowest of the three, taking 12 hours to complete the aeration. To help explain the order of reaction rate the pK_a values for these compound are 4.44,

4.73 and 5.08 for the *ortho*-, *meta*- and *para*- substituted structures (Lide, 1996). These pK_a values are close together so it was not surprising that the graph lines for each compound's slurry were in close proximity. The only deviation from the expected results, by order of pK_a values, was that the *para*- compounds slurry was the fastest aeration catalyst rather than the slowest. The reasoning behind this observation was that the pK_a value relates only to the acid dissociation. This constant does not consider the ability of an ionic iron (II) ion to approach the compound, so steric hindrance by a functional group may still have a major effect on the complex ion formation. In the case of the *ortho*-, and the *meta*- compound, to a lesser extent, the methyl group causes steric hindrance. This was not believed to be the case with the *para*- compound so its slightly higher pK_a value was counter balanced by its lack of steric hindrance to give an approximately equal rate of aeration to that for the *ortho*- compound.

In a final comparison the data for *para*- compounds from the chloroaniline hydrochloride, nitroaniline hydrochloride and the toluidine hydrochloride were drawn from their respective sections to be compared in Figure 5.6.

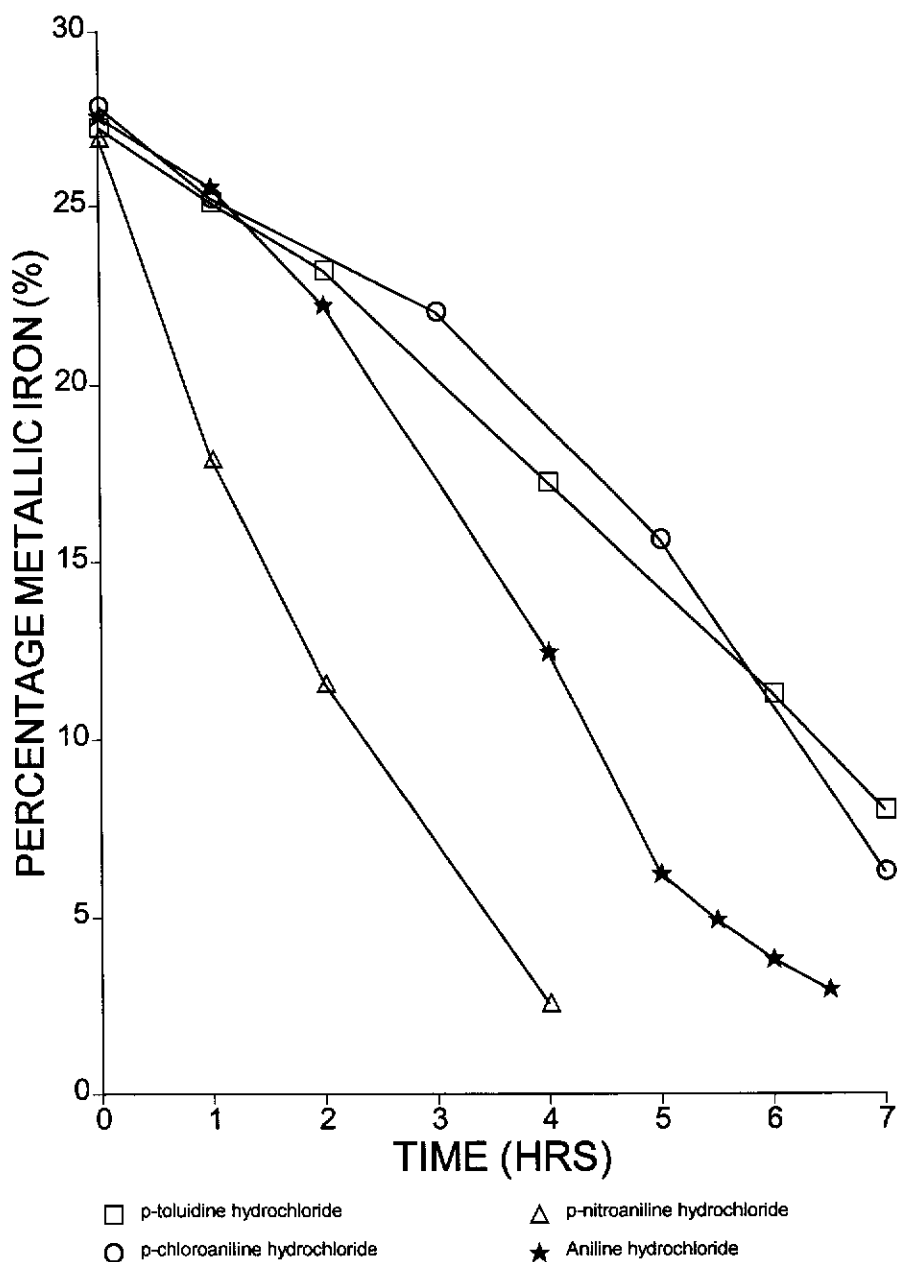


Figure 5.6: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using *para*-toluidine hydrochloride, *para*-chloroaniline hydrochloride and *para*-nitroaniline hydrochloride as catalytic reagents.

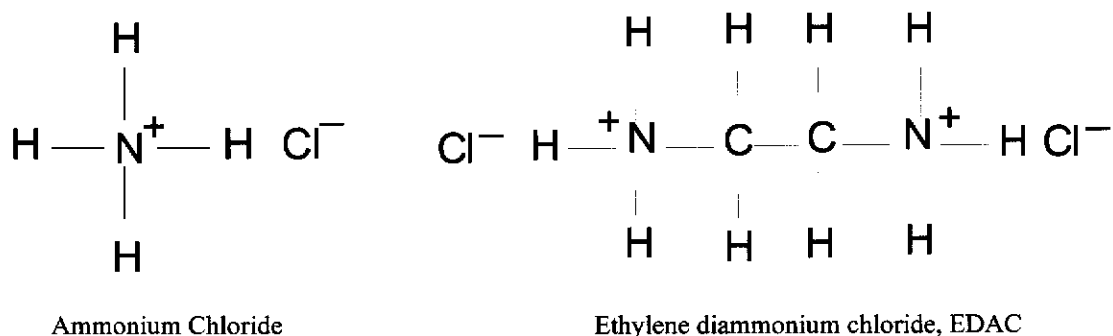
In the comparison shown in Figure 5.6 the order of increasing aeration times was found to be related to the increasing pK_a values. The observed order of increasing aeration times was nitroaniline hydrochloride followed by the chloroaniline hydrochloride and finally the (methyl substituted) toluidine hydrochloride. The increasing pK_a values were 1.0, 4.15 and 5.08 for the nitro-, chloro- and methyl-compounds respectively. Finally, although not a linear

relationship, it can be seen that the greater difference in the pK_a values the larger the difference in the aeration rates observed. Unsubstituted aniline hydrochloride, of pK_a 4.62, does not fit this pattern perfectly, but this may be due to the absence of steric effects.

5.5 Ethylene diammonium hydrochloride

5.5.1 Introduction

Previous work (Farrow and Ritchie, 1985) (Crisafio *et al*, 1994) (Lewis, 1994) has yet to explain how the ammonium chloride actually takes part in the mechanism of leaching reduced ilmenite with oxygen. In this work ethylene diammonium chloride has been investigated as an alternative catalyst. The choice of ethylene diammonium chloride (EDAC) as a comparison against ammonium chloride was based on the similarities between the two substances:



One difference between these two compounds is the number of nitrogen-hydrogen bonds possible per nitrogen atom. The other observable difference is that the EDAC had two ammonium groups and therefore twice the possible reactive sites when compared to ammonium chloride. This is reflected in the well known metal complexing ability of ethylenediamine as a chelating ligand (Cotton, *et al*, 1987)

5.5.2 Effect of air flow rate on aeration

In order to remove the metallic iron from the reduced ilmenite grain the metallic iron must first be oxidised by some form of oxidant - in this case the oxidant was oxygen in the form of air. If the effects on aeration rate caused by the variation in catalysts are to be measured, the air flow rate must already be at its optimum so that it has no influence on the catalyst performance. Consequently the optimum air flow rate was examined for the ethylene diammonium chloride (EDAC) slurries.

A standard slurry mixture consisting of 300 grams of reduced ilmenite, 1.8 litres of water, 16.79 grams of ethylene diammonium chloride was held at a temperature between 75 and 85 degrees Celsius and aerated at a given air flow rate between 0.3 litres to 1.0 litres per minute. The results of these tests can be seen in graphical form in Figure 5.7.

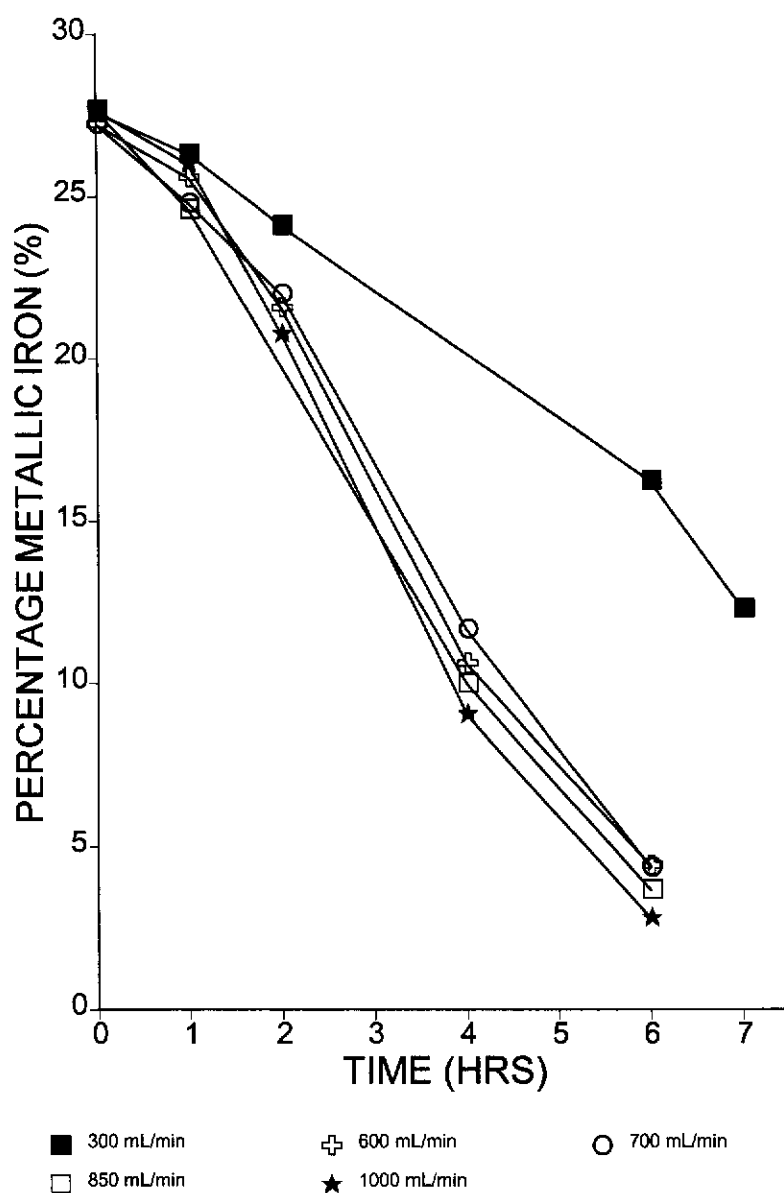


Figure 5.7 The effect of the air flow rate on the catalytic action of EDAC

Figure 5.7 shows that any flow rate lower than 0.60 litres per minute is insufficient to reach a minimum residual metallic iron level in a 6.0 hour period. At flow rates from 0.60 litres to 1.0 litres per minute a similar metallic iron level was reached in 6.0 hours but as the air flow rate increased in this range only a small decrease in the residual metallic iron were observed. These results were such that, although there was only a small change in the residual metallic iron between 0.60 litres and 1.0 litres, this change was considered to be significant enough, that is, greater than the calculated experimental errors, that the 1.0 litres per minute flow rate was chosen as the preferred air flow rate.

5.5.3 Aeration as function of the catalyst concentration

Previous experimental work using ammonium chloride as a catalyst had found a concentration of 0.093 M to be the optimum concentration required to leach a reduced ilmenite slurry (section 3.4.1). This series of experiments has determined the optimum concentration of EDAC, which was then compared with the performance of ammonium chloride.

The procedure used for this series of tests was the same as in section 5.5.2 with exception of the variations in the catalyst concentration. The range of concentrations tested was from 0.1395 M to 0.0233 M. The results of these tests are shown in Figure 5.8.

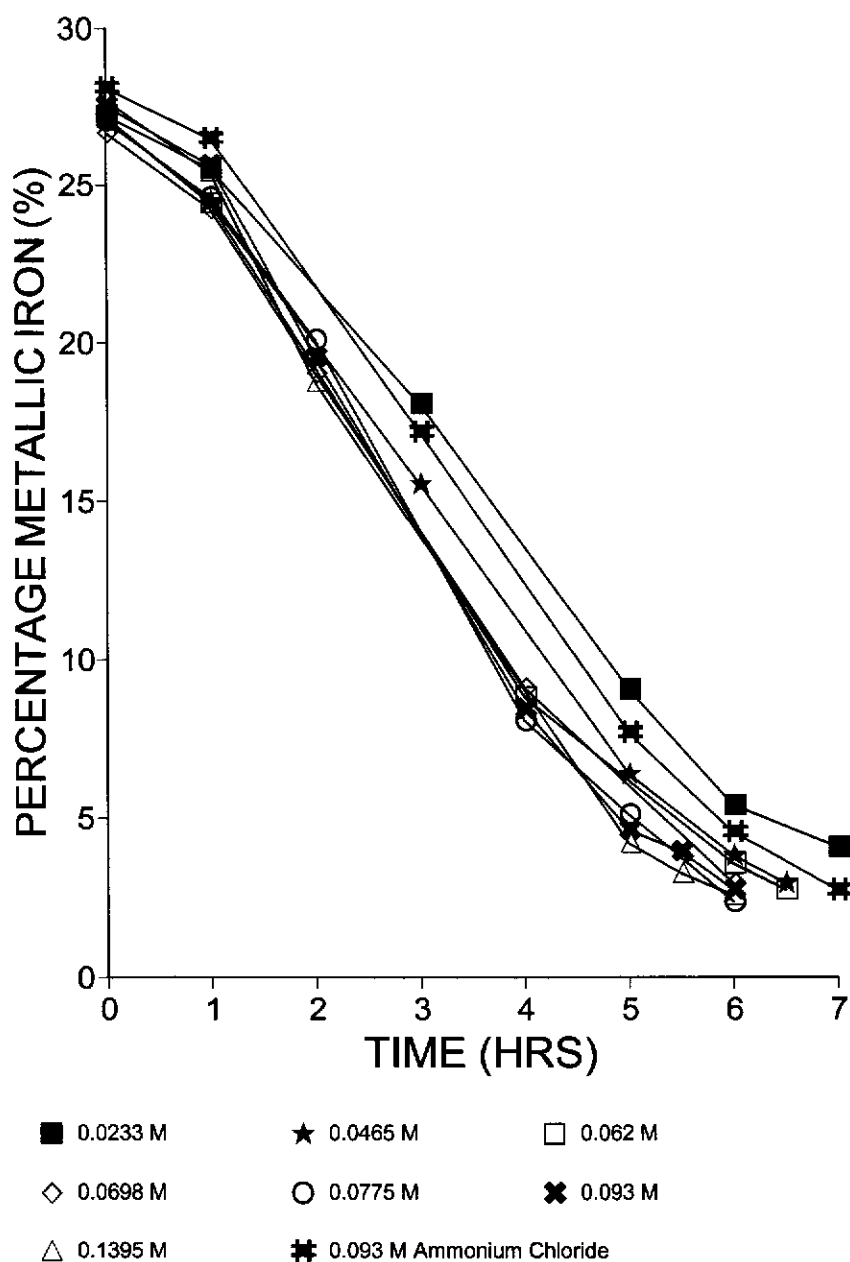


Figure 5.8: The effect of concentration of EDAC (and ammonium chloride) on the leaching rate of metallic iron in reduced ilmenite

The graph shown in Figure 5.8 indicates a slowly decreasing trend in the amount of residual metallic iron present as the concentration of ethylene diammonium chloride increases to a value of 0.0698 M. At concentrations higher than 0.0698 M it was found, within the normal variation of replicate results, that the same level of iron removal had occurred in the same amount of time as for the lower concentration of 0.0698 M. This indicates that the use of concentrations in excess of 0.0698 M achieved no further advantages in the leaching rate of metallic iron.

A comparison of the ammonium chloride aeration at 0.093 M concentration and ethylene diammonium chloride indicates significant differences between the two catalysts. The first difference was the optimum concentration for leaching and the second was the amount of time taken to reach a minimum level of residual metallic iron.

Results in Chapter Three have shown that the most appropriate concentration for the ammonium chloride leaching was 0.093 M. If the ammonium groups alone were the deciding factor in the rate of metallic iron removal then, as EDAC has twice the active ammonium units of ammonium chloride, the optimum concentration, would be expected to be half that of the required ammonium chloride concentration. If the ammonium groups were not contributing the primary function of the removal of metallic iron then the concentrations of the two catalysts would probably be the same. The actual results obtained show the optimum EDAC concentration to be 75 per cent (0.068 M) of that for the ammonium chloride. It was first considered that adsorption of EDAC on to the surface of the iron oxides could be a contributing factor, thereby decreasing the effective concentration in solution. To test this hypothesis the concentrations were monitored by taking liquor samples before and after 7.0 hours aeration from ammonium chloride and EDAC slurries at their optimum concentrations. Those samples of solution were then analysed for nitrogen concentration by the Kjeldahl method and the results are shown in Table 5.3.

Table 5.3: Nitrogen concentrations in solution before and after leaching with ammonium chloride and EDAC

SAMPLE	% NITROGEN (TOTAL)
ammonium chloride (Before)	0.132
ammonium chloride (After)	0.148
EDAC (Before)	0.168
EDAC (After)	0.180

As is evident from the data in Table 5.3 the concentration of the ammonium ion in both the ammonium chloride and EDAC leaches did not decrease after a 7.0

hour aeration. The small increase in concentration maybe attributed to the evaporation which occurs from the aeration vessel.

The most likely explanation then seems to be that steric hindrance in the larger molecule prevents the amine groups from complexing the iron to a certain extent. Alternatively, in some instances both amine groups from a single EDAC molecule may bond in a chelating manner with an iron ion while only one of the amine groups may in bond in another case. Further evidence of this occurrence can be found from a comparison of the pK_a values for the 2 catalysts. The pK_a for ammonium chloride is 9.25 (Stark and Wallace, 1976) while ethylene diammonium chloride has a value of 7.56 (Lide, 1996) for its first dissociation. In keeping with the relationship between pK_a and aeration rate shown earlier in this Chapter, the ethylene diammonium chloride is expected to catalyse the aeration more effectively than ammonium chloride in terms of the first dissociation. The second pK_a value for the ethylenediammonium chloride is 10.71 (Lide, 1996) which is higher than the value for ammonium chloride which indicates this dissociation will be more difficult than the one for ammonium chloride. Hence the ethylene diammonium chloride is likely to be more efficient than ammonium chloride, but not as much as twice as efficient.

5.5.4 Effect of temperature on aeration

Temperature in the ammonium chloride slurry had a significant effect on its leaching capabilities so the effect of temperature changes on aeration with the ethylene diammonium chloride slurries was investigated.

The temperature ranges used for this study included 50 - 60, 60 - 70, 70 - 80, 80 - 90 degrees Celsius and a test involving a slurry that was started at temperature of 50 degrees Celsius and then allowed to run its course with no heating provided. The slurries used for this series of experiments were the same as those used in section 5.5.2 with an air flow rate of 1.0 litre per minute passing through the slurries. These data are shown in Figure 5.9.

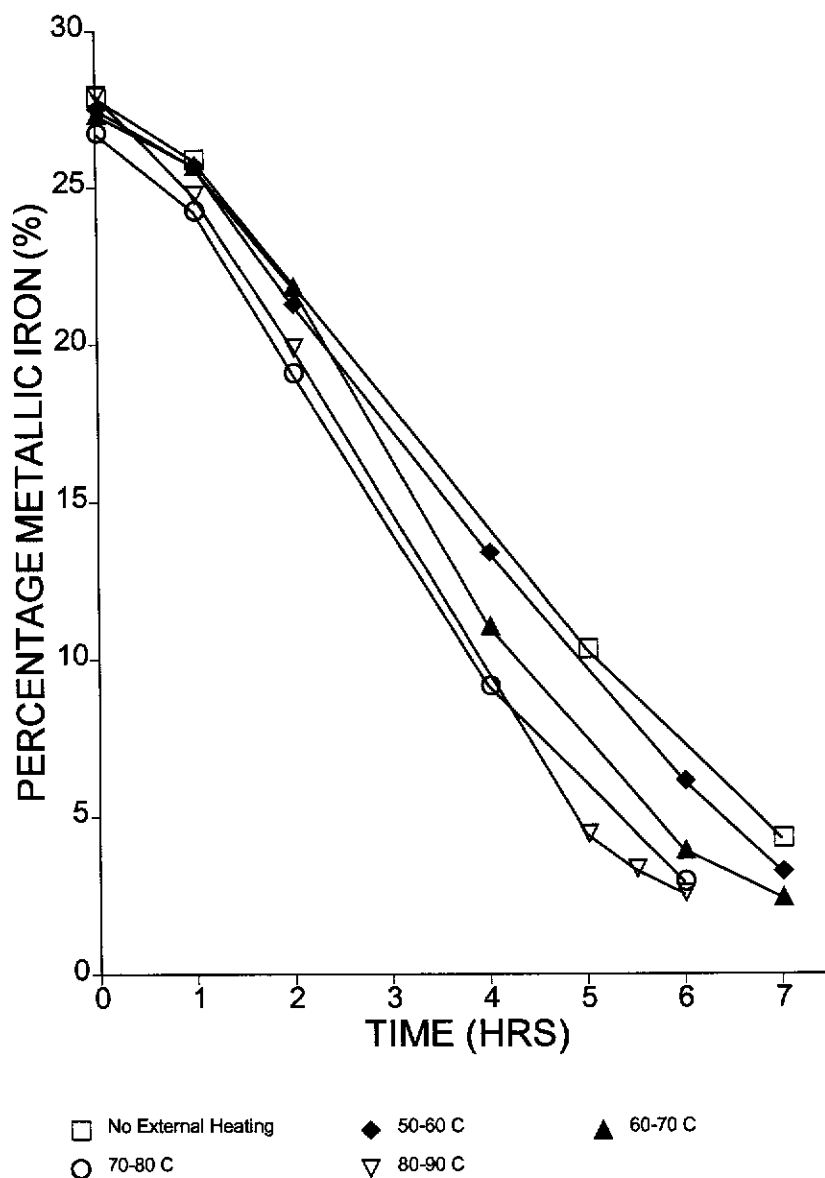


Figure 5.9: The effect of temperature on the leaching of reduced ilmenite with the use of EDAC as catalyst

Figure 5.9 demonstrates the effect of variations in temperature on the aeration rate. The residual metallic iron level after the completion of the 6th and 7th hour can be used to highlight this point. The lowest residual metallic iron value with the fastest leaching rate was achieved at a temperature range of 80 - 90 degrees Celsius, but when considering the possible experimental error the 70 - 80 degrees Celsius experiment was found to produce the same final metallic iron level after 6.0 hours of aeration. At the other extreme, after 6.0 hours of aeration without heating of the slurry, was a residual metallic iron level of 7.0 per cent. The other major factor to

note was the additional hour it took to 'complete' the aeration once the temperature dropped below 70 degrees Celsius.

A similar spread in results across the temperature ranges was found for aerations based on ammonium chloride in section 3.5. Reaction rates appear to be the only major difference between the two catalysts, that is the EDAC slurry had taken only 6.0 hours of leaching to reach the same stage of completion as ammonium chloride in 7.0 hours. The best results for the EDAC slurries were found in the temperature range of 80 -90 degrees Celsius, with the 70 - 80 degrees Celsius range only slightly less successful. By contrast, when using the ammonium chloride the results show conclusively that the 70 - 80 degrees Celsius range was far superior.

5.5.5 The effect of pH on aeration

As already explained, EDAC was chosen because of its chemical similarities to ammonium chloride. It was considered that it may be possible to alter the leaching rate of metallic iron from reduced ilmenite by altering the pH to values similar to the ammonium chloride system or closer to some other buffering point for the ammonium - ammonia reaction.

In this series of experiments the pH was varied by using ethylene diamine instead of EDAC, which would then need to be neutralised with sodium hydroxide, resulting in the presence of sodium ions. Stock solutions of ethylene diamine were combined with the necessary amounts of hydrochloric acid to alter the pH of the solution before the reduced ilmenite was added. Each slurry mixture in this case consisted of 300 grams of reduced ilmenite, 1.8 litres of water and 8 millilitres of ethylene diamine (at density of 0.9 grams per millilitre), which would make the solution a concentration of 0.066 M. This original slurry with no hydrochloric acid added had a pH of 10.74. Two different approaches were taken to assess the effect of pH alone in variations in leaching rates. In this first case the aeration was carried out for a 7.0 hour period with 1.0 litre per minute of air flowing through the slurry at a

temperature between 70 and 80 degrees Celsius. In the second case a calculated amount of sodium chloride was added to create a constant ionic strength equivalent to a solution of ethylene diammonium chloride at a pH of 6.45 (the pH at which an ammonium chloride slurry leaches).

To follow the second procedure the initial pH was dropped with the use of hydrochloric acid and then the appropriate amount of sodium chloride was added to keep the total chloride ion concentration constant. This trend was continued until the pH values reached 6.45 and below, from which point sodium chloride was no longer added. The results of both tests are expressed in a graphical form in Figure 5.10.

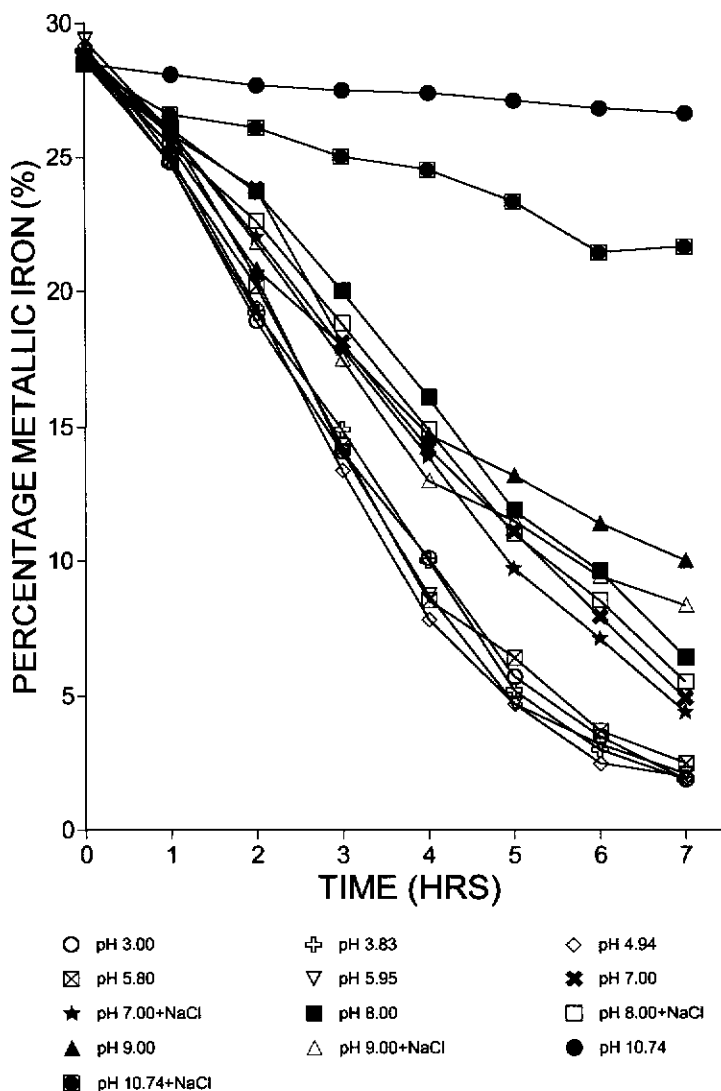


Figure 5.10: Variations in the leaching of metallic iron from reduced ilmenite using EDAC as a function of initial pH

The first trend, to observe in Figure 5.10, was the effect the chloride ion, in the form of sodium chloride, had on the leaching ability at any given pH. The most obvious illustration of this was at the pH of 10.74. Very little metallic iron was removed from the pH 10.74 slurry over a 7.0 hour period, while at pH 10.74 with the additional sodium chloride the metallic iron level from the reduced ilmenite decreased by 5.5 per cent over a 7.0 hour period. This seems to suggest that the extra chloride ion was playing a role in leaching the metallic iron and/or its oxides.

The other trend found in Figure 5.10 was that as the pH dropped the rate of reaction increased to a maximum at a pH of approximately 6.5. Thereafter the decrease of pH contributes very little to increase in the rate of reaction. A clarification of this behaviour can be found in the pH profiles in Figure 5.11.

NB: The pH labels in the following graph are the pH of the solution of ethylenediamine and acid before the reduced ilmenite was added. The first pH measurement on the graph for each line was actually measured 3 to 4 minutes into the aeration.

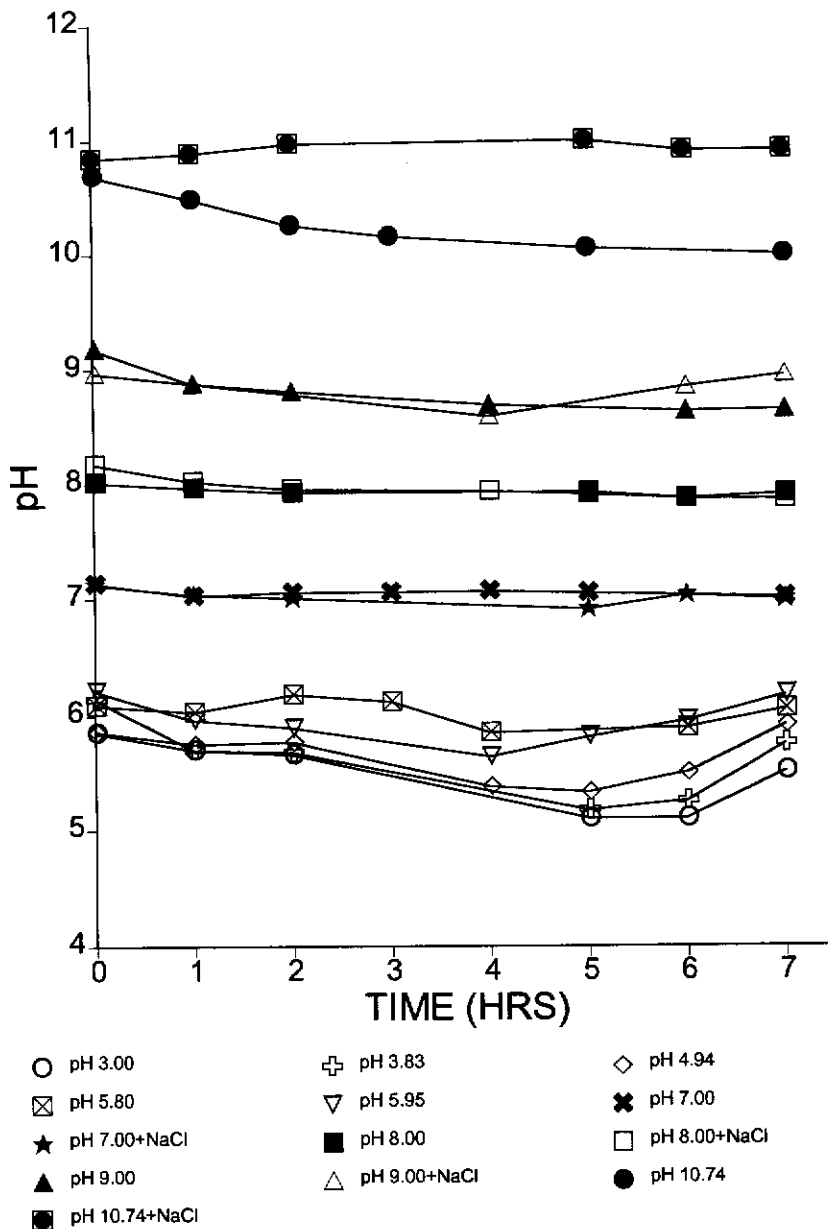


Figure 5.11: The pH profiles for the leaching trials using EDAC as a leaching agent with various values of initial pH

The results in Figure 5.11 show that at initial pH values above 6 there was some variation in the pH over the 7.0 hour period but no more than a variation of half a pH unit. At initial pH values lower than 6 a very quick change in pH value occurred to change to a pH of approximately 5.8. These slurries also had much more variation in the following 7.0 hour period but they all followed a similar pathway toward their final pH value. The second trend suggests that all the slurries that began with a pH lower than 6.0 had acid leaching occurring at some time soon after the reduced

ilmenite was added. It is believed this small amount of acid leaching would contribute to a small increase in the reaction rate in the first hour of aeration.

The other significant observation during the aeration studies was that the odour of hydrogen sulfide was given off in the first hour by the slurries with a pH of 5.5 or lower. The hydrogen sulfide was created by acid attack on manganese sulfide present in the reduced ilmenite matrix. This signifies the presence of free acid that can leach either metallic iron or manganese (from manganese sulfide) that was present in the reduced ilmenite.

The evidence suggested from the pH profiles that the lower pH slurries had some acid leaching occurring and thereby changed the pH to approximately 6 where the maximum rate of reaction could be found. This pH value also corresponds with the optimum leaching conditions for ammonium chloride where the ammonium groups can participate in an equilibrium with ammonia and thereby buffer the system.

5.5.6 The effect of oxygen partial pressure on aeration

As has been shown in Chapter Three, an increase in the oxygen partial pressure in a constant flow rate of gas successfully increases the rate of reaction while using ammonium chloride as the catalyst. As ethylene diammonium chloride (EDAC) has been found to be a faster catalyst than ammonium chloride, the prospect of combining EDAC with a gas flow that has a higher proportion of oxygen should produce faster aerations.

The conditions previously used for the ammonium chloride tests (section 3.7) were 70 to 80 degrees Celsius with a gas flow of 300 mL per minute. These tests used a standard slurry of 300 grams of reduced ilmenite, 1.8 litres of water and nine grams of ammonium chloride. The test involving the use of EDAC and a gas flow of 300 mL per minute gave a slower rate of reaction (Figure 5.7) than when using ammonium chloride. This indicated that a total gas flow of 300 mL per minute would

not be high enough for the EDAC catalyst to complete leaching in 6.0 hours or less. As shown in Figure 5.7 a flow rate of 1.0 litre per minute is the optimum air flow rate to completely remove the metallic iron in a 6.0 hour period. It was therefore decided to use a total gas flow rate of 1.0 litre per minute for these experiments. Six different tests were carried out using different partial pressures of oxygen. The standard slurry used in all six cases consisted of 300 grams of reduced ilmenite, 1.8 litres of water and 16.79 grams of ethylenediammonium chloride. Each of these tests was carried out between 75 and 85 degrees Celsius. Samples were taken periodically to evaluate the metallic iron content in the reduced ilmenite. The results of the metallic iron analyses of these six tests are shown in Figure 5.12.

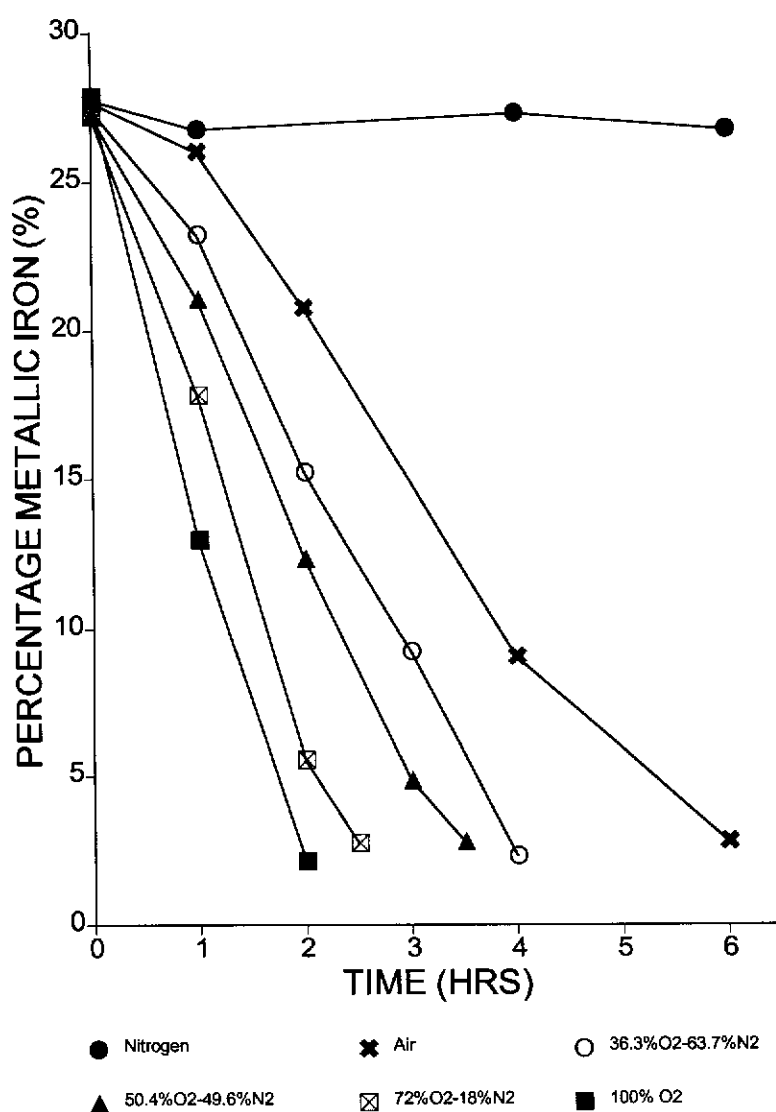


Figure 5.12: The removal of iron from reduced ilmenite at various oxygen partial pressures at a total gas flow rate of 1.0 litre per minute, using EDAC as the catalyst

The results shown in Figure 5.12 clearly demonstrate the positive effect of increasing the partial pressure of oxygen. Under normal air the complete removal of all the available metallic iron took place in a 6.0 hour period. In comparison, the use of 100 per cent oxygen took only 2.0 hours to reach the same level of metallic iron. There was a progressive increase in the rate of reaction with increasing oxygen partial pressure all the way to the 100 per cent oxygen test. This also agrees with the trend found for ammonium chloride when increasing the oxygen partial pressure.

The question of whether the ammonium chloride or the EDAC was the better catalyst, especially under the conditions of increased oxygen partial pressure, was addressed by repeating the ammonium chloride tests using the total gas flow rate of 1.0 litre per minute. The same gas mixtures were used for these tests as for the EDAC and the results are shown graphically in Figure 5.13.

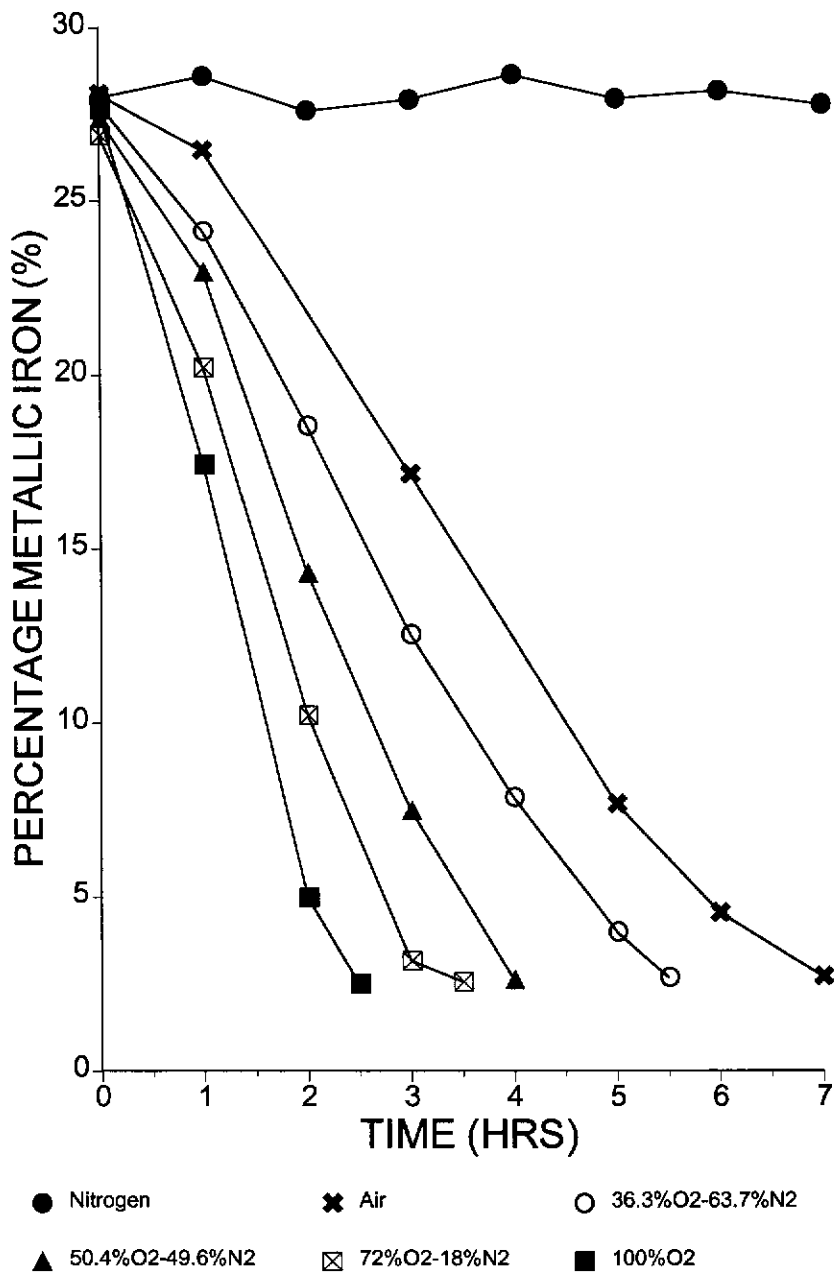


Figure 5.13: The effect of the oxygen partial pressure on iron removal at a constant total gas flow rate of 1.0 litre per minute, using ammonium chloride as the catalyst

By comparison of Figure 5.12 and Figure 5.13 it can be seen that EDAC catalyst gives a faster rate of reaction than ammonium chloride. For each gas mixture the time for complete reaction for the ammonium chloride catalyst was observed to be longer than for the EDAC, by approximately 0.5 hours in most cases.

The other important factor can be seen in the comparison between Figures 3.8 and 5.13 for 100 per cent oxygen gas flow in each graph. The higher gas flow rate

shown in Figure 5.13 shows that the leaching of metallic iron can be completed in 2.5 hours (Figure 5.13) compared to 4.0 hours of aeration at the lower gas flow rate (Figure 3.8). The use of a 300 mL per minute flow rate was chosen from previous test work that showed no difference in the aeration rates of ammonium chloride slurries when air was the aeration gas.

5.5.7 Reproducibility of results using ethylene diammonium chloride

In previous work with ammonium chloride as a catalyst a standard experiment was completed several times to investigate the reproducibility of experiments using one source of reduced ilmenite. Those experiments concluded that the experiment was readily reproduced. The purpose of the repeat experiments in this section is to prove that another catalyst can also reproduce results, based on a single source of reduced ilmenite.

The four slurries tested with ethylene diammonium chloride were all operating under optimum conditions for the this catalyst; that is, 0.068 M EDAC in 1.8 litres of water at 70 to 80 degrees Celsius. The results of the aerations are arranged graphically in Figure 5.14.

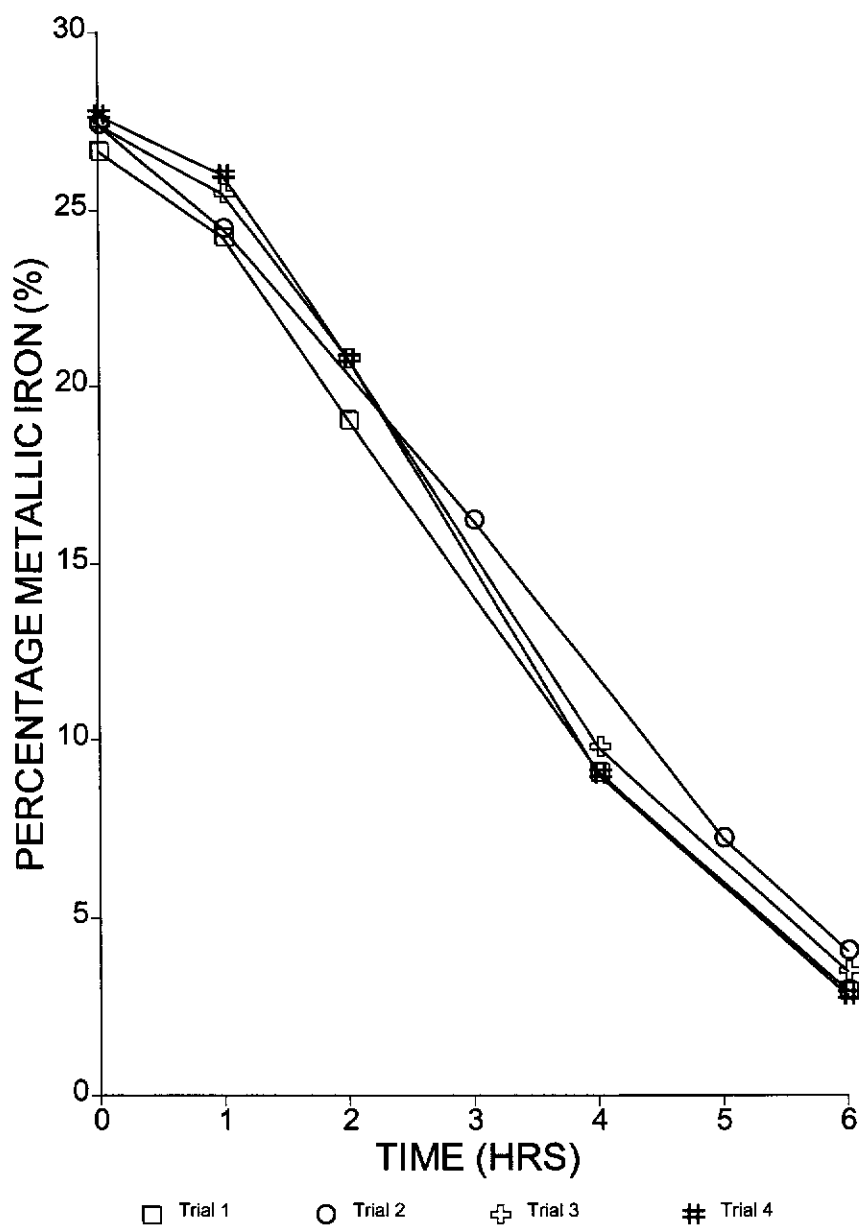


Figure 5.14: The ethylene diammonium chloride experiment under optimum conditions repeated four times to assess the reproducibility of the experiment.

The repetition of the ethylene diammonium chloride experiment has shown that the results of the experimental procedure are easily reproducible. All four slurries were able to be aerated in 6.0 hours with residual metallic iron values all within 1.0 per cent of one another. Each of the experiments also followed a similar pathway throughout the entire aeration. These experiments yielded results with a mean of 2.6 per cent metallic iron with a standard deviation of 1.6 per cent. Further calculations yielded an error of ± 1.8 per cent from a 95 per cent confidence level.

The results presented in Figure 3.10 and 5.14 have demonstrated that the experimental procedure for two different catalysts, under different conditions, yields produce reproducible results when the reduced ilmenite was from the same source in each instance.

5.6 Conclusions

By observing compounds related to ammonium chloride through structure and functional groups, it has been determined that the pK_a of a catalyst in the aeration slurry for reduced ilmenite can assist in rationalising the rate of reaction. This means that the lower the pK_a value for a given catalyst, the faster the rate of aeration of the slurry will proceed.

The other factor discovered involved the steric hindrance of a compound around the nitrogen of the amine group. If a compound has large atoms or functional groups in the vicinity of the functional amine group steric hindrance can occur to hinder a complex forming between the ionic iron (II) and the amine compound as was shown by Martell and Handcock (1996) for the methyl R_3N series. If this happens, the rate of aeration was significantly reduced, even if the compound had a low pK_a value.

With these explanations in mind, it becomes obvious why ammonium chloride is so effective at aerating reduced ilmenite: it has a reasonably low pK_a value and minimal steric hindrance around the nitrogen when the ammonium ion was deprotonated to ammonia. This explanation can be extended to explain why *para*-nitroaniline hydrochloride was an even better catalytic reagent. The amine group in *para*-nitroaniline hydrochloride was only sterically hindered in the direction of the benzene ring while still having three small hydrogen atoms bound to it. The nitro functional group was bound to the connecting benzene ring in such a way that the nitro group could not cause any steric hindrance to the deprotonated amine group. Finally, the compound had such a small pK_a value that it would be expected to aerate

much faster than ammonium chloride on this basis, provided that steric hindrance was not a major factor. A search through the literature found that no work had yet been compiled on the stability constants of the substituted aniline compounds with iron (II) (Lewis and Wilkins, 1960) (Martell and Hancock, 1996) (Martell and Smith 1975, 1977, 1982, 1989) (Greenwood and Earnshaw, 1986) (Schwarzenbach and Sillen, 1957) (Perrin, 1979).

The initial comparison between the ammonium chloride and ethylene diammonium chloride showed that ammonium chloride had an optimum concentration of 0.093 M and that ethylene diammonium chloride had an optimum concentration of 0.068 M. This concentration of ethylene diammonium chloride was 75 per cent of the ammonium chloride concentration. The reason for this lower concentration requirement could be due to a combination of factors. One mole of ethylene diammonium chloride has twice the ammonium groups that may complex with the iron, but this may be balanced against possible steric hindrance caused by the ammonium group being attached to a carbon chain.

The effect of temperature on both the ammonium chloride and the ethylene diammonium chloride catalysed aerations was very similar. The optimum results for ethylenediammonium chloride were found in the 70 to 90 degrees Celsius range, whereas ammonium chloride found its optimum temperature range at 70 to 80 degrees Celsius.

By varying the pH of the ethylene diammonium chloride catalytic system a preferential buffering pH at approximately 5.8 was found, close to the buffering point of ammonium chloride. These experiments with constant chloride ion concentration also showed that ethylene diammonium chloride depends on the chloride ion present to stop iron passive films forming (Denholm, 1962).

If the partial pressure of oxygen was varied while using a constant gas flow rate the reaction rate could be considerably increased as the partial pressure increased. By using a 1.0 litre per minute flow rate, at 100 per cent oxygen,

ammonium chloride could complete an aeration in 2.5 hours, while ethylenediammonium chloride could complete an aeration in 2.0 hours. This tended to show ethylene diammonium chloride as the better reagent but when the total gas flow rate was dropped from 1.0 litre to 300 mL per minute ammonium chloride was shown to use the oxygen more effectively.

The speed at which these two catalysts complete the aeration of the reduced ilmenite under normal air flows and slurry conditions differed by an hour. The ethylenediammonium chloride takes 6.0 hours compared to 7.0 hours for ammonium chloride. This suggests some potential advantages in the use of EDAC in place of ammonium chloride. The lower volatility of ethylene diamine should also result in less loss of catalyst in the vapour, as ammonia is known to be lost when ammonium chloride is used (Farrow *et al*, 1987).

Chapter Six

Other organic catalysts for the Becher process

6.1 Introduction

The objective of this chapter is to examine some alternative catalysts based on the criteria described previously for ammonium chloride, that is its buffering and complexation ability. For this investigation three compounds were chosen which possess metal - binding capabilities (Wilkinson, *et al*, 1987) and buffering capacities. These three compounds are tartaric acid, citric acid and oxalic acid, which are di- and tri- carboxylic acids and have at least twice as many bonding sites, per mole, as ammonium chloride. In addition to the use of these alternative leaching reagents the prospect of combining ammonium chloride with these other complexing compounds to form mixed leaching agents was examined, since the chloride ion has been suggested to play a role in the prevention of passive iron films forming on the surface (Farrow and Ritchie, 1985), and ammonium ion has been shown to be particularly effective in leaching iron (Chapter Four).

6.2 The use of citric acid and its salts as aeration catalysts

A series of tests was conducted to compare citric acid to the ammonium chloride as a catalyst. A superior catalyst may be found by using alternative complexing agents to ammonium chloride, such as a mixture of citric acid and its sodium salts. The citrate ion has three possible active sites that may complex the ionic iron(II) and the citric acid / trisodium citrate is a known buffer that buffers at a similar pH to that of ammonium chloride.

6.2.1 Changes in the aeration rate caused by varying pH

The experiments used a standard slurry of 300 grams of reduced ilmenite, 1.8 litres of water, to which a mixture of citric acid and the trisodium citrate was added to make up a total combined concentration of 0.1 M. The citric acid and the trisodium citrate would then equilibrate to the appropriate mixture of citrate salts depending on the relative amounts added. These slurries were then aerated for 7.0 hours with the use of a 1.0 litre per minute air flow. Throughout this 7.0 hour period the temperature was held between 70 and 80 degrees Celsius. Regular testing of the metallic iron content through the aeration gave the results represented graphically in Figure 6.1.

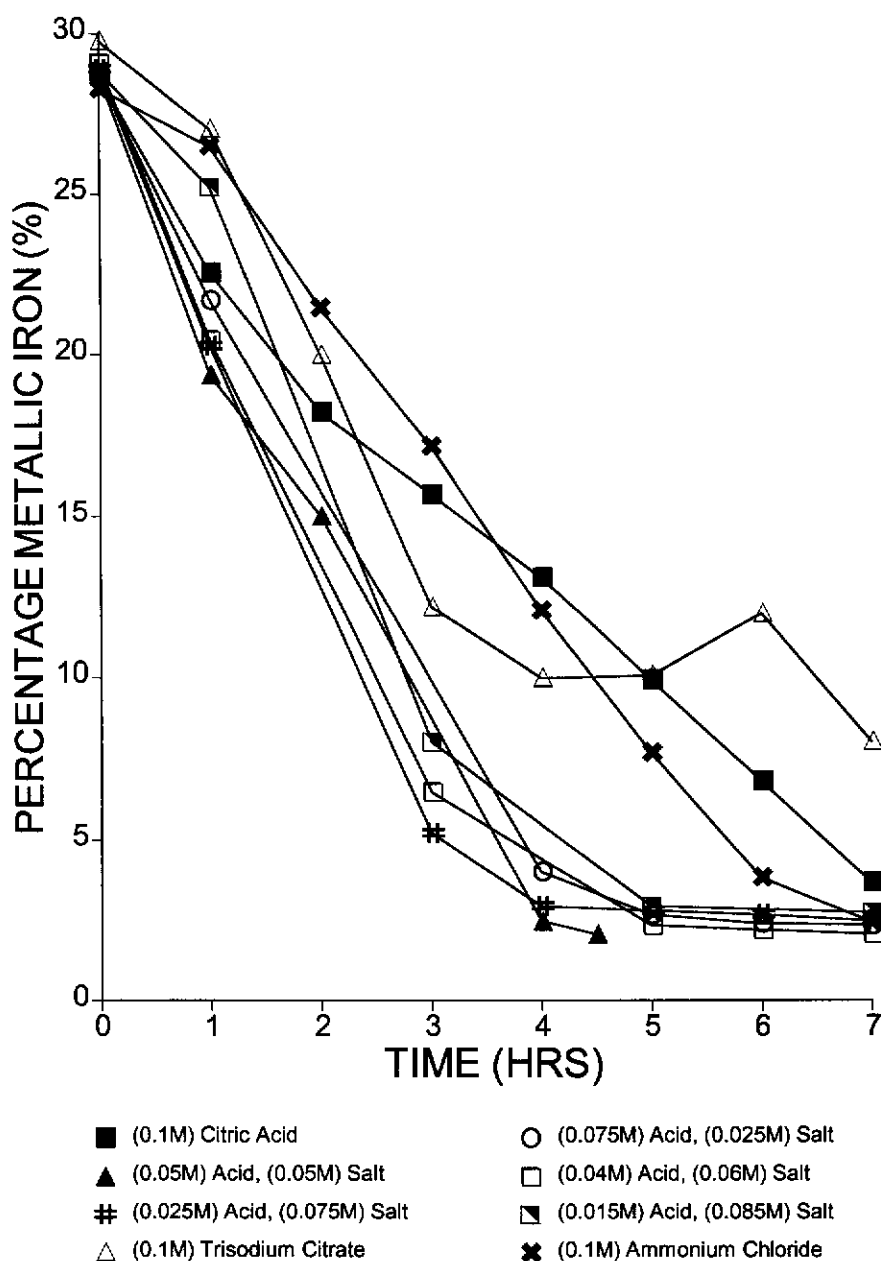


Figure 6.1: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using ammonium chloride, citric acid, trisodium citrate and mixtures of citric acid and trisodium citrate as catalytic reagents.

The results shown in Figure 6.1 indicate that all the mixtures of citric acid with trisodium citrate reached the minimum level of metallic iron at a faster rate than either pure 0.1 M citric acid or pure 0.1 M trisodium citrate. The mixture with the fastest aeration rate was found to be 0.05 M citric acid / 0.05 M trisodium citrate which took only 4.5 hours to reach a 1.6 percent residual metallic iron level. The pure citric acid and pure sodium citrate had not reached the same level of metallic

iron removal at the end of a 7.0 hour aeration period. An important point to note about this series of experiments is that the slurries that finished the aerations at pH values of 6 or higher created very fine or soluble oxide. This oxide was found to be difficult to separate from the liquor so several methods of separation were attempted, as described in section 6.2.2. All met with little success due to the very small size of the particles.

A probable explanation of the success of various mixtures was obtained by comparing the pH profile for the leaching period to a similar profile for ammonium chloride. These profiles are shown in Figure 6.2. The 0.05 M citric acid / 0.05 M trisodium citrate mixture, as an example, had a rapid change in pH in the first hour, and then varied only slightly for the next three hours between pH 8 and 10 to finish at pH 8.1. All the other citric acid and trisodium citrate mixtures followed a similar trend and had leached most of the iron in a 5.0 hour period. The initial increase in pH can be attributed to some degree of acid participation in the leaching of iron. After the first hour of aeration the high rate of aeration remained. This high rate could no longer be attributed to acid leaching. Rather, it seems likely that a complex ion is formed between the citrate ion and the ferrous ion at a pH between 9.4 and 8.0. This complexation must have occurred in the reduced ilmenite grain and then transported the ferrous ion to the bulk solution, which was at the same high pH itself. As the bulk solution was also at a high pH, this would explain why the oxide /complex was impossible to recover from the slurry solution.

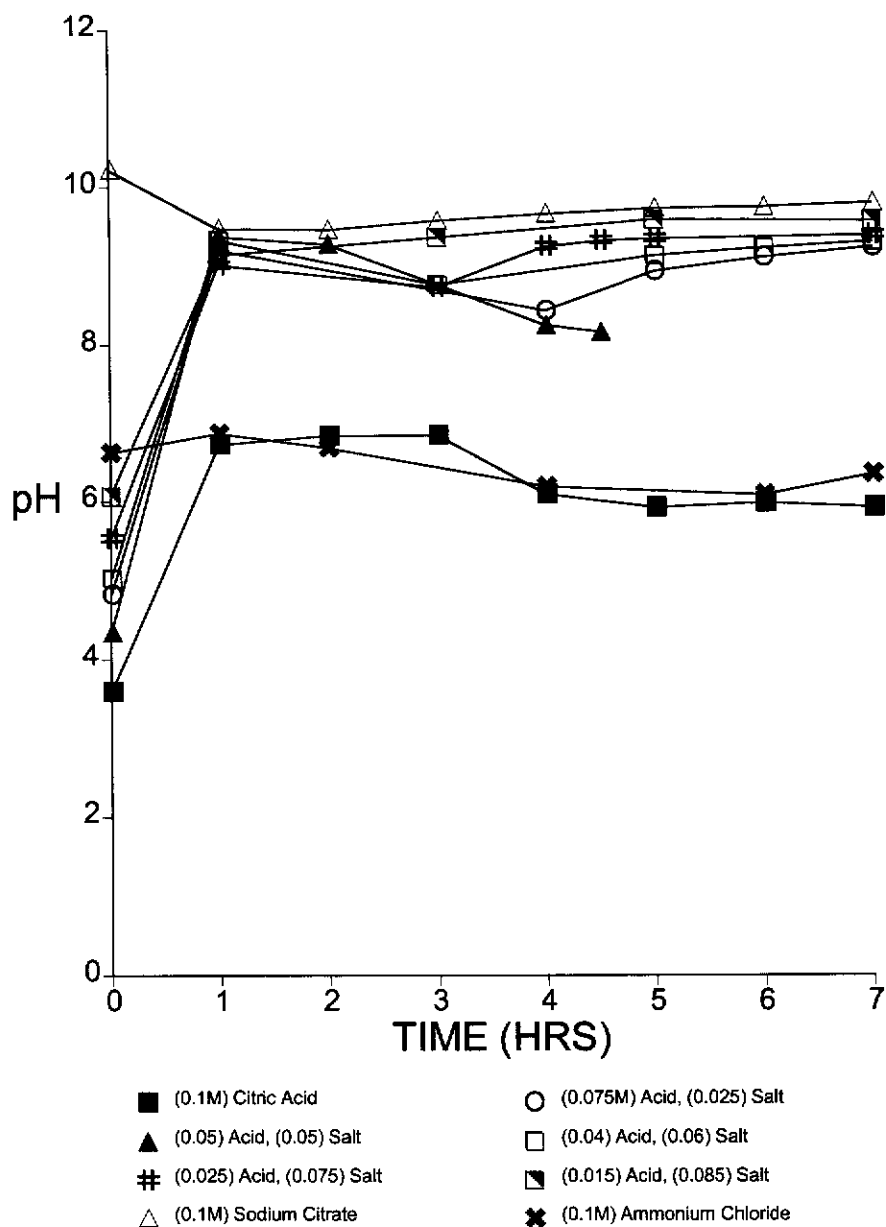


Figure 6.2: Graph of time vs pH in the aeration of reduced ilmenite using ammonium chloride, citric acid, trisodium citrate and mixtures of citric acid and trisodium citrate as catalytic reagents.

The pH pathway for the 0.1 M citric acid shows clearly that the first hour of aeration was due mainly to acid leaching. Most of the reactive protons from the 0.1 M citric acid were consumed in the first hour as the pH rose to 6.8. The pH then ranged between pH 6 and 7 for the next 6.0 hours. Although the pH did vary somewhat, the rate of iron leaching appeared to remain constant for the 0.1 M citric acid over the 7.0 hour period. This pH profile, except for the first hour, followed a near identical

pathway to the ammonium chloride and leaching finished in the same time as the ammonium chloride slurry. This seems to indicate that the citric acid, at the right pH conditions, was also able to complex the ferrous ion and transport it in to the bulk solution where the complex could then break apart at a rate similar to ammonium chloride.

As the 0.05 M citric acid and 0.05 M trisodium citrate catalyst produced such a rapid aeration it was decided to investigate the possibility of recycling the liquor for further aerations. Problems arose when the liquor could not easily be separated from the very fine iron oxide product. Methods involving centrifugation, agglomeration, pressure filtration, flocculation and magnetic separation were all tried, but to no avail. As the oxide was not easily removed, the experiment was continued with the excess iron oxide present in the recycled liquor. The result of this experiment is compared to the fresh liquor experiment in Figure 6.3.

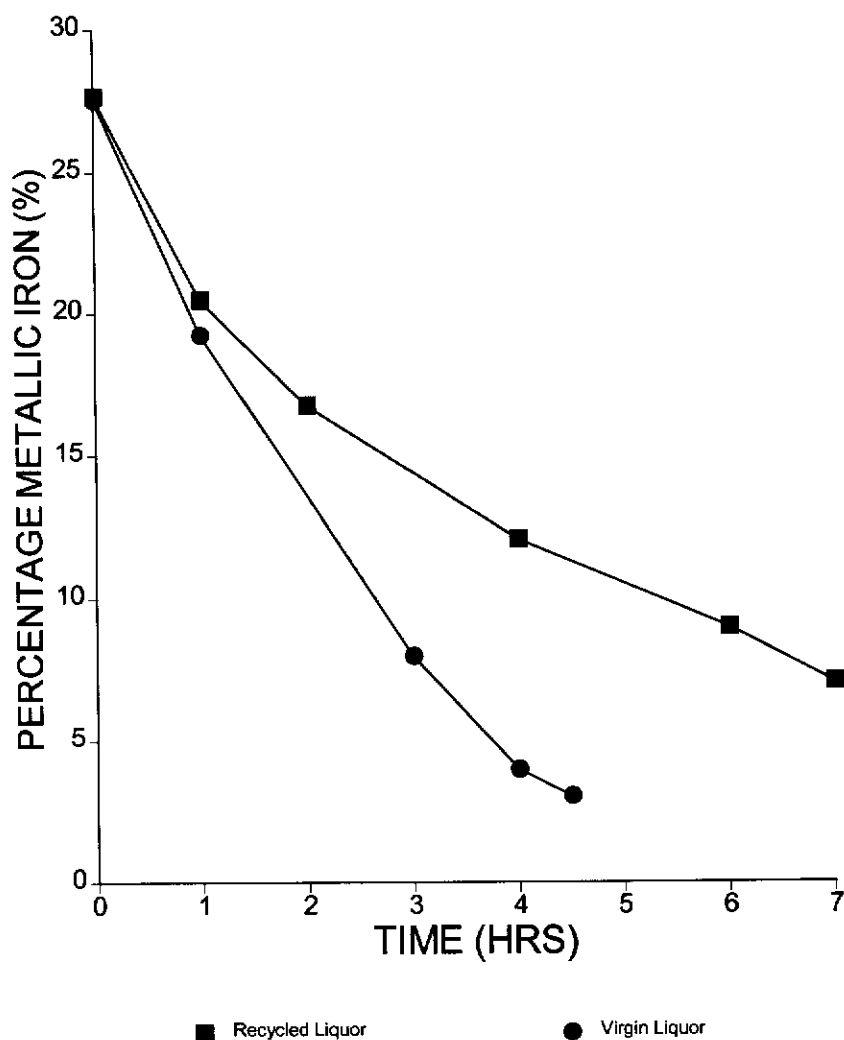


Figure 6.3: A comparison between the leaching ability of freshly made catalyst solution (Virgin) and reused catalyst solution (Recycled), where 0.05 M citric acid and 0.05 M trisodium citrate is used as the catalyst in both cases.

The graph in Figure 6.3 has shown that the slurry using recycled liquor required 7.0 hours to reach a metallic iron content of 7.1 per cent. In the case of the virgin liquor it only required 4.5 hours to reach a metallic iron level of 4.7 per cent. This has shown that the recycled liquor experiment had a marked decrease in the reaction rate. It is not known whether the presence of the iron oxide or the lack of acid caused this slowing of the leaching rate, but observations shown in the pH profile in Figure 6.4 may assist.

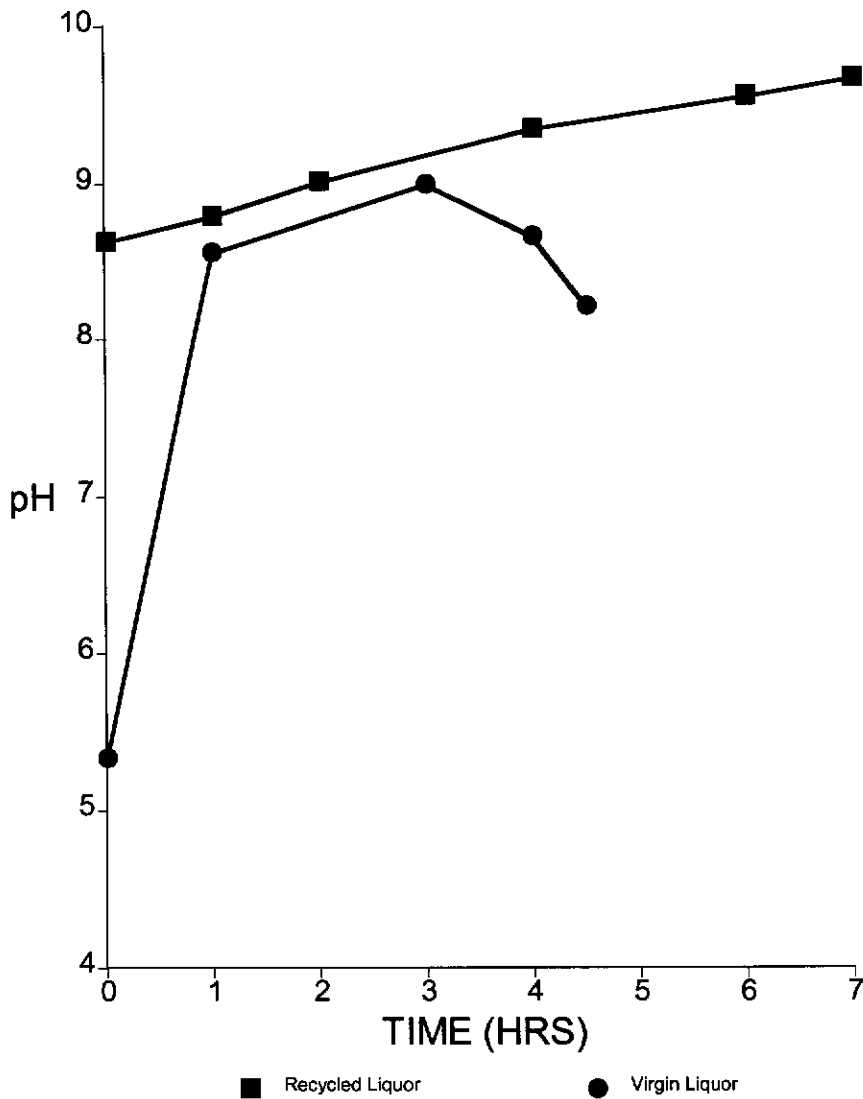


Figure 6.4: A pH profile of freshly made catalyst solution (Virgin) and reused catalyst solution (Recycled), where 0.05 M citric acid and 0.05 M trisodium citrate is used as the catalyst in both leaching trials

Figure 6.4 shows that, for the virgin liquor, most of the pH change occurs in the first hour with a rise in pH of 3 units. This rise indicates the consumption of acid in leaching various materials from the reduced ilmenite. The aeration with recycled liquor undergoes a relatively moderate and constant pH rise from approximately 8.6 to 9.6 in 7.0 hours. By using these facts in conjunction with Figure 6.3 it can be assumed that all the acid leaching that occurred in the virgin liquor was in the first hour. In that same hour the recycled liquor's leaching rate was similar to the virgin liquor. It was only after the first hour that the aeration rates began to differ between the two trials with the recycled liquor aerating at a slower rate. It therefore appears

that the acid leaching plays a very small role in the initial rate of aeration for the virgin liquor. The acid may preferentially interact with the sulfur and other impurities first, so that the difference in the two trials must have been caused by other factor such as the presence of the iron oxide in the recycled liquor.

6.2.2 Iron oxides produced through varying the citric acid / trisodium citrate composition

The citric acid leach produced an extremely fine brown oxide after 7.0 hours of aeration, but for the first 6.0 hours of aeration the oxide was a blue/green colour and made the slurry far more viscous. Attempts to separate the blue/green oxide resulted in the colour changing to dark brown. The oxide from the trisodium citrate slurry aeration was initially a dark brown colour which faded through the course of the aeration to a light brown colour. Finally the 0.05 M citric acid / 0.05 M trisodium citrate mixture was used as representative of the all the other mixtures because they all started with a viscous blue/green oxide, after one hour of aeration, that was replaced by a dark oxide within 2.0 further hours of aeration.

All three oxides were analysed by X-ray powder diffractometry, the results of which can be found in Table 6.1.

Table 6.1: Table of the iron oxides produced by various aeration catalysts

Slurry Catalyst	Dominant Oxide	Minor Oxide
0.1 M citric acid	synthetic maghemite	ferrihydrate
0.1 trisodium citrate	ferrihydrate	synthetic maghemite
0.05 citric acid / 0.05 trisodium citrate	ferrihydrate	synthetic maghemite

Dominant - greater than 50 %, Minor - up to 10 %.

synthetic maghemite $\gamma\text{-Fe}_2\text{O}_3$

ferrihydrate $\text{Fe}_3\text{HO}_8 \cdot 4\text{H}_2\text{O}$

The results shown in Table 6.1 have shown that the slurries using 0.1 M trisodium citrate and 0.05 citric acid / 0.05 trisodium citrate as catalysts produced the

same oxides in much the same proportions. This was most likely because the two slurries operated at a similar pH range throughout the aeration. The 0.1 M citric acid operating at a much lower pH still produced the same iron oxides but in far different proportions.

6.3 Ammonium chloride and citric acid mixtures as aeration catalysts

The success of using citric acid as an aeration catalyst in the previous section encouraged further experimentation in the area. As ammonium chloride is already the best known and most widely used leaching and buffering agent for this process, a combination of both catalysts may create an even faster aeration rate than either component on its own.

The main aim of these experiments was to examine the effect of substituting citric acid in place of some of the ammonium chloride. The central question to be addressed by this investigation was: does the citric acid increase the rate of reaction and does the citric acid complex iron (II) in the same way as the ammonium chloride?

6.3.1 The effect of a mixed composition

This series of experiments used the same slurry composition and conditions as those outlined in section 6.2.1, with a combination of ammonium chloride and citric acid to give a total concentration of 0.1 M. The results of these tests are shown in Figure 6.5 as a plot of the percentage of metallic iron remaining in the reduced ilmenite as a function of aeration time.

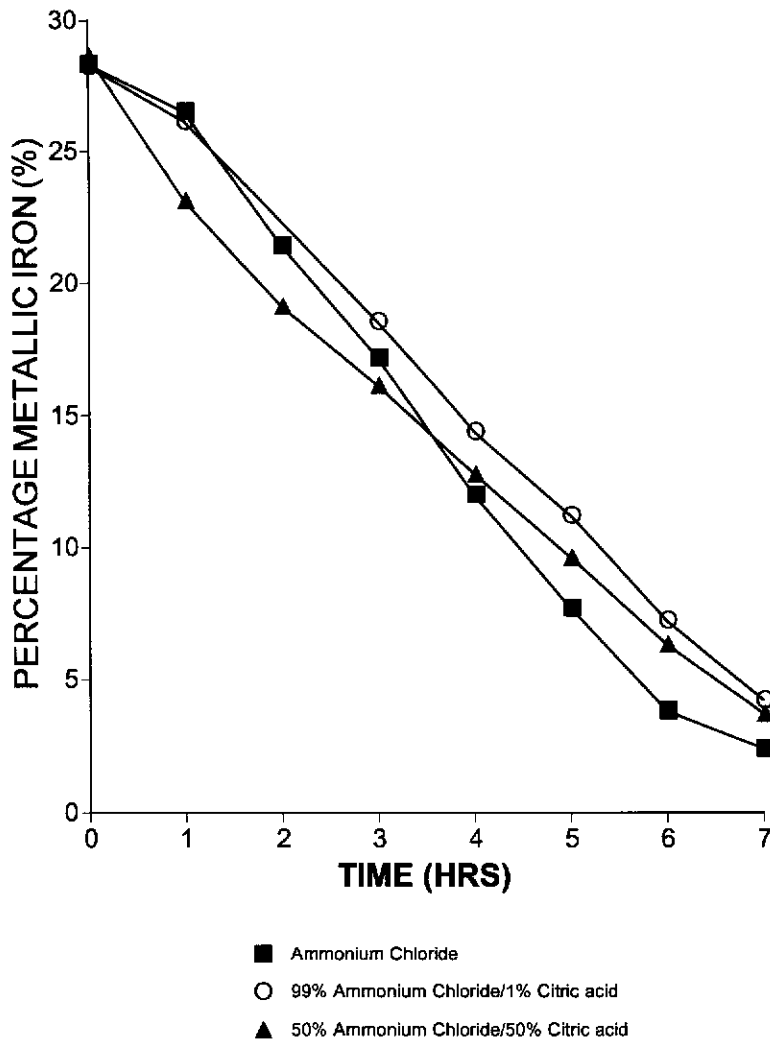


Figure 6.5: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using mixtures of ammonium chloride, citric acid and trisodium citrate as catalytic reagents.

Upon examining the results in Figure 6.5 it is apparent that after 7.0 hours of aeration there is more metallic iron remaining in the slurries containing some citric acid along with ammonium chloride. The pure ammonium chloride experiment had a residual 2.4 percent metallic iron level in the upgraded ilmenite product after the standard 7.0 hour leaching period, compared with a range of 3.7 to 4.2 percent residual metallic iron in the two ammonium chloride / citric acid mixtures. It was also found that the 0.05 M citric acid / 0.05 M ammonium chloride mixture had a higher initial leaching rate than the other two aerations. This was believed to be caused by acid leaching. The aeration rate of this mixture was then seen to slow in comparison to the other aerations after all the acid was consumed. A comparison of gradients between the three aerations, excluding the first hour where the slurry with

the high citric acid concentration underwent acid leaching, was made to determine which catalyst was the most effective. The gradient of the slurry containing the pure ammonium chloride catalyst was found to be -4.56 ± 0.40 , while the slurry with 99 per cent ammonium chloride / 1 per cent citric acid as a catalyst had a gradient of -3.76 ± 0.24 and the slurry using 50 per cent ammonium chloride / 50 per cent citric acid as a catalyst had a gradient of -3.31 ± 0.25 . These gradients and errors were all calculated in Microsoft Excel V5 by the least squares method. From these results it can be seen that the more citric acid that is added to slurry in the place of ammonium chloride the slower the aeration rate becomes.

Clearly, from these results, the substitution of part of the ammonium chloride concentration with citric acid slows the rate of the leaching process. The effect of ammonium chloride concentration on the leaching process has been investigated previously as described in Chapter Three. When the rate of reaction, obtained for the 0.05 M ammonium chloride and 0.05 M citric acid mixture, was compared to the rate of reaction of just 0.05 M ammonium chloride the residual metallic iron levels were similar. This seems to indicate that citric acid either does not assist the ammonium chloride to leach the iron from the reduced ilmenite, or only assists in the leaching to a very minor extent. Unfortunately, the reduced ilmenite samples came from different batches and direct comparison may not be reliable. For a clearer analysis of the effect of the citric acid, the previous results were normalised. The results from the previous work in Chapter Three were expressed as the ratio of the residual percentage metallic iron for the 0.1 M ammonium chloride leach test to the percentage metallic iron for the 0.05 M ammonium chloride leach test. This ratio can then be compared with the 0.1 M ammonium chloride leach test normalised against a mixture of 0.05 M citric acid / 0.05 M ammonium chloride leach test residual percentage metallic iron at the same hourly intervals. The reduced ilmenite used for calculating each ratio was from the same batch. This graph is shown in Figure 6.6.

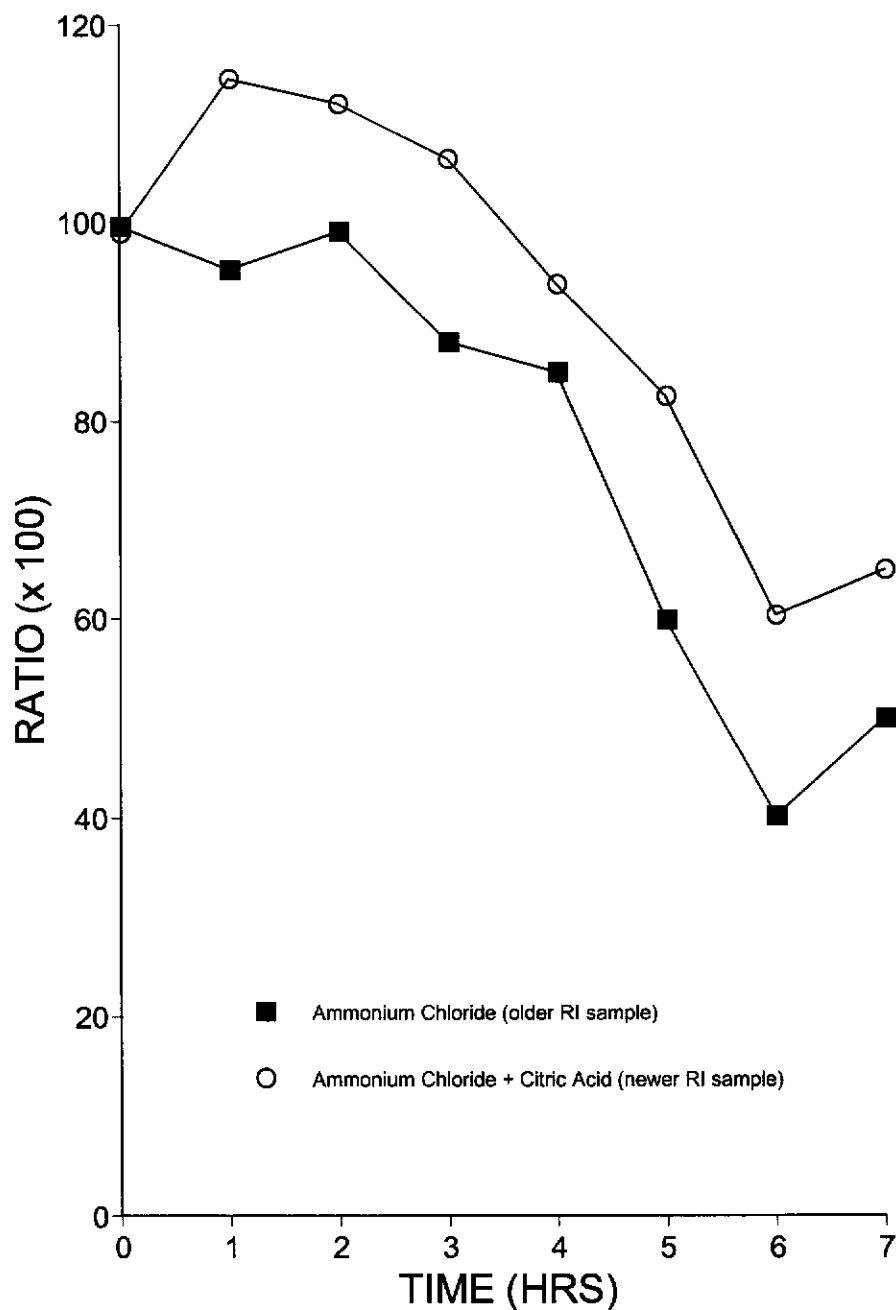


Figure 6.6: Graph of time vs a ratio of the extent of leaching with 0.1 M ammonium chloride to the extent of leaching with 0.05 M ammonium chloride with and without citric acid.

Since there is an inverse relationship between the amount of iron remaining and the rate of leaching, the results shown in the format of Figure 6.6 indicate that the 50 : 50 citric acid / ammonium chloride mixture had a somewhat faster rate of reaction, at every hourly interval, than the pure 0.05 M ammonium chloride.

As the concentration of the citric acid is increased, while the total catalyst concentration remained constant (ie the ammonium chloride concentration decreased), the rate of reaction (leaching) decreases. The cause of this decrease could be due to citric acid poisoning active sites or simply due to the parallel decrease in the ammonium chloride concentration. In the 50 : 50 ammonium chloride and citric acid mixture the residual metallic iron was found to be 3.7 percent. This value was substantially higher than the 2.4 percent obtained using pure ammonium chloride at 0.1 M. This trend was found to be consistent with earlier work in section 3.4 on the effect of ammonium chloride concentration, in which it was found that decreasing the concentration of ammonium chloride from 0.1 M to 0.05 M doubled the residual metallic iron. From the information observed in Figure 6.6, citric acid did actively increase the rate of reaction. Although the citric acid did increase the rate of reaction when mixed with ammonium chloride at lower concentrations it did not leach to the same extent as pure ammonium chloride at 0.1 M concentration, which suggests that the citric acid acted as a poison.

Further combinations of ammonium chloride with citric acid and trisodium citrate failed to leach the reduced ilmenite in a 7.0 hour period. The test conducted used 0.05 M ammonium chloride / 0.025 M citric acid / 0.025 M trisodium citrate, which only leached the metallic iron level to 9.7 per cent. Finally, the use of 0.1 M ammonium citrate failed, only producing a blue solution and ammonia gas. As a result the experiment was stopped an hour after commencement.

6.3.2 Iron oxides produced

The 99.0 per cent ammonium chloride and 1.0 per cent citric acid slurry produced a black oxide in the first hour of aeration and remained that colour all the way through the reaction. On X-ray diffraction analysis, the oxide was reported to be over 50 per cent haematite ($\alpha\text{-Fe}_2\text{O}_3$), 10 to 50 percent magnetite (Fe_3O_4) with 2 to 10 percent content of goethite ($\alpha\text{-FeOOH}$). These results were consistent with previous analyses completed for a 100 per cent ammonium chloride slurry (section 3.5.1).

The 0.05 M ammonium chloride / 0.05 M citric acid slurry created a black iron oxide in the first hour of aeration but as the aeration continued the colour of the oxide gradually changed to a brown colour by the time the aeration finished. As previously mentioned, the oxide was an extremely fine material that could not be separated even after long periods of settling. After gently heating the solution to evaporate the liquid the remaining solid was analysed with the use of an X-ray diffractometer. The oxide was found to be poorly crystalline but was confirmed as being predominantly (greater than 50 per cent) ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$). This type of oxide was also found to be created from the slurries in section 6.1 that also contained citrate ion, but no ammonium chloride.

6.4 Tartaric acid and its salts as aeration catalysts

The use of tartaric acid as a catalyst for aeration was chosen because of its possible ability to offer twice the complexation sites of ammonium chloride, and also because when mixed with its salts, it may offer a buffering action to assist the aeration. A racemic source of tartaric acid was used in all the following experiments.

6.4.1 The effect of pH

These three experiments used the same slurry content and conditions as those outline in section 6.2.1 using a total of 0.1 M of the catalyst. Tartaric acid, disodium tartrate and a 0.05 M tartaric acid/ 0.05 M disodium tartrate mixture were used to compare their catalytic capabilities against the catalyst used industry, ammonium chloride. The results of these assays are shown in Figure 6.7.

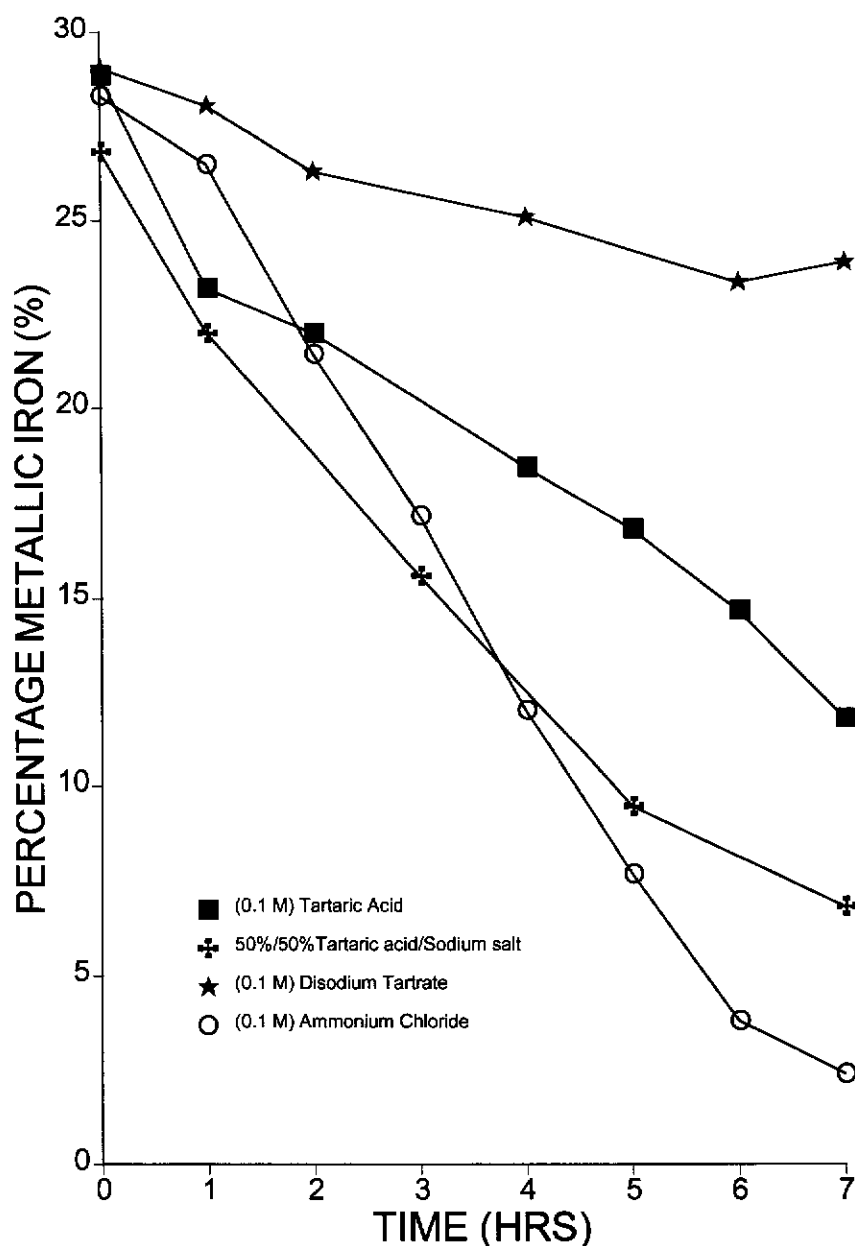


Figure 6.7: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using ammonium chloride, tartaric acid, disodium tartrate and mixtures of tartaric acid and disodium tartrate as catalytic reagents.

The results of these three experiments, shown in Figure 6.7, indicated that neither the tartaric acid nor the disodium tartrate were able to catalyse the leaching of metallic iron to the same extent, in a 7.0 hour period, as ammonium chloride. The mixture of 50 per cent tartaric acid and 50 per cent disodium tartrate performs much better than either the acid or the salt alone, but still had a slower aeration rate than the ammonium chloride slurry. The disodium tartrate was unable to promote the leaching of the reduced ilmenite to a level lower than 23 per cent residual metallic iron over

the 7.0 hour period, while the tartaric acid reached a level of 11.4 per cent in the same time period. The tartaric acid / disodium tartrate mixture managed to reach a residual metallic iron level of 6.8 per cent in the same 7.0 hour period. The difference in the tartrate compounds may be due to the acid groups present in tartaric acid. The acid coming from the tartaric acid may be able to oxidise the metallic iron to iron (II) ions and increase the leaching rate until all the acid was consumed, as shown by the comparatively steep initial slope in Figure 6.7. Once the acid was consumed the rate slowed considerably. This is reinforced by the pH profile during leaching shown in Figure 6.8.

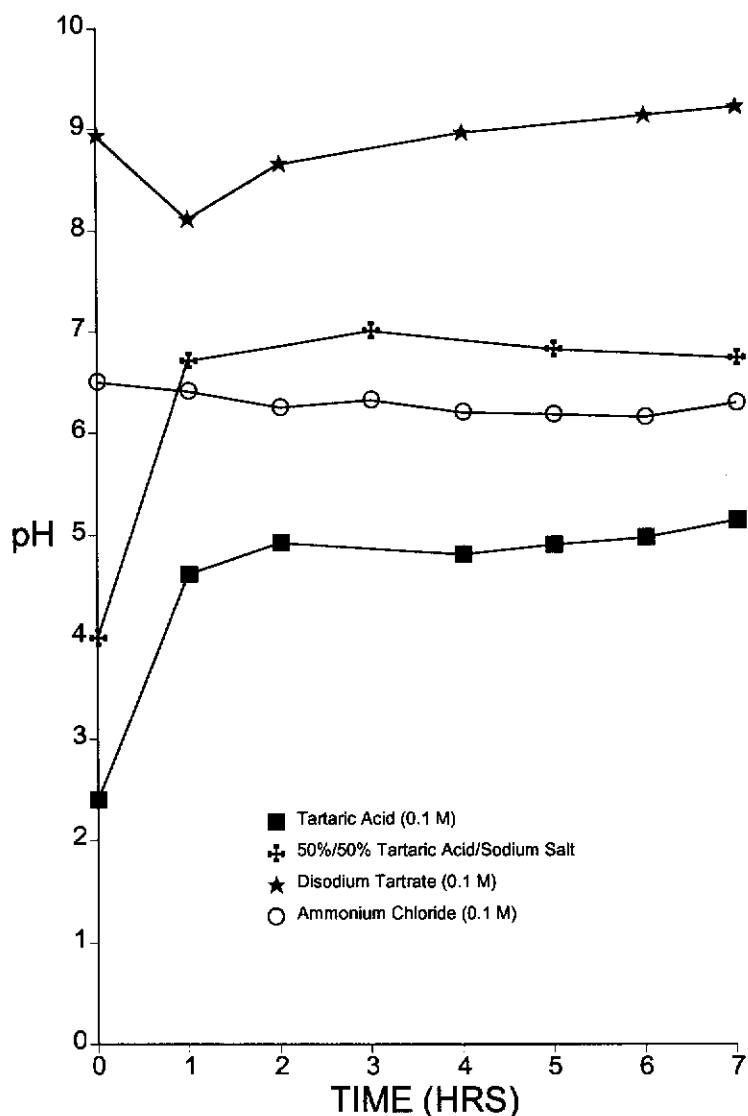


Figure 6.8: Graph of time vs pH in the aeration of reduced ilmenite using ammonium chloride, tartaric acid, disodium tartrate and mixtures of tartaric acid and disodium tartrate as catalytic reagents.

As the pH profile shown in Figure 6.8 suggests, the free acid in the tartaric acid slurry was quickly consumed in the first hour of the aeration, which corresponds to the higher aeration rate in the first hour. For the 0.05 M tartaric acid / 0.05 M disodium tartrate mixture the increased rate of reaction was not entirely due to acid leaching as it was for the tartaric acid alone because the mixture only had half the amount of acid present. After the first hour the mixture slurry had reached a pH very close to the pH of the ammonium chloride slurry. Working in this pH range probably allowed the mixture to reach conditions where the complex compounds present could begin to transport the ionic iron (II) out of the grains.

Overall, the tartrate systems as catalysts were found to be generally ineffective when compared to the ammonium chloride system, although when a 50 per cent tartaric acid / 50 per cent disodium tartrate mixture was used, far better results were obtained. However, this mixture was still not as effective as ammonium chloride.

6.4.2 Iron oxides produced

A brown coloured oxide was collected for both the tartaric acid slurry and the disodium tartrate slurry. As the oxides for both appeared to be the same colour and texture, only the oxide produced using tartaric acid was taken for further analysis. In the case of the 50 per cent tartaric acid / 50 per cent disodium tartrate mixture the oxide produced appeared to be a soluble brown oxide. Due to the difficulty of separation it was decided that the oxide was inaccessible for analysis.

The oxide from the tartaric acid slurry, was analysed using X-ray powder diffractometry. The results of this analysis indicated that the oxide contained predominantly, greater than 50 per cent, ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) and a major portion, 10 to 50 per cent, of synthetic maghemite ($\gamma\text{-Fe}_2\text{O}_3$).

6.5 Ammonium chloride and tartaric acid mixtures as aeration catalysts

From the previous section the use of tartaric acid by itself or in combination with disodium tartrate was proven to be too slow as an aeration catalyst. In this work a combination of tartaric acid mixed with ammonium chloride was investigated. The purpose behind these experiments was to examine whether ammonium chloride's buffering or complexation abilities may assist the tartrate ion's own complexation abilities thereby producing a faster aeration.

6.5.1 The effect of varying the mixture composition on aeration rates

This series of experiments used the same slurry composition and conditions as those outlined in section 6.2.1, with a combination of ammonium chloride and tartaric acid to give a total concentration of 0.1 M. The results of these tests are shown in Figure 6.9 as a plot of the percentage of metallic iron remaining in the reduced ilmenite as a function of aeration time.

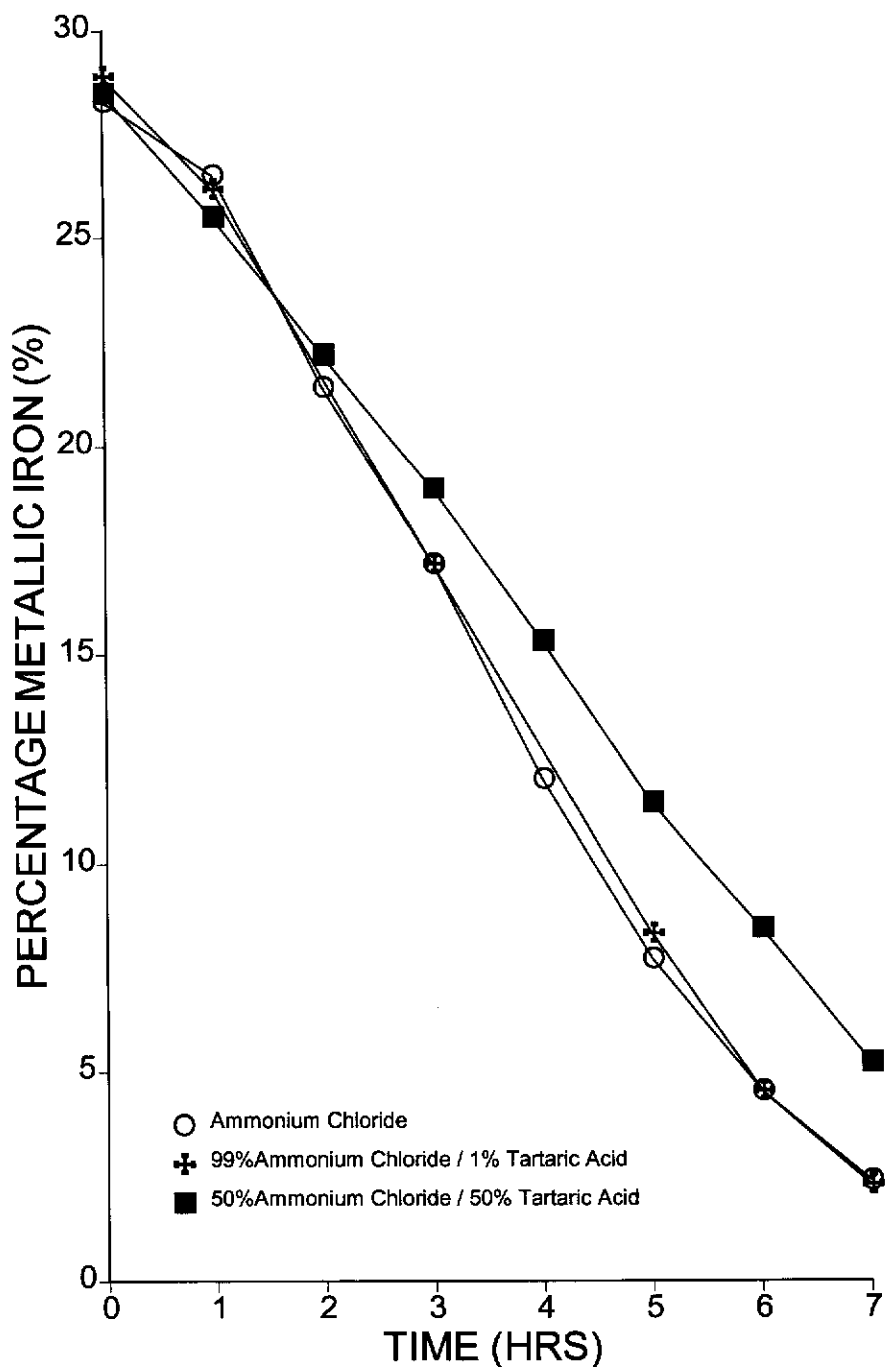


Figure 6.9: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using mixtures of ammonium chloride, tartaric acid and disodium tartrate as catalytic reagents.

The immediate trend, shown in Figure 6.9, that can be observed is the slower rate of leaching with higher concentrations of tartaric acid. The residual metallic iron level increased from 2.4 per cent, from the pure ammonium chloride test, to 5.2 per cent, when the leaching solution was 50 : 50 tartaric acid / ammonium chloride.

Clearly the ammonium chloride aeration and the 99% ammonium chloride / 1% tartaric acid aeration are very similar and within the normal variation of replicate results. In the case of the 50% ammonium chloride / 50% tartaric acid aeration the aeration rate is markedly different from the first two aerations. As a further comparison between the three aerations the gradient of each line was found by the least squares method used in Microsoft Excel V5. The slurry using 100 per cent ammonium chloride as its catalyst had a gradient of -4.46 ± 0.62 while the 99 per cent ammonium chloride / 1 per cent tartaric acid catalyst produced an aeration gradient of -4.35 ± 0.33 and the 50 per cent ammonium chloride / 50 per cent tartaric acid catalyst produced an aeration gradient of -3.46 ± 0.23 . Statistically this shows that the catalysts with the higher ammonium chloride concentrations (100% and 99%) perform at the same rate, well within experimental error, while the lower ammonium chloride concentrations give significantly lower rates.

The critical issue in this case, as it was with citric acid, is whether the decrease in the rate of reaction is due to the presence of tartaric acid as a poison, or simply due to the decrease in the ammonium chloride concentration. The residual metallic iron level obtained from the mixture of the 0.05 M tartaric acid / 0.05 M ammonium chloride was found to be comparable with the level of metallic iron of test using only 0.05 M ammonium chloride, after 7.0 hours. Again, the reduced ilmenite samples came from different batches and could not be readily compared in this direct manner. For a clearer analysis of the effect of the tartaric acid the results were normalised as described in section 6.3.1. The results from the previous work in Section 3.4 were expressed as the ratio of the residual percentage metallic iron for the 0.1 M ammonium chloride concentration to the residual percentage metallic iron for the 0.05 M ammonium chloride concentration. This ratio was then compared with the 0.1 M ammonium chloride leach normalised against the residual metallic iron from a mixture of 0.05 M tartaric acid / 0.05 M ammonium chloride at the same hourly intervals. This graph was placed in Figure 6.10. The reduced ilmenite used for obtaining each ratio came from the same batch.

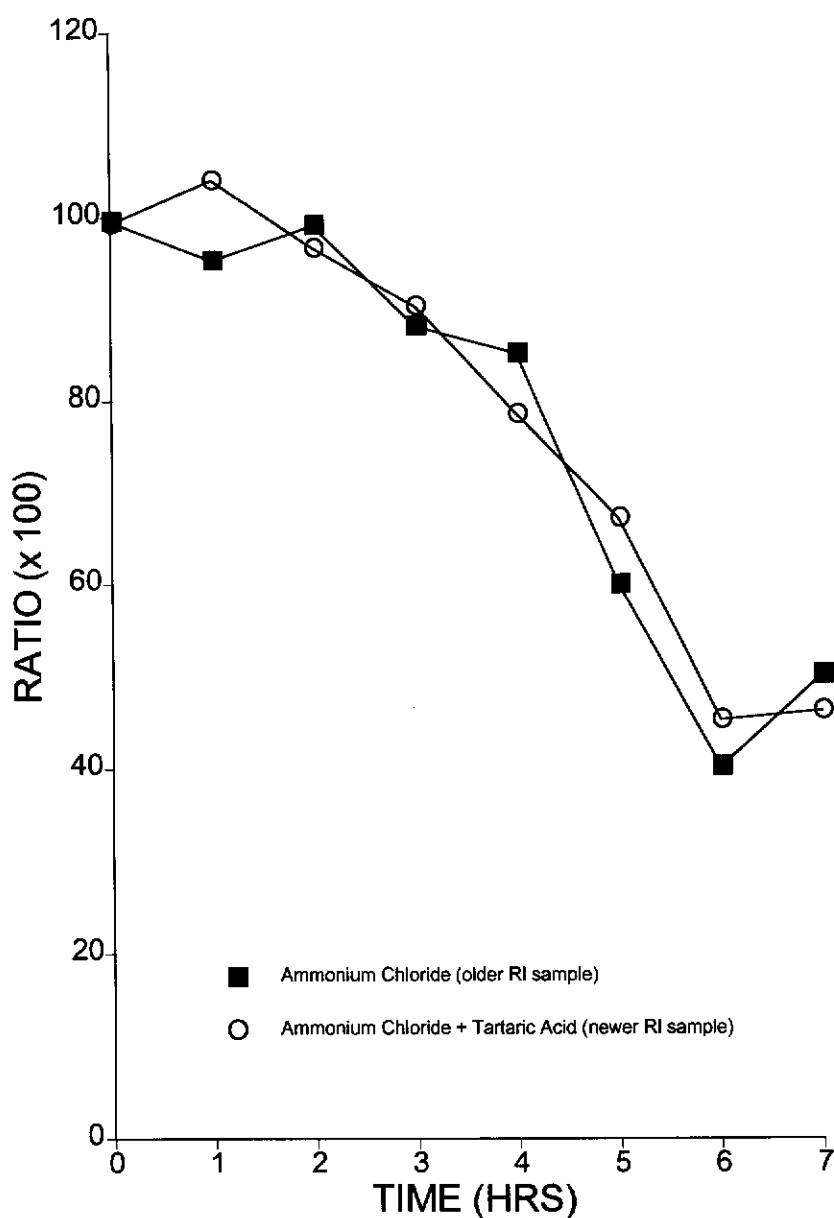


Figure 6.10: Graph of time vs a ratio of the extent of leaching with 0.1 M ammonium chloride to the extent of leaching with 0.05 M ammonium chloride with and without tartaric acid.

The resultant graph in Figure 6.10 indicates that the ratios of the pure ammonium chloride system and the tartaric acid / ammonium chloride system are very similar. This indicates that the tartaric acid neither assists nor inhibits the ammonium chloride in leaching the metallic iron from the reduced ilmenite. In the case of the 1 per cent tartaric acid / 99 per cent ammonium chloride mixture there was clearly little difference between the levels of metallic iron at all points on the graph shown in Figure 6.9, compared with 100 per cent ammonium chloride.

It appears that the tartaric acid, unlike the citric acid, plays no role in the removal of the metallic iron from the reduced ilmenite when used in conjunction with ammonium chloride. Furthermore, it appears likely that the sole cause of variation in the rates is the change in ammonium chloride concentration arising from the experimental design of maintaining a constant total concentration of leaching agent.

6.5.2 Iron oxides produced for the different mixtures

The 99 per cent ammonium chloride and 1 per cent tartaric acid slurry mixture produced a brown coloured oxide in the first hour of aeration that darkened further over the following hours to eventually produce a black oxide. The oxide was then analysed using X-ray diffraction (XRD), the results of which show the oxide to be made up of greater than 50 per cent haematite ($\alpha\text{-Fe}_2\text{O}_3$), between 10 to 50 per cent magnetite (Fe_3O_4) and between 2 and 10 per cent goethite ($\alpha\text{-FeOOH}$). The same analysis was made for the pure ammonium chloride slurry and the same oxides were produced in the same proportions.

In the case of the 0.05 M ammonium chloride / 0.05 M tartaric acid slurry mixture the oxide produced in the first hour of aeration was a mustard brown that changed to a dark brown during the course of the aeration. On analysis by XRD the oxide was found to contain 50 per cent or greater ferrihydrite ($\text{Fe}_5\text{HO}_8\cdot 4\text{H}_2\text{O}$), between 2 and 10 per cent magnetite (Fe_3O_4) and between 2 and 10 per cent maghemite ($\gamma\text{-Fe}_2\text{O}_3$). This analysis was consistent with the analyses for other tartrate ion slurries found in section 6.4.

6.6 Oxalic acid and its salts as aeration catalysts

Oxalic acid was the last of the carboxylic acids that was examined as a possible aeration catalyst. Oxalic acid, simply being two carboxylic acid groups joined together, has the same potential complexation ability as tartaric acid without the added problems of a larger molecular structure. The possible use of the sodium oxalate salts in combination with the acid may also cause a buffering effect that assists in the complexation and removal of the metallic iron.

6.6.1 Changes in the aeration rate caused by varying pH

The first series of experiments used the same slurry composition and conditions as those outlined in section 6.2.1 using oxalate to a total catalyst concentration of 0.1 M. To make up the total oxalate ion concentration of 0.1 M different combinations of oxalic acid and disodium oxalate were mixed together. The results of these experiments are shown in Figure 6.11.

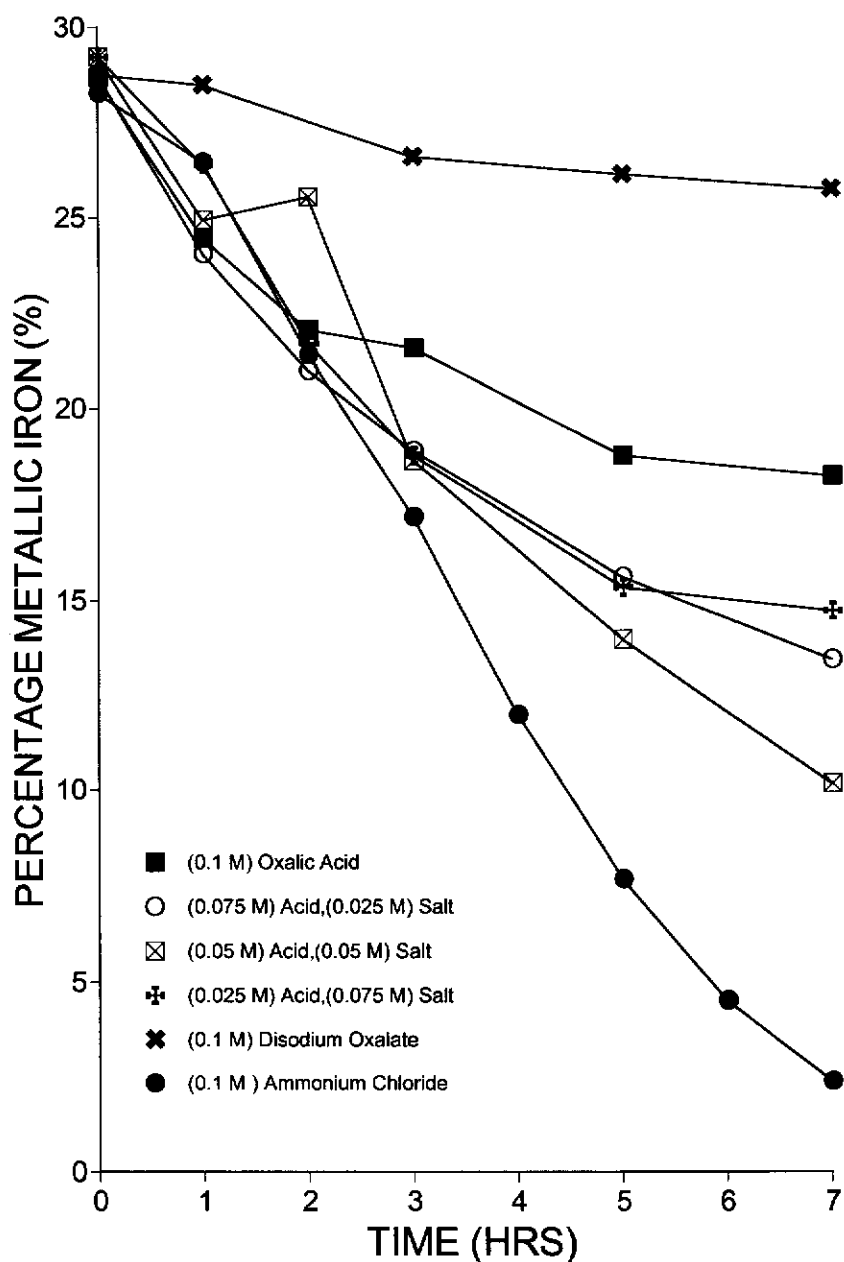


Figure 6.11: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using ammonium chloride, oxalic acid, disodium oxalate and mixtures of oxalic acid and disodium oxalate as catalytic reagents.

The graph, featured in Figure 6.11, has shown that all of the combinations of oxalic acid and disodium oxalate had a slower rate of aeration than the standard ammonium chloride slurry. Of the oxalate slurries, the two using either 100 per cent oxalic acid or disodium oxalate had the slowest rates of aeration. The pure disodium oxalate slurry removed very little of the metallic iron, the small amount that was leached was attributed to aerial oxidation and a small amount of *in situ* rusting.

In the case of the oxalic acid slurry the reaction profile shown in Figure 6.11 suggested a fast rate of reaction for the first 2 hours of aeration then a much slower rate of reaction for the remainder of the aeration time. The faster aeration rate was attributed to the oxalic acid leaching the metallic iron by means of its acid groups. This was confirmed by examination of the pH profiles for these experiments in Figure 6.12. After the acid leaching had been exhausted the aeration rate became very slow and very similar to the disodium oxalate slurry over the last 5 hours of the experiment.

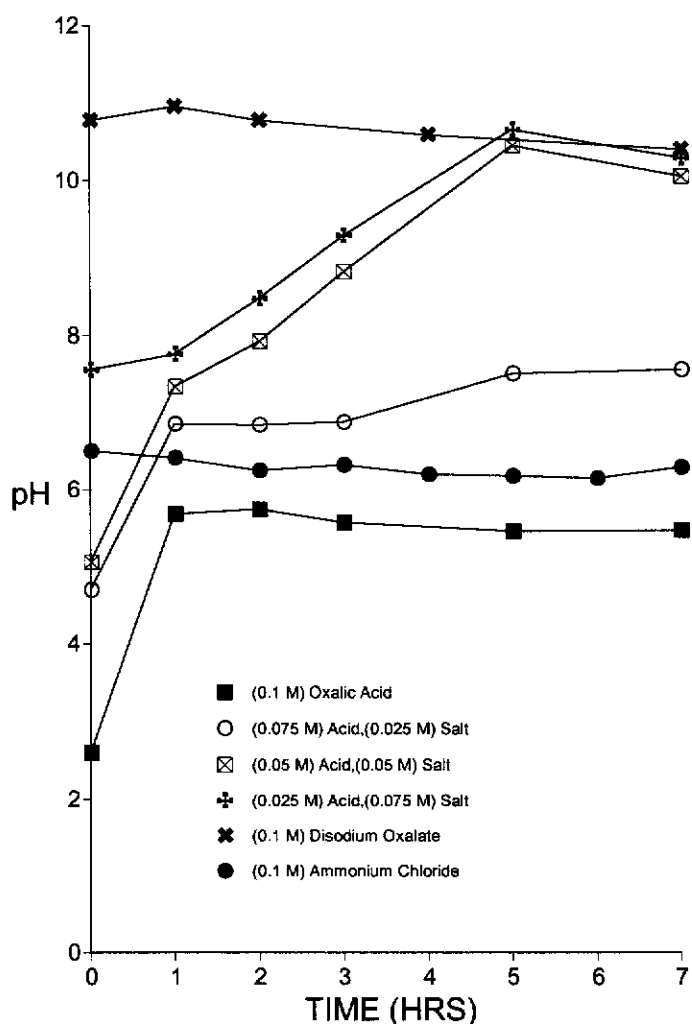


Figure 6.12: Graph of time vs pH in the aeration of reduced ilmenite using ammonium chloride, oxalic acid, disodium oxalate and mixtures of oxalic acid and disodium oxalate as catalytic reagents.

The combinations of oxalic acid and disodium oxalate yielded faster rates of reaction than either of the components alone. In each case the rate of reaction slowed to some extent as the reaction progressed. The amount of acid present did not result in any great difference between the reaction rates for the three mixtures of oxalic acid and disodium oxalate. The pH profile, in Figure 6.12, showed that while the slurry containing 0.075 M oxalic acid did rise in pH, indicating that the acid was being consumed. The rate of reaction did not change after the first hour when the pH stopped rising, which seemed to indicate that iron complexation was occurring. In the case of the 0.05 M oxalic acid and 0.05 M disodium oxalate slurry the pH did rise for 5 hours before stabilising at just under pH 11. It is believed that at high pH levels the iron complexes were unable to form. The same behaviour was observed for the slurry employing 0.025 M oxalic acid and 0.075 M disodium oxalate as its pH rose steadily through most of the aeration time. The distinct advantage the mixtures had over the single component catalysts was the ability to form such species as monohydrogen oxalate that may have formed iron complexes in the intermediate pH range.

The only slurry to show any tendency to act as a buffering reagent was the one containing 0.075 M oxalic acid and 0.025 disodium oxalate. Even then the pH rose for an hour before coming to a fairly steady pH value of around pH 8. Due to the lack of buffering of the oxalate ion, even if it was capable of complexation with the ferrous ion, the rate of aeration decreased due to the ever changing pH conditions which affected when a complex could form.

6.7 Ammonium chloride and oxalic acid mixtures as aeration catalysts

The oxalic acid and disodium oxalate combinations were shown to be poor aeration catalysts in the Becher process. To investigate the slow reaction rates of the oxalate ion a further series of tests involving the addition of ammonium chloride and sodium chloride was conducted. These tests were designed to investigate the possible changes introduced by a buffering agent (ammonium ion), and an agent that prevents passive oxide films forming on metallic iron (chloride ion), in combination with the use of oxalate mixtures as a catalyst.

6.7.1 The effect of a mixed composition

This series of experiments used the same slurry composition and conditions as those outlined in section 6.2.1 with combinations of oxalic acid, disodium oxalate, ammonium chloride and sodium chloride as catalyst at a total concentration of 0.1 M. These results were then graphed and placed in Figure 6.13.

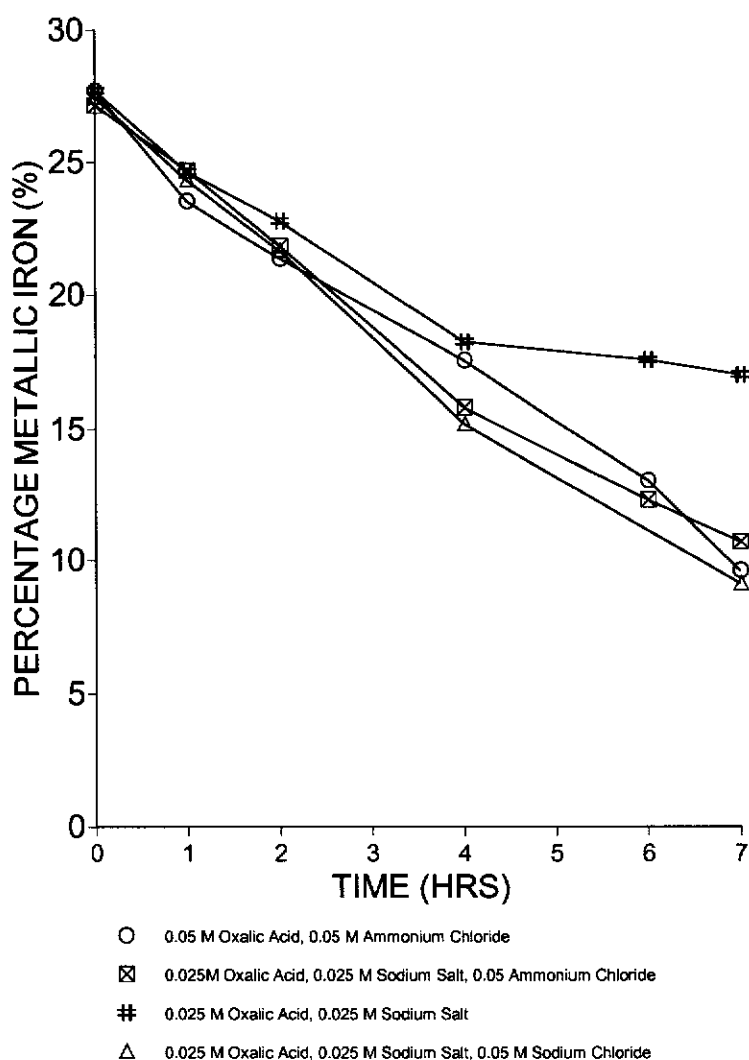


Figure 6.13: Graph of time vs percentage metallic iron in the aeration of reduced ilmenite using mixtures of ammonium chloride, oxalic acid and disodium oxalate as catalytic reagents.

The graph shown in Figure 6.13 indicates that the use of 0.05 M ammonium chloride with a 0.025 M oxalic acid, 0.025 M disodium oxalate mixture in a slurry reached a residual metallic iron value of 10.7 per cent after 7.0 hours. This value was only very slightly higher than the value of 10.2 per cent for the 0.05 M oxalic acid / 0.05 M disodium oxalate slurry used in section 6.6.1. This comparison indicated that the presence of ammonium chloride achieved nothing in the way of increasing aeration rates or it managed to act in such a manner to compensate for only having half the amount of oxalic acid and disodium oxalate present. To find out exactly what the ammonium chloride achieved in the slurry the same experiment was repeated without the ammonium chloride, using only 0.025 M oxalic acid and 0.025 M

disodium oxalate. The result was a significantly slower reaction with a residual metallic iron level of 17.0 per cent after the 7.0 hours of aeration. This information would seem to show the ammonium chloride was acting to increase the rate of aeration compared with the low rate achieved with oxalate alone.

The slurry using 0.05 M oxalic acid with 0.05 M ammonium chloride also reached a similar residual metallic iron value of 9.6 per cent. This would seem to indicate that the ammonium ion may have assisted by buffering the system, or the chloride ion may have decreased passive iron oxide layer formation, because the aeration rate was increased compared to the 0.1 M oxalic acid slurry (section 6.6.1).

The use of 0.05 M sodium chloride with 0.025 M oxalic acid / 0.025 M disodium oxalate as an aeration catalyst was then considered to establish which component of the ammonium chloride could promote an increase in the aeration rate. As the graph in Figure 6.13 suggests, the slurry with 0.05 M ammonium chloride and 0.05 M oxalic acid follows a very similar reaction pathway to the 0.05 M sodium chloride / 0.025 M oxalic acid / 0.025 M disodium oxalate slurry. This evidence suggests that the presence of chloride ion was causing the aeration rate to increase. To confirm that this was the only effect of the ammonium chloride a pH profile graph was drawn (Figure 6.14).

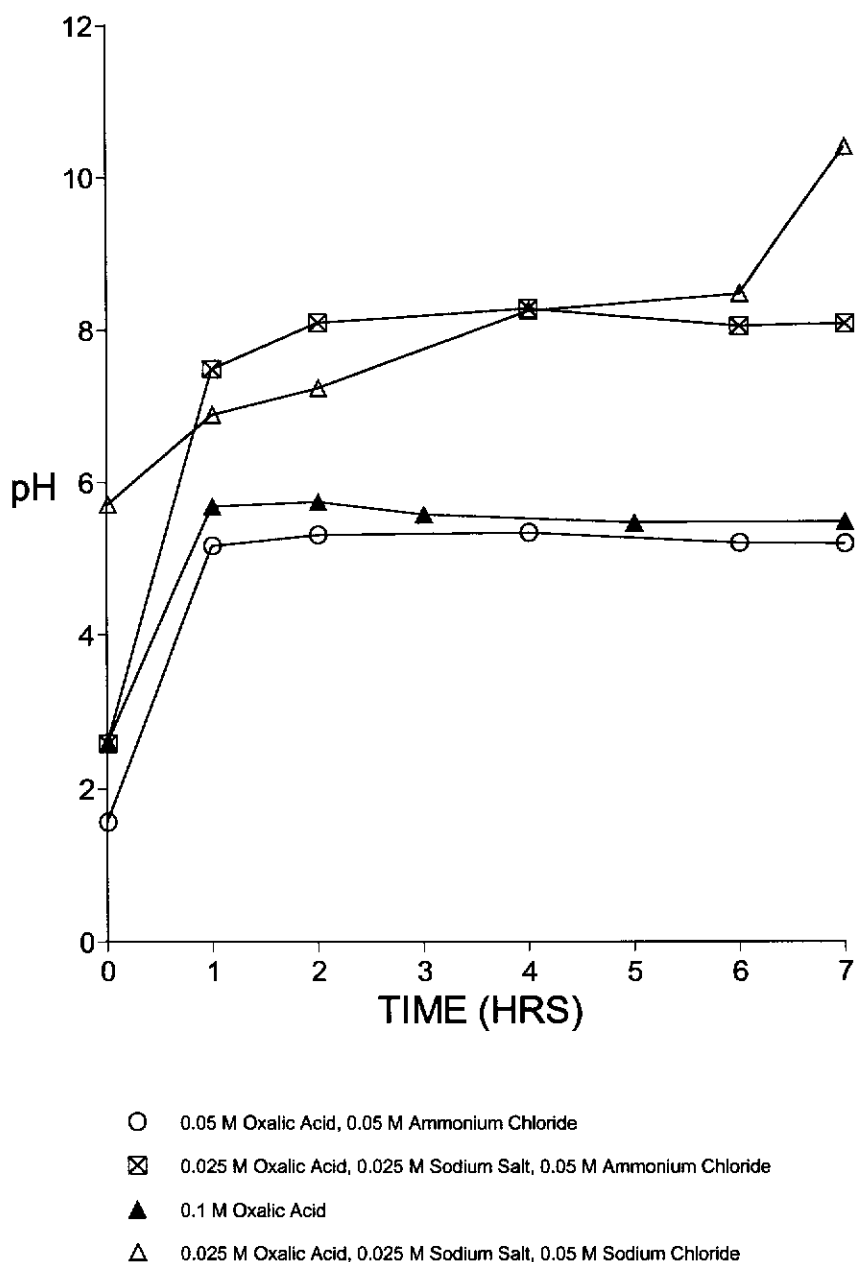


Figure 6.14: Graph of time vs pH in the aeration of reduced ilmenite using mixtures of ammonium chloride, oxalic acid and disodium oxalate as catalytic reagents.

The graph presented in Figure 6.14 shows that the buffering offered by the ammonium ion was not effective in these experiments. In the case where the 0.05 M ammonium chloride / 0.05 M oxalic acid slurry was compared to the 0.1 M oxalic acid slurry the pH profiles are near identical. This meant that the ammonium ion can not be buffering the slurry to the same extent as it does in ammonium chloride only. In the experiments using 0.025 M oxalic acid / 0.025 M disodium oxalate with ammonium chloride the pH profile becomes constant at a pH value too high for the

ammonium ion to exist because ammonia would be prevalent. Finally the slurry that used sodium chloride as part of its catalyst did not show any buffering action, as would be expected.

It was then apparent that any increase in the aeration rate of the oxalate catalyst by addition of ammonium chloride was brought about by the ability of chloride ion decrease the degree of passivation achieved by iron oxides on the surface of the iron.

6.8 Conclusions

The mechanism of the Becher process involves the use of ammonium chloride as the catalyst for aeration. The actual role of the ammonium chloride in this mechanism has been found to be more complex as further studies are carried out. The role that ammonium chloride plays in this process includes that of a buffer and a complexing agent. In these experiments other compounds which have similar buffering and / or complexing abilities were examined.

Pure tartaric acid and disodium tartrate showed a much slower rate of leaching when compared to ammonium chloride. The levels of metallic iron present after a 7.0 hour leaching period were 11.4 per cent for the tartaric acid, 23 per cent for the disodium tartrate, and 2.4 per cent for the ammonium chloride. The difference between the tartaric acid and the disodium tartrate was due to the acid groups participating in the leaching process.

The investigation involving citric acid and its salts found that the mixtures of citric acid and trisodium citrate had a faster reaction rate when compared to the ammonium chloride system. The 0.05 M citric acid / 0.05 M trisodium citrate mixture reached the same level of metallic iron, in 4.5 hours, as the ammonium

chloride system did in 7.0 hours. Although the rate of leaching was faster for the citrate slurry it was also found that a significant part of the leaching was carried out by free acid which would not be advantageous for continual processing as additions of fresh acid would be required at the beginning of each leach.

The experiments involving oxalic acid and its sodium salts found that the oxalate ion, in any of its salt forms, did not work well as a catalyst, as it could only complex weakly to iron, if at all. The slurry that was aerated fastest used 0.05 M oxalic acid and 0.05 M disodium oxalate, giving a residual metallic iron level of 10.2 per cent after 7.0 hours of aeration.

The attempt to gauge the leaching capabilities of citric acid and tartaric acid by combining them individually with ammonium chloride to a total concentration of 0.1 M indicated that the citric acid, at high concentrations, does participate in the leaching of metallic iron from reduced ilmenite but not as well as pure 0.1 M solution of ammonium chloride. At lower concentrations citric acid simply acts as a poison to the leaching. These tests also indicated that the tartaric acid neither hinders or assists in the leaching of metallic iron in an ammonium chloride solution.

The oxalate ion mixed with ammonium chloride proved to be able to slightly increase the rate of aeration to a residual metallic iron level of 9.6 per cent, when compared with aerations involving oxalate ion alone. The aeration rate for the oxalate ion and ammonium chloride was still not able to completely aerate 300 grams of reduced ilmenite in 7.0 hours, as ammonium chloride alone could.

Chapter Seven

Inverted cone aerator

7.1 Introduction

There were three objectives in building an inverted cone aerator. The first was to increase the speed of experimental tests compared with the aerator already in use. The second was to use another style of aerator to examine the similarities and differences in leaching between the two aerator designs and finally to create an aerator that used a smaller amount of sample but still produced meaningful results.

The final inverted cone reactor was a modified design based on the aerator used by Farrow and Ritchie (1985) for use with small quantities of reduced ilmenite sample. The major design difference was the circulating mechanism that pumped the liquid in a circuit to make the aerator a fluidised bed. This aerator was used to repeat several of the experiments already completed with the 5.0 litre aerator to compare the results and effectiveness of each aerator.

7.2 Aeration at different pulp densities

The optimisation of the slurry conditions in the inverted cone reactor was part of the initial investigation to ensure that the optimum results could be obtained in the shortest time possible. For these initial tests an ammonium chloride slurry was used to assess the optimum operating conditions of the aerator. The first of these optimisation examinations was the amount of reduced ilmenite that could be added to the aerator to be leached in the smallest possible time.

In these experiments the slurry consisted of 1.0 litre of water and 5.0 grams (0.093 M) of ammonium chloride. Various amounts of reduced ilmenite, 5.0 to 100 grams, were added to each slurry and then aerated. The aerations were carried out at a temperature of 75 degrees Celsius, as the aerations are in industry, and consistent with the optimum results found in section 3.5. An air flow of 1.0 litre per minute was used after initial observations indicated that higher flow rates caused too much turbulence. A more accurate assessment of air flow rate was completed following these experiments. Due to the small amounts of reduced ilmenite being used in most cases, samples could not be removed hourly, for metallic iron analysis, without causing a major change in the pulp density. To avoid this problem each trial consisted of 5 to 7 separate aerations, the first aeration for 1.0 hour the second for 2.0 hours and so on until they were completely leached, or 7 hours had passed. The results of these analyses are shown graphically in Figure 7.1.

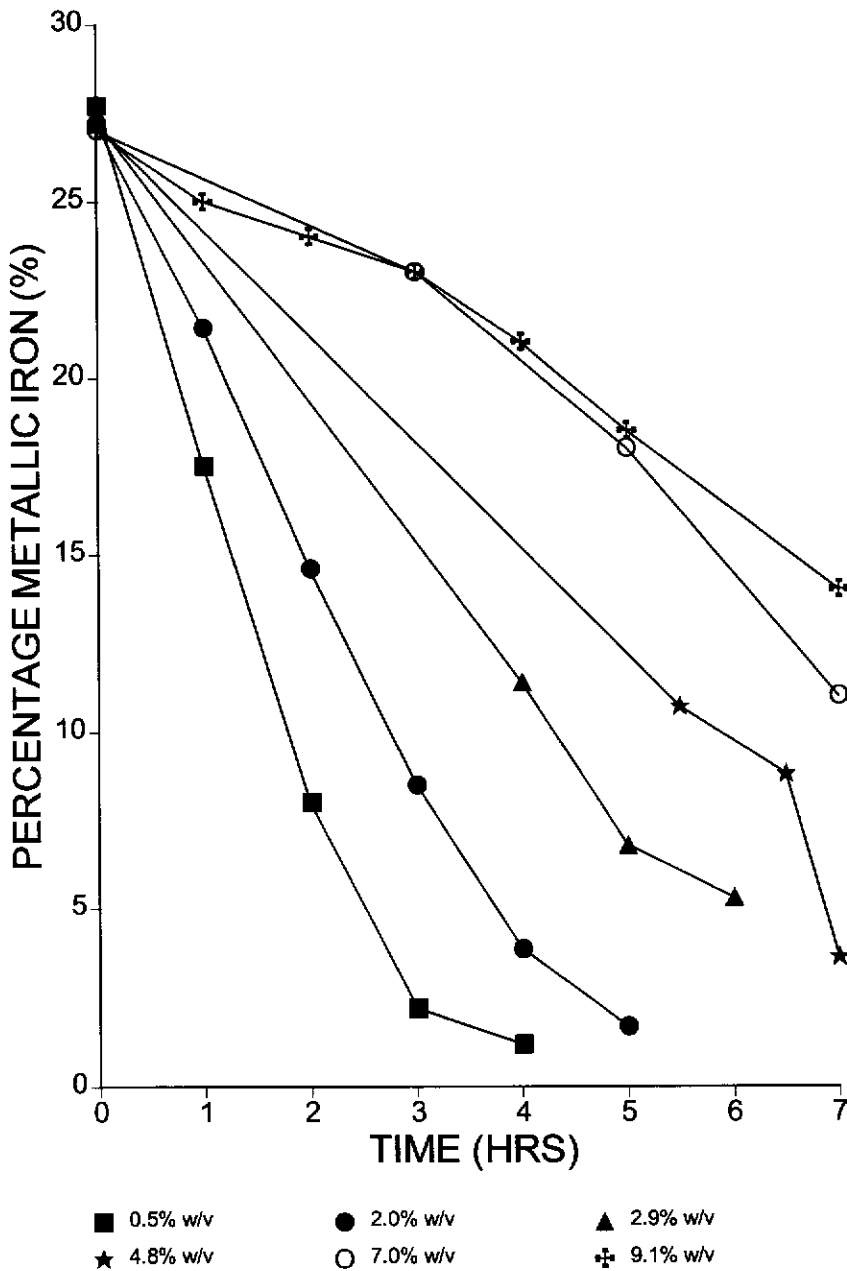


Figure 7.1: Graph of time vs percentage metallic iron using different pulp densities in ammonium chloride slurries.

The graph in Figure 7.1 indicates that the slurries containing 30 grams (2.9% w/v) or more of reduced ilmenite did not complete the leaching of the metallic iron in a 7.0 hour period. As one of the purposes of the inverted cone reactor was to create faster leaching conditions than the 5.0 litre reactor, the aeration time of a slurry in the inverted cone needed to be less than 7.0 hours with ammonium chloride as the catalyst. The only slurries that aerated to a residual metallic iron level and fall into this time restriction were the 5 gram (0.5% w/v) and 20 gram (2.0% w/v) slurries.

The 5 gram slurry reached a residual metallic iron level of 1.2 per cent in 4.0 hours while the 20 gram slurry reached a residual metallic iron level of 1.7 per cent in 5.0 hours.

Although the mass of the reduced ilmenite in the two successful slurries differed by a factor of four the aeration times only differed by 1.0 hour. This suggests that the higher pulp density utilised the oxygen at a greater efficiency than the lower pulp density, consistent with results discussed for the 5.0 litre aerator in section 3.3.

From these results it was decided to continue the further investigations with the use of 20 grams (2.0% w/v) of reduced ilmenite. This was decided because the higher pulp density would give a better representation of any changes in aeration rates caused by other variations in characteristics than would a lower pulp density.

7.3 Aeration at different air flow rates

The air flow used for the inverted cone reactor had two purposes, the first is to assist in the suspension of the solids in the slurry and secondly to deliver the oxygen to the reduced ilmenite so the metallic iron can be oxidised. These points became important because, if the air flow rate was allowed to become too great the air was also capable of pushing the reduced ilmenite up into the liquid pumping zone of the aerator where the solids would then flow through the pump and be crushed by the pumping mechanism. Alternatively if the air flow was too small, the solids would block the inlet flow point at the bottom of the reactor. Due to these constraints, finding the optimum air flow rate was much more difficult.

These slurries were aerated with an air flow between 0.5 and 3.5 litres per minute. These experiments used the same procedures, slurry composition and conditions as those described in section 7.2 with a 20 gram mass of reduced ilmenite. The results are shown in a graph in Figure 7.2.

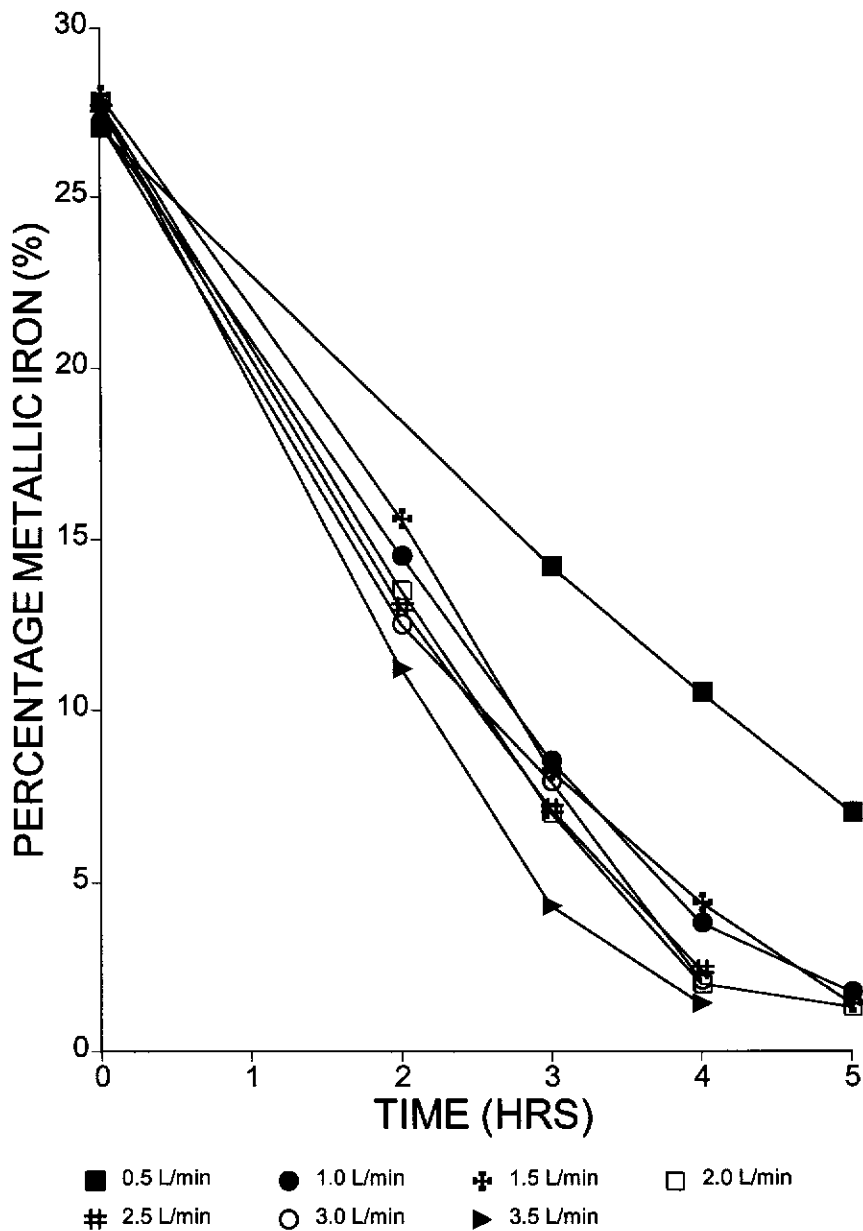


Figure 7.2: Graph of time vs percentage metallic iron using different air flow rates for standard ammonium chloride slurries

The results in Figure 7.2 clearly showed that any flow rate of 1.0 litre per minute or greater could achieve complete aeration in a 5.0 hour period. Of those air flow rates that fell into this category, those above 2.0 litres per minute were almost completely aerated in 4.0 hours. There was a general relationship evident between the air flow rate and the aeration rate. This relationship infers that the higher the air flow rate the faster the aeration rate will be. This relationship is seen in the initial aeration rates shown at all the flow rates up to and including 3.5 litres per minute.

The discussion thus far has only looked at the possibility of increasing the aeration rate. The other factor that required observation was the effect of turbulence in the inverted cone aerator. As the air flow rate was increased from 0.5 litres per minute the reaction vessel was observed to note the first signs of excessive turbulence caused by the air flow that could cause some of the reduced ilmenite to be pushed higher up the cone, thereby becoming accessible to the pumping inlet line. Observations made during these experiments indicated that the turbulence did not become excessive until flow rates of 2.0 litres and above were used. The excessive turbulence at these higher flow rates caused reduced ilmenite to be passed through the pumping system, partially crushing the solids. This occurrence could explain why the rate of removal of iron jumped by some degree between the flow rate of 1.5 and 2.0 litres per minute (see Figure 7.2). The crushing of the particles could cause a breakdown in size and therefore a more exposed surface for oxygen to oxidise metallic iron.

As a result of the unwanted particle breakup the air flow rate needed to be held below 2.0 litres per minute. If the reaction were to finish within a 5.0 hour time frame the air flow rate needed to be 1.0 litre per minute or higher. These results left a choice between an air flow rate greater than or equal to 1.0 litre per minute but less than 2.0 litres per minute. The 1.0 and 1.5 litre per minute profiles in Figure 7.2 were near identical so that a flow rate of 1.0 litre per minute was chosen.

7.4 Aeration as a function of temperature

Evidence from previous tests carried out, and industry practice, have shown that the optimum temperature for a standard 0.1 M ammonium chloride aeration was between 70 to 80 degrees Celsius. As the inverted cone reactor had a better control of the temperature, (namely +/- 0.5 degrees), than the 5.0 litre reactor (+/- 5 degrees), experiments were carried out to establish a more accurate optimum temperature. With this more accurate temperature control the region of 70 to 80 degrees was investigated more thoroughly, while experiments were also conducted on temperatures outside the range to use as a comparison.

The temperature used in these experiments ranged from 30 to 87.5 degrees Celsius. These experiments used the same slurry composition and conditions as those described in section 7.2. These results are graphed in a graph in Figure 7.3.

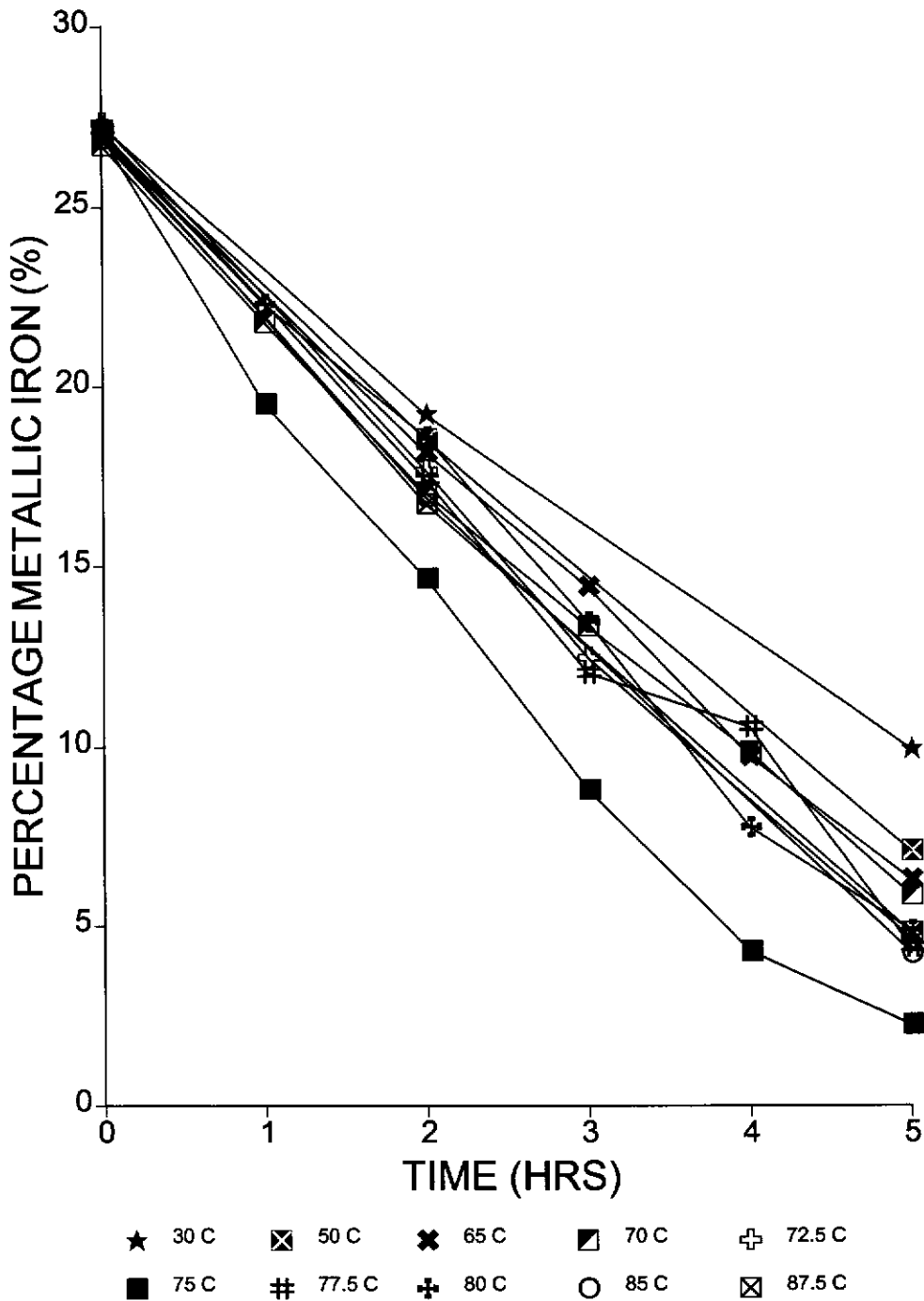


Figure 7.3: Graph of time vs percentage metallic iron of reduced ilmenite aerations at different temperatures using standard ammonium chloride slurries

Aeration at 75 degrees was the fastest, the reaction reaching a residual metallic iron level of 2.2 per cent after 5.0 hours, while the closest of the other slurries was still at 4.2 per cent after 5.0 hours. Temperatures of 70 degrees and below did not achieve a metallic iron level less than 5.8 per cent after the 5.0 hours of aeration while those temperatures above 75 degrees varied between 4.3 to 4.8 per cent residual metallic iron. The effect of temperature was seen more clearly when a graph of temperature vs the residual metallic iron content was constructed in Figure 7.4.

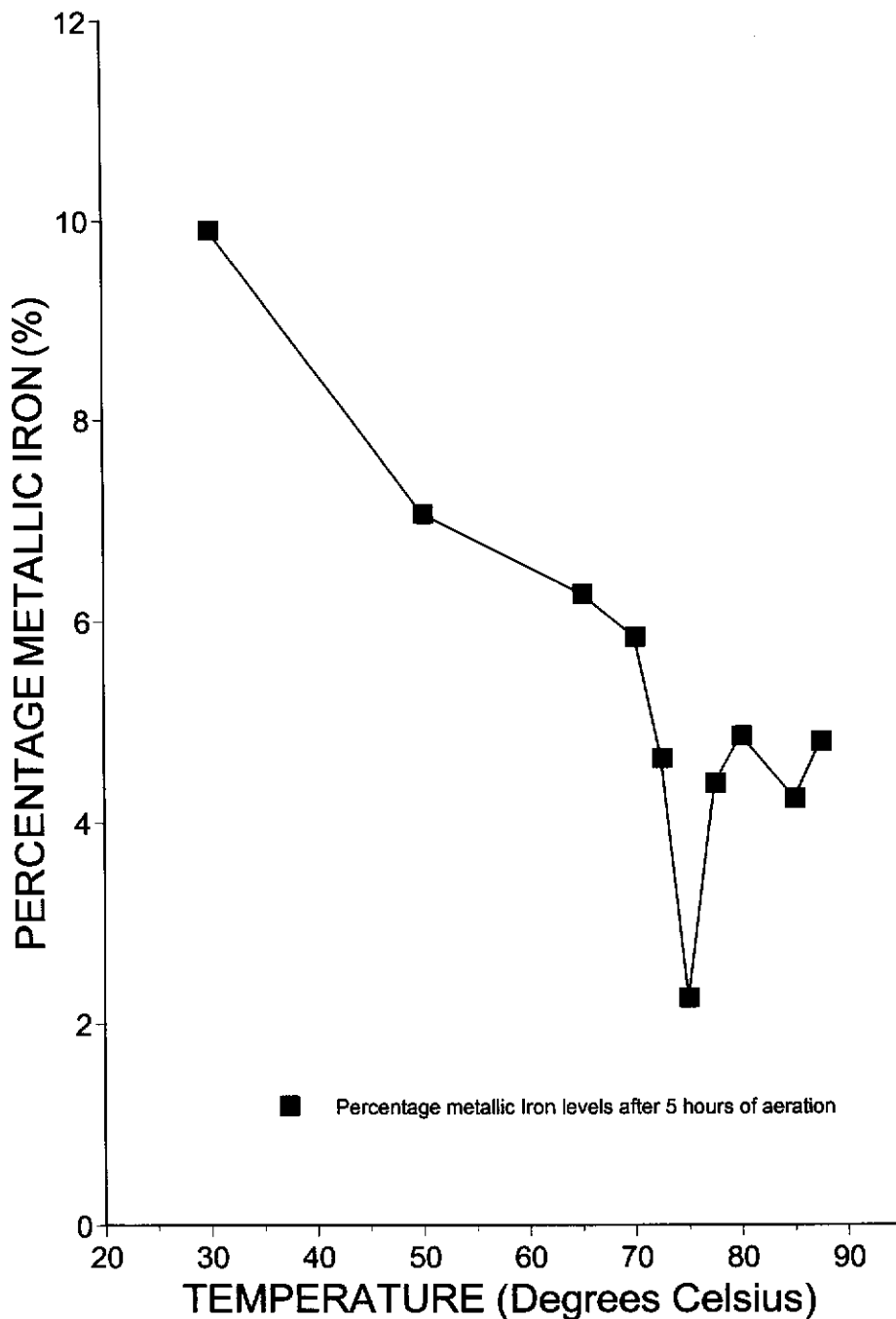


Figure 7.4: Graph of temperature vs residual metallic iron level (after 5.0 hours) for standard aerations run at temperatures between 30 and 90 degrees.

The effect of slight changes in temperature, just 2.5 degrees, was observed, in Figure 7.4. These small changes in temperature caused significant differences in the residual metallic iron level of the slurries. The lowest metallic iron values and greatest deviations occurred in the 70 to 80 degree range as was expected. The slurries operating at temperatures of 72.5, 77.5, 80 and 85 degrees resulted in similar residual metallic iron levels. At a temperature of 75 degrees the slurry was taken to a

residual metallic iron level of 2.2 per cent which was 2.0 per cent less than any other temperature. It was because of this clearly definable improvement that the temperature of 75 degrees Celsius was used in the following experiments. These results were repeated to confirm the effect of minor temperature changes in the inverted cone aerator.

7.5 Aeration as a function of oxygen partial pressure

It is known that variations in the oxygen partial pressure have a large effect on the aeration rates. This is due to the oxygen diffusion to the metallic iron, in the reduced ilmenite grains, being considered as the rate determining stage in the aeration. It was therefore thought that if there was an increase in the oxygen percentage in the aeration gas, more oxygen would dissolve and diffuse so leaching would proceed at a faster rate.

Four trials were prepared to be aerated at different oxygen partial pressures. These experiments used the same slurry composition and conditions as those described in section 7.2. Each aeration was aerated with 1.0 litre per minute of a gas mixture. The aeration gas varied in composition, the first was air (approximately 21 per cent oxygen), the second was pure oxygen, the third was pure nitrogen and the last was a 50 per cent oxygen and 50 per cent nitrogen mixture. These results are shown in Figure 7.5.

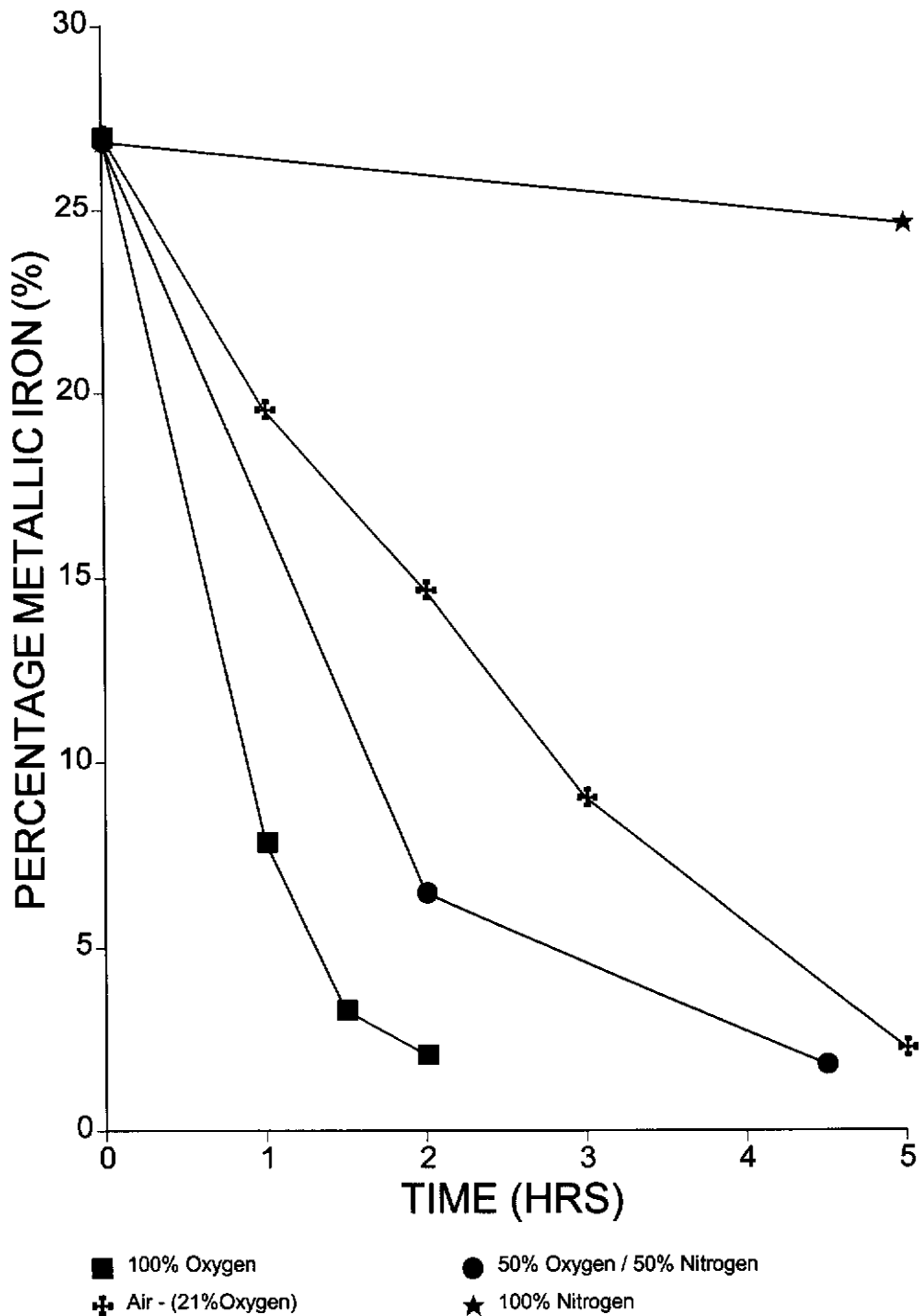


Figure 7.5: Graph of time vs percentage metallic iron for four standard ammonium chloride slurries that were aerated at different oxygen partial pressures.

The apparent trend in Figure 7.5 was that as oxygen partial pressure increased the rate of aeration increased with it. The pure nitrogen aeration, which was known to purge all the oxygen from the solution, showed very little removal of metallic iron at all over the 5.0 hours. This further confirmed that the oxygen was essential to increase the rate of reaction. This trend agreed with that found for oxygen partial

pressure for the 5.0 litre reactor (in section 3.7). Where the two aerators differed was the actual relationship between the oxygen partial pressure and the aeration rate. In Figure 7.6 a graph comparing the rate of aeration of each trial against the percentage of oxygen in the gas flow, was drawn.

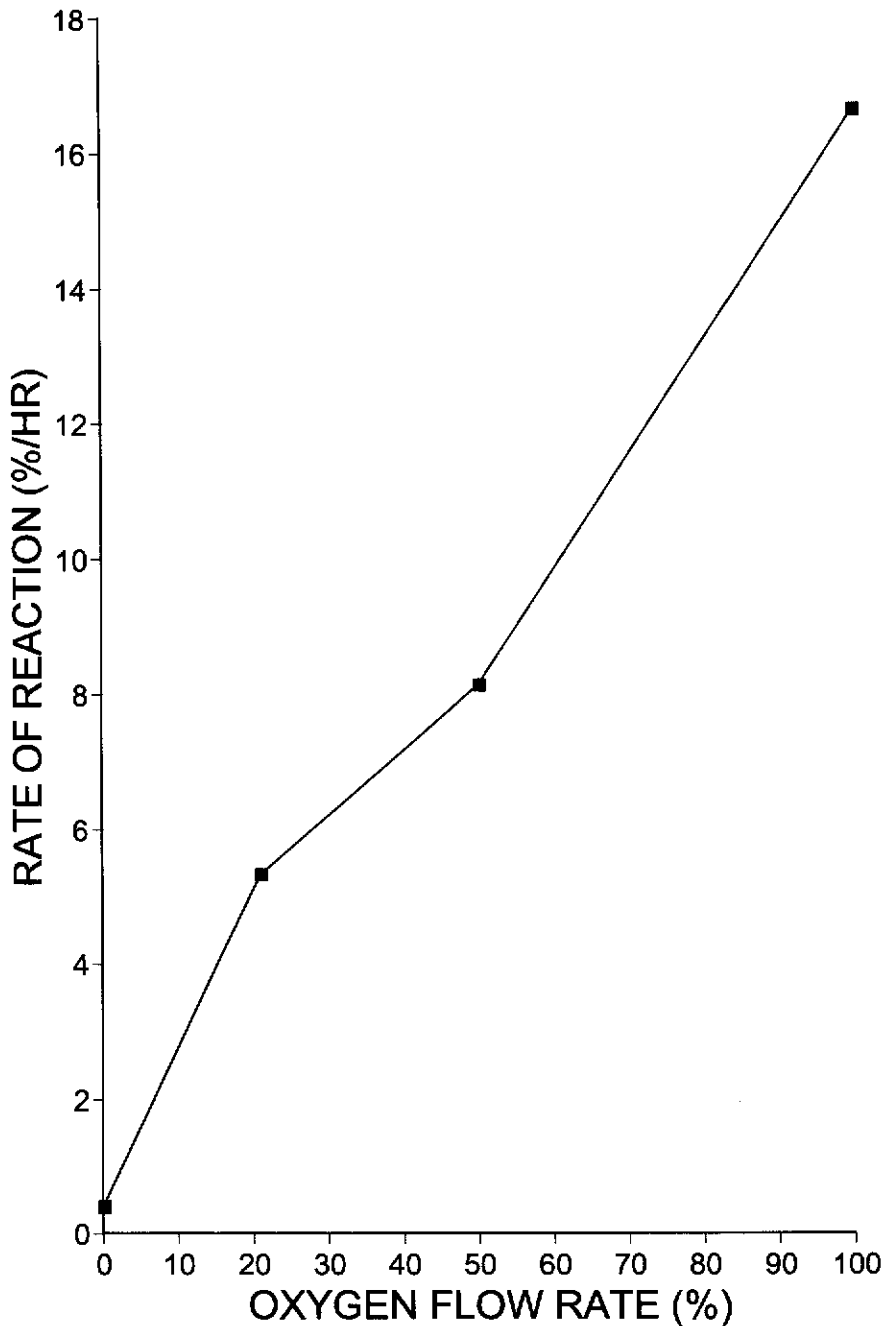


Figure 7.6: Graph of oxygen percentage vs rate of reaction for four separate trials.

The relationship, in Figure 7.6, is seen as almost linear, that is, that if the oxygen content of the gas was increased the aeration rate would increase in direct

proportion. This also indicated that the increase in the amount of oxygen does not have any adverse effects such as passivation. The 5.0 litre reactor also had these characteristics when the oxygen partial pressure was increased but there was not a linear relationship between the oxygen flow rate and the aeration rate. This was due to a lack of efficient mixing, making dissolution of the oxygen gas less efficient, giving less contact with the particles in the 5.0 litre reactor.

7.6 Citric acid / trisodium citrate mixture as a catalyst

7.6.1 Aeration with 20 grams of solids

From previous experiments using the 5.0 litre aerator, a 50 per cent citric acid 50 per cent trisodium citrate buffer was used in place of ammonium chloride as a catalyst to great effect. The use of this catalyst in conjunction with the inverted cone aerator was a valuable comparison between the two aerators.

These experiments used the same slurry composition and conditions as those described in section 7.2 with 0.05 M citric acid, 0.05 M trisodium citrate in place of the ammonium chloride. These results were placed in a graph in Figure 7.7.

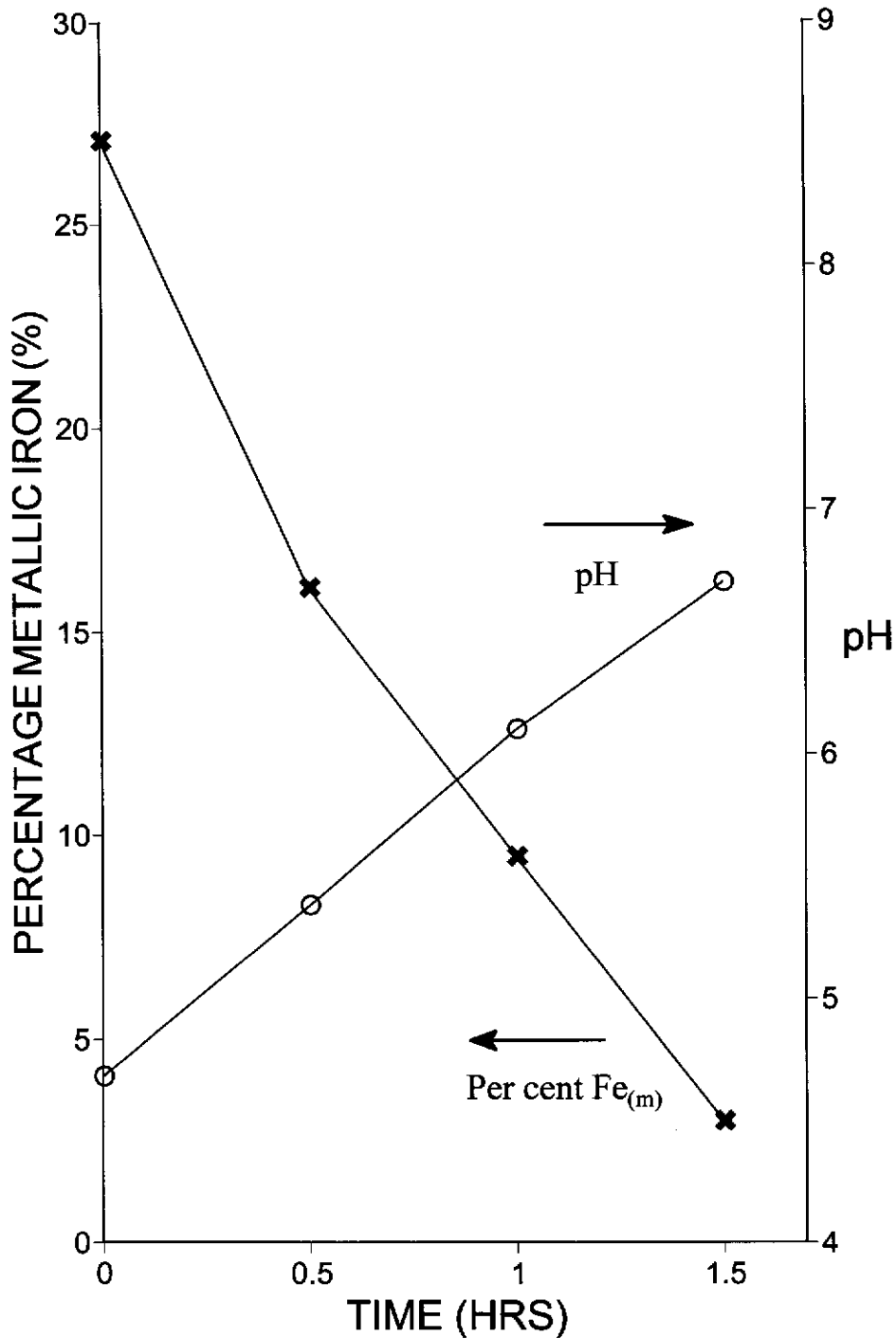


Figure 7.7: A combined graph of time vs percentage metallic iron and time vs pH for the aeration of 20 grams of reduced ilmenite with a citric acid / trisodium citrate catalyst and an air flow of 1.0 L / min

The data shown in Figure 7.7 indicated that the citric acid / trisodium citrate mixture proved to be an exceptional catalyst in the leaching of the metallic iron from the reduced ilmenite. The citrate buffer took only 1.5 hours to remove all the accessible metallic iron whereas the standard ammonium chloride took 5.0 hours to leach the same amount of iron as previously discussed in this chapter.

The pH profile shown in Figure 7.7 also indicated that the pH continually rose during the aeration. This indicated that the metallic iron was being acid leached while the citrate buffering system was equilibrating. This same type of profile was noted when similar experiments were conducted in the 5.0 litre in section 6.2. Where this experiment and pH profile in section 6.2 begin to differ was after the initial acid leaching. In this experiment all the iron was dissolved before the acid leach was completed; in section 6.2 the citrate ion started to facilitate the catalytic leaching of the metallic iron after the initial acid leaching.

7.6.2 Aeration with 100 grams of solids

To further investigate the leaching abilities of the citrate ions in the inverted cone aerator another experiment was conducted with the use of 100 grams of reduced ilmenite instead of the standard 20 grams, so that there would be a considerable excess of metallic iron that the initial acid leaching stage could not account for. The experiment was run in the same manner, with the exception of the amount of reduced ilmenite added to the inverted cone aerator. The results of this aeration is shown graphically in Figure 7.8.

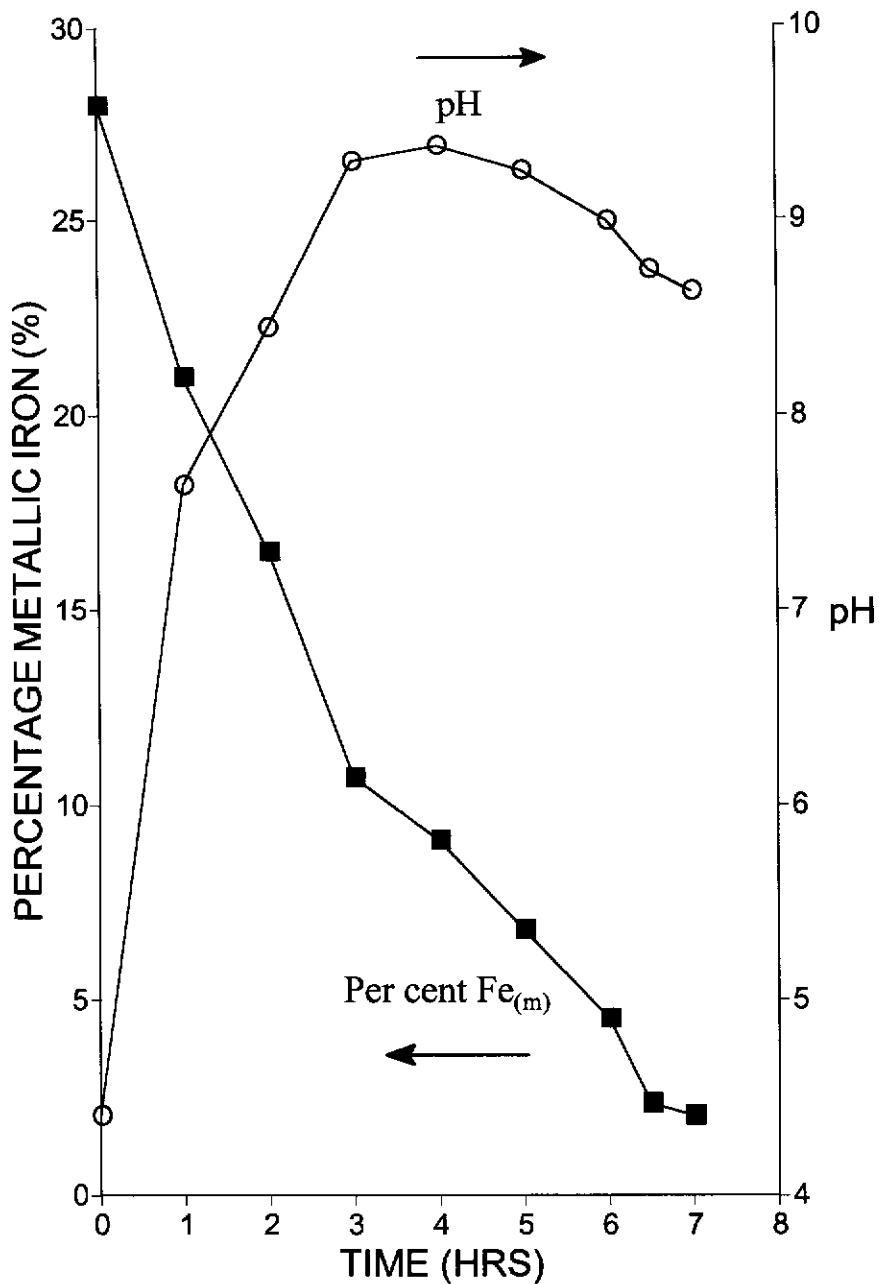


Figure 7.8: A combined graph of time vs percentage metallic iron and time vs pH for the aeration of 100 grams of reduced ilmenite with a citric acid / trisodium citrate catalyst

Figure 7.8 has shown that the citrate ion buffer did succeed in completing the aeration of the 100 gram sample in a 7.0 hour period. The similar test conducted with ammonium chloride managed to only reach a residual metallic iron level of 14 per cent, which was about half of the original content. These results only further show that the citrate ion buffer was a superior catalyst under these conditions. The other point worthy of note was the 2 apparent rates of reaction in Figure 7.8, the faster rate occurred between in the first 2.5 hours of aeration then the rate slowed to some

extent for the rest of the aeration. The change in rate occurred at the same time that the pH stopped rising. This indicated a change in the leaching mechanism from predominantly acid leaching to citrate-iron complexation. The minor fall in pH after this point was attributed to the precipitation of iron oxides that consumes hydroxide ions.

The pH profile which was also shown in Figure 7.8 demonstrates a very similar profile to the profile for the citrate ion buffer in section 6.2. This profile indicated an initial rise in pH due to the consumption of acid followed by a constant pH in the later part of the aeration indicating the catalytic effect of the citrate buffer.

In terms of a comparison between the two aerators these experiments have shown that the inverted cone needs to work with a higher charge to observe true behaviour of the slurry if there were several changes to the mechanism of leaching expected. In this particular case the higher charge managed to show both the acid leaching and the catalytic leaching while the lower charge only showed the acid leaching before most of the metallic iron was removed.

7.7 Ethylene diammonium chloride as a catalyst

The last catalyst to be examined in the inverted cone aerator was ethylene diammonium chloride. The catalyst was investigated because of its similarities to ammonium chloride and therefore its different aeration mechanism to the citrate ion buffer system.

These experiments used the same slurry contents and composition as those described in section 7.2 with 13.3 grams of ethylene diammonium chloride in place of the ammonium chloride. These results were placed in a graph in Figure 7.9.

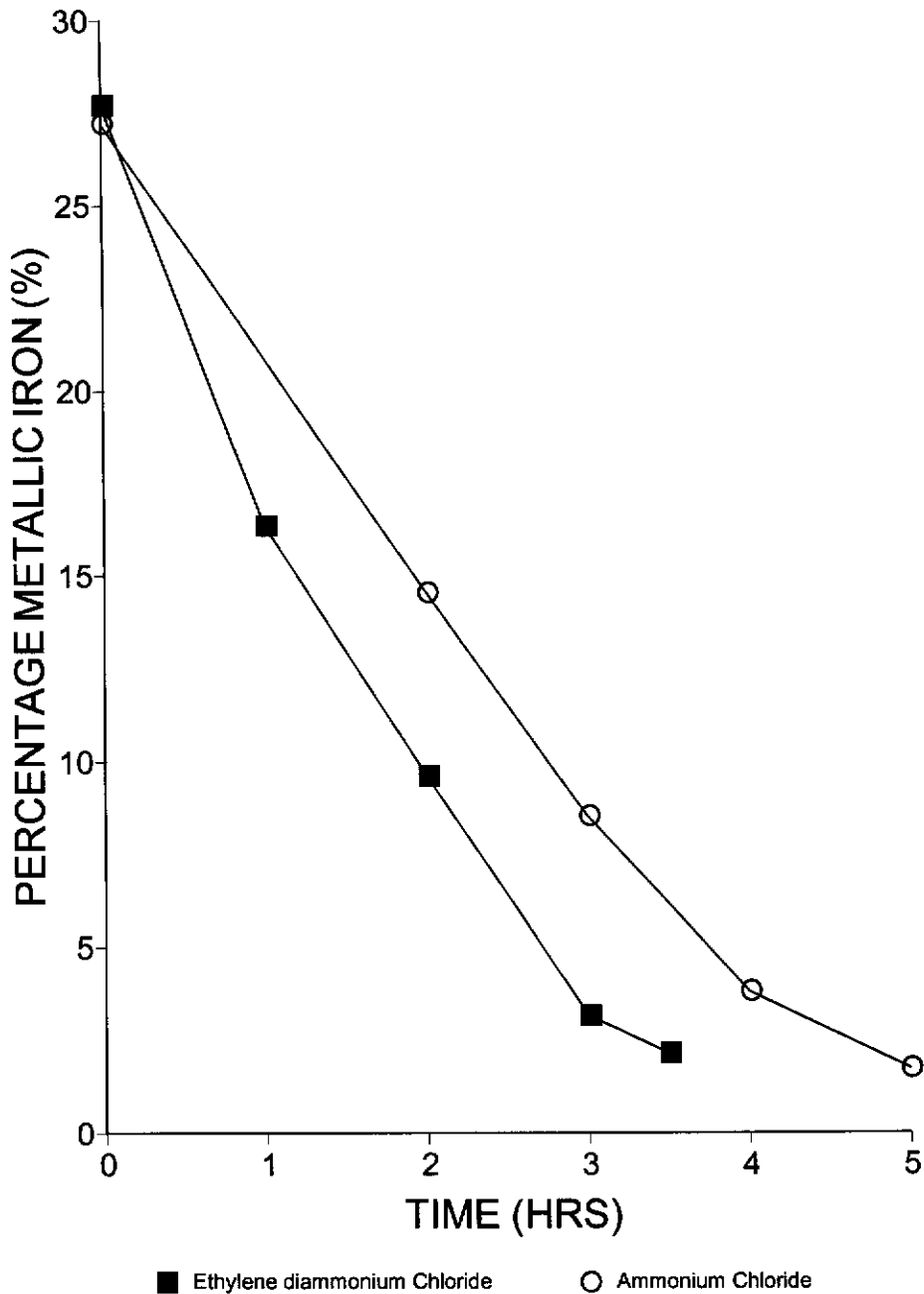


Figure 7.9: Graph of time vs percentage metallic iron comparing an ethylene diammonium chloride slurry to an ammonium chloride slurry

In comparison to ammonium chloride, the ethylene diammonium chloride catalyst has shown a faster rate of aeration in Figure 7.9. The ethylene diammonium chloride slurry completed the aeration in 3.5 hours while the standard ammonium chloride slurry took 5.0 hours to complete aeration. The increase in the aeration rate could be attributed to two reasons. These include the two active ammonium groups available for complexation in the ethylene diammonium chloride compared to one

group in ammonium chloride. Secondly the pK_a values of 7.56 and 10.71 (Lide, 1996) for ethylene diammonium chloride which are compared to 9.25 for ammonium chloride (Stark and Wallace, 1976). These values indicate that the ethylene diammonium chloride will catalyse the leaching of metallic iron to a greater extent, than ammonium chloride, as it has a lower initial pK_a value as was discussed in Chapter Five.

7.8 Conclusions

The inverted cone aerator has shown that the results obtained from experiments with ammonium chloride match those results from the 5.0 litre aerator. These results include the optimum aeration temperature of 75 degrees and 100 per cent oxygen gas flow to reach the highest aeration rate.

The two aerators differ in that the inverted cone can be adversely effected by increasing the gas flow rate past 1.0 litre per minute due to turbulence while the 5.0 litre aerator was not affected in this manner. The inverted cone aerator also has a much more precise control on the temperature so that the effect of temperature could be monitored more closely. The inverted cone can aerate a smaller amount of sample faster than the other aerator but risks missing changes in the leaching mechanism if more than one mechanism is possible in a system, as was shown with the citrate ion buffer.

If the inverted cone is used with an known single mechanism system such as ethylene diammonium chloride, experiments can be done faster and with less sample than the 5.0 litre aerator.

Chapter Eight

Reduced ilmenite from alternative sources

8.1 Introduction

All experimental work described in this thesis up to this point has used one supplier of similar reduced ilmenite samples (S1) to obtain a consistent feedstock. The purpose of using samples from a single batch was to ensure that all the experiments could be compared with each other. As a result of this, any conclusions thus far made may only be in regards to that one batch. This chapter looks at assessing some other reduced ilmenite samples by repeating a certain number of the more successful experiments with the different types of reduced ilmenite.

The graphs in section 8.2 are presented as the results of aerations with 4 different catalyst systems for each type of reduced ilmenite. They are presented in such a manner to avoid overlapping and to show a clear trend between the type of reduced ilmenite and the order of aeration for each of the catalysts.

8.2 The influence of using reduced ilmenite from different producers

As the characteristics of reduced ilmenites vary depending on the consistency of the original ilmenite mined in a given area and the particular reduction conditions of the kiln used, it must be considered whether different samples of reduced ilmenite may aerate at different rates or to different extents than others.

8.2.1 Comparison between the different reduced ilmenite under four different aeration conditions against a standard

To examine if various reduced ilmenites did affect the aeration rates, three new samples were obtained from 3 different plants in Western Australia. These 3 samples had slightly different metallic iron percentages of 29.5 (S2), 27.9 (S3) and 24.5 (S4) per cent compared to the 27.5 per cent (S1) of the standard sample used for all the other experiments. As a consequence of the difference in the metallic iron values, probable different surface areas and probable different amounts of metallic species bound into the structure that could not be removed through normal aeration, results from different reduced ilmenites were not expected to be identical. To overcome this restriction, each of the 3 samples was aerated under 4 different sets of conditions. These 4 aerations were then graphed and compared to the results of the same 4 aerations using sample S1. The four aerations chosen for this study were; ammonium chloride catalyst (0.093 M) aerated with air, ammonium chloride catalyst (0.093 M) aerated with oxygen, ethylenediammonium chloride (0.0698 M) aerated with air and citric acid (0.05 M) / trisodium citrate (0.05 M) catalyst aerated with air.

The results of these 4 aerations that were conducted with the original sample (S1) were redrawn in Figure 8.1.

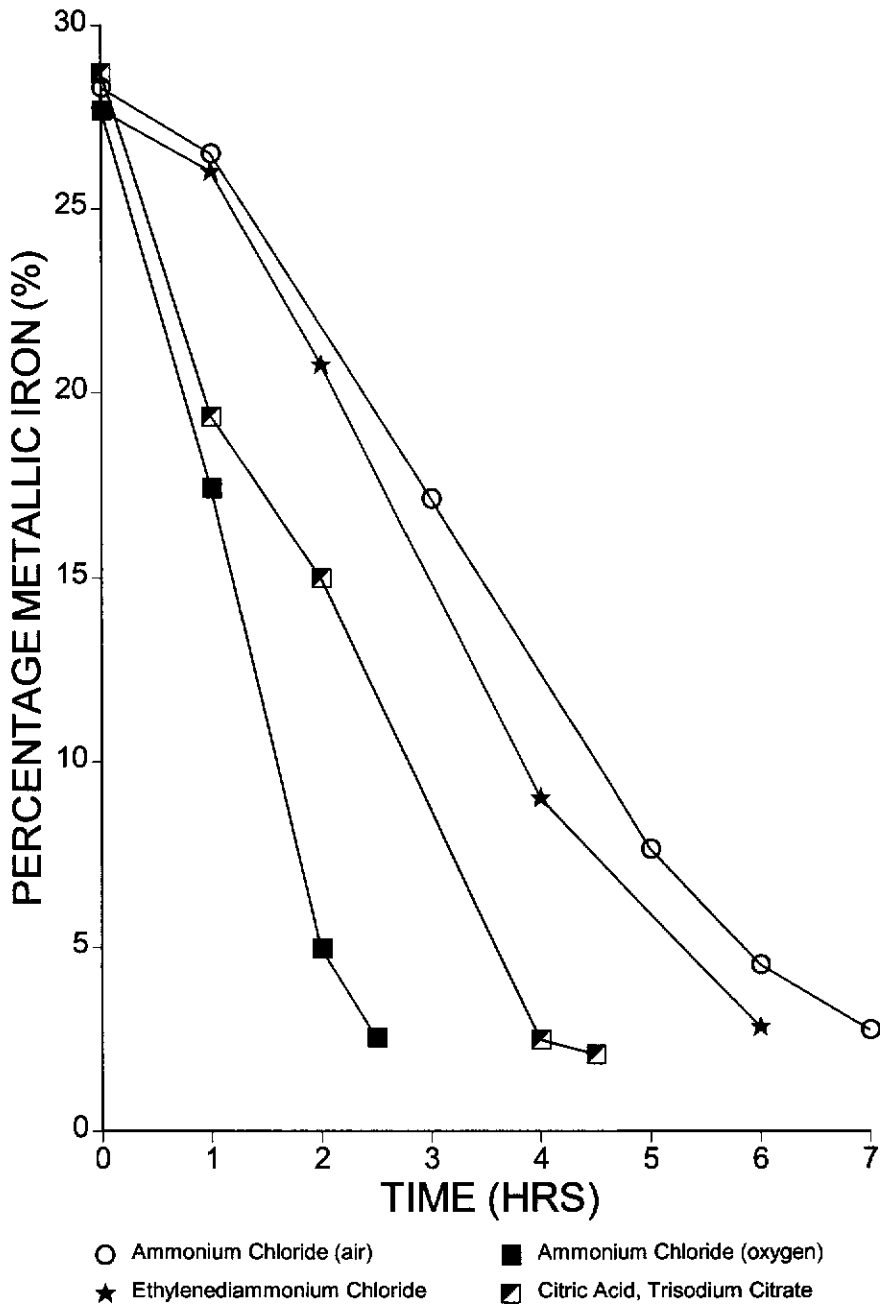


Figure 8.1: Four standard slurries using ammonium chloride with air, ethylenediammonium chloride, 0.05 M citric acid / 0.05 M sodium citrate and ammonium chloride with oxygen as aeration catalysts with reduced ilmenite sample S1.

Using the results in Figure 8.1 as a standard basis for comparison, further aerations were completed with the sample labelled S2. The results of the aerations with reduced ilmenite S2 were graphed in Figure 8.2.

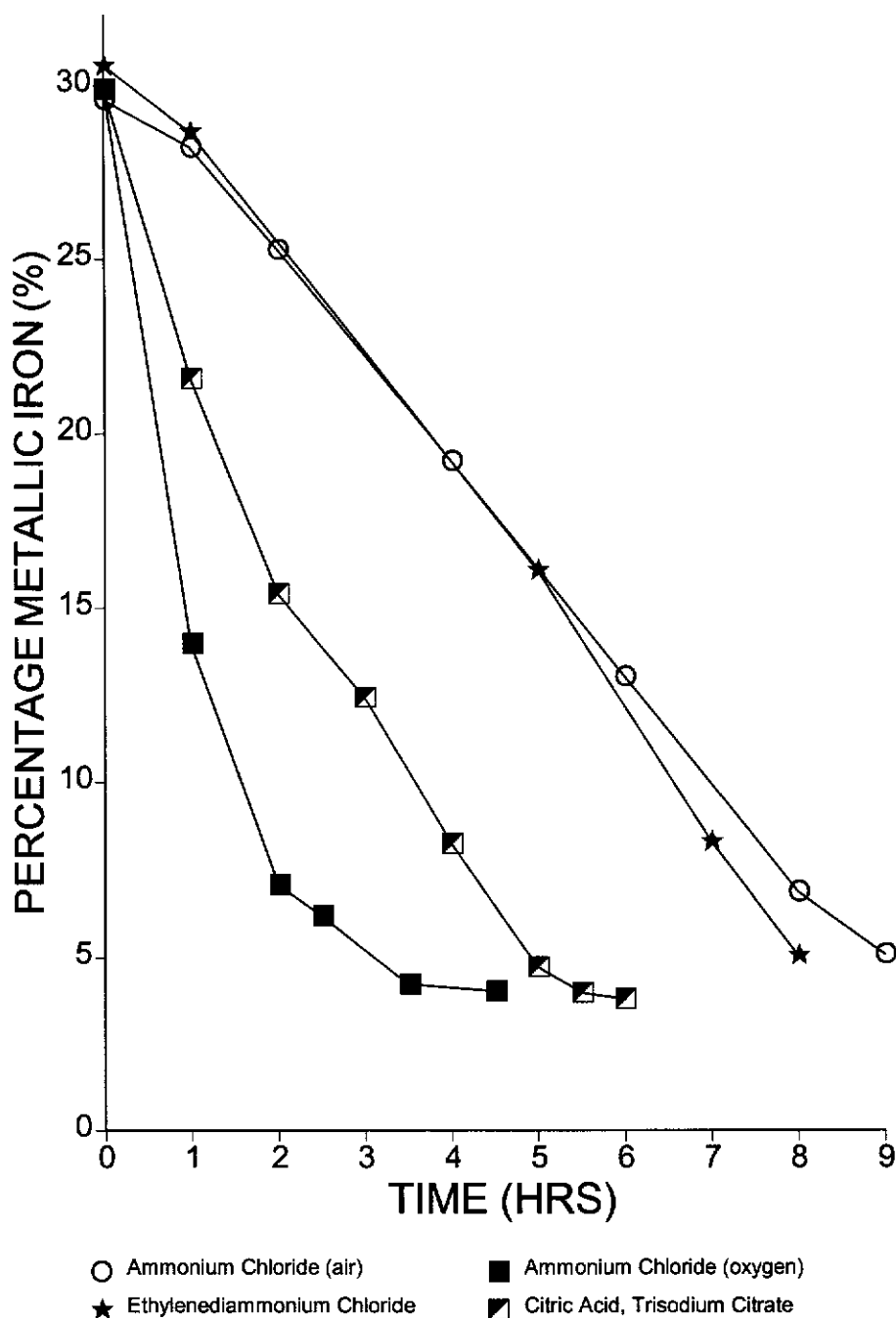


Figure 8.2: Four standard slurries using ammonium chloride with air, ethylenediammonium chloride, 0.05 M citric acid / 0.05 M sodium citrate and ammonium chloride with oxygen as aeration catalysts with reduced ilmenite sample S2.

From a comparison of the results found in Figure 8.1 and Figure 8.2 the relative leaching rate for each of the leaching conditions was found to be in the same order. This means the ammonium chloride aeration, with air, took the longest of the 4 in both cases. The ethylenediammonium chloride aeration rate was 1.0 hour faster than the ammonium chloride aeration (air) with both types of

reduced ilmenite. The use of the 0.05 M citric acid / 0.05 M sodium citrate as a catalyst was approximately 1.5 hours faster than the ethylenediammonium chloride aeration in both cases. Finally the aeration involving the ammonium chloride catalyst with oxygen as the aeration gas was the fastest of all the aeration, being approximately 1.5 hours faster than the next fastest aeration.

The major difference between the 2 types of reduced ilmenites is seen in a comparison of aeration times. Although there may be similar relativities between the individual aeration times, eg the difference between the ethylenediammonium chloride and the ammonium chloride (air) aeration of 1.0 hour, the aeration of S2 took longer to complete for each catalyst. The other important factor was the difference in the residual metallic iron levels, for S1 the residual level was approximately 2.7 per cent while S2 had a residual level of approximately 5.1 per cent. Most of these differences can be attributed to S2 having a higher initial metallic iron level to begin with. Of course, each of the reduced ilmenites originates from a different area and it is likely to have different structural porosity, differing minor elemental composition and different amounts of passivating films formed on the reduced ilmenite surface (Marinovich, 1997).

A further comparison was made between sample S3 and the original sample S1 by comparing the graph in Figure 8.1 to the results for the aeration of S3 in Figure 8.3.

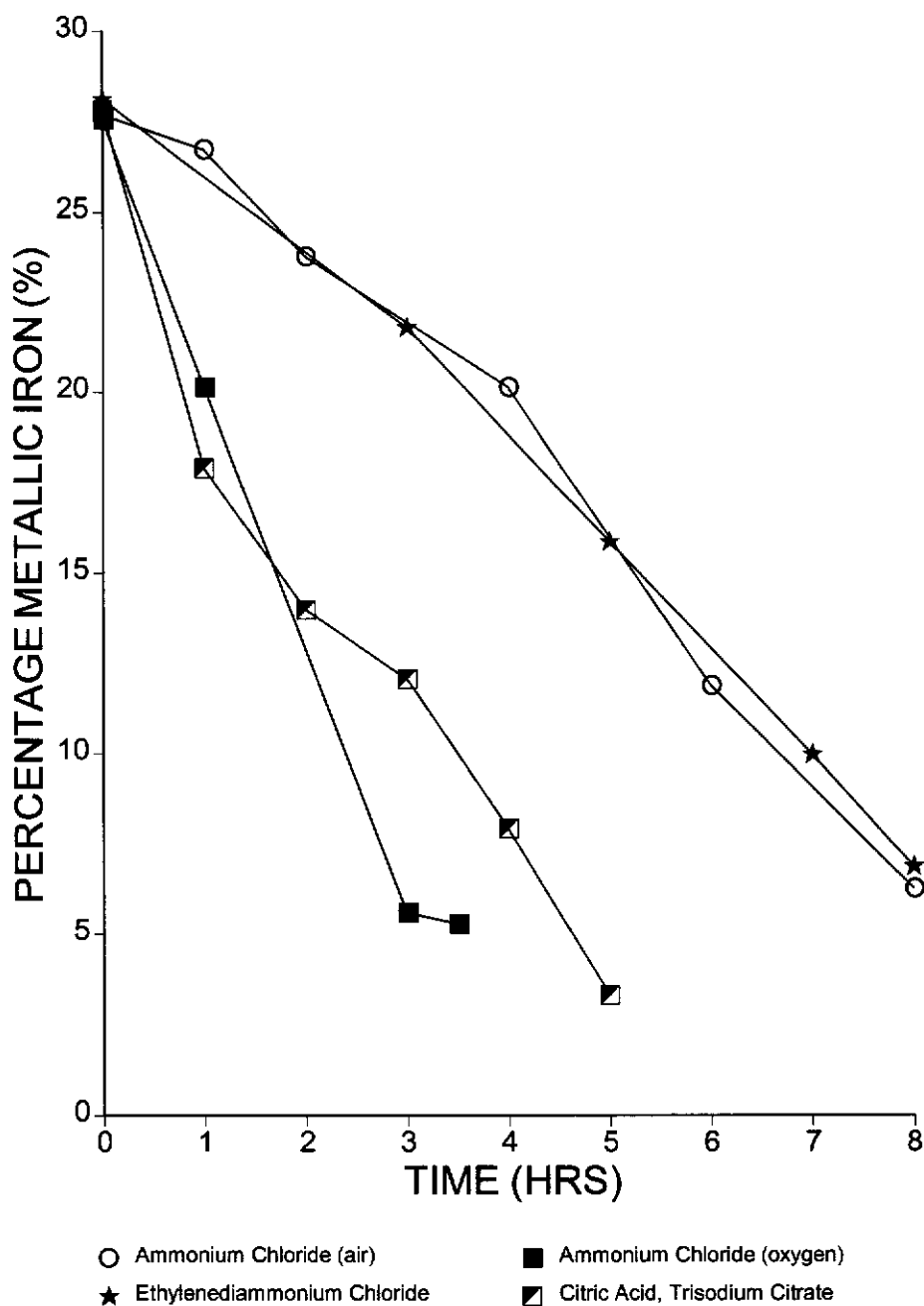


Figure 8.3: Four standard slurries using ammonium chloride with air, ethylenediammonium chloride, 0.05 M citric acid / 0.05 M sodium citrate and ammonium chloride with oxygen as aeration catalysts with reduced ilmenite sample S3.

The order of effectiveness of the aerations of sample S3 was found to decrease from ammonium chloride with oxygen, followed by the 0.05 M citric acid / 0.05 M sodium citrate, followed by the ethylenediammonium chloride and the ammonium chloride aeration with air being equally the slowest. The obvious difference between the aeration catalysts for reduced ilmenites S1 and S3 is that

the ethylenediammonium chloride leached S1 faster than the ammonium chloride (air) while with S3 they both leached at approximately the same rate. There was also no apparent correlation between the time differences for each of the aeration catalysts while using S3 and S1. The last difference between the two samples was the residual metallic iron levels. S1 reached an approximate residual level of 2.7 per cent iron in each aeration whereas S3 could manage to reach an approximate level of 3.5 to 6.2 per cent.

The final comparison between sample S4 and the original sample S1 was made by inspection of the graphs in Figure 8.4 and 8.1 for the respective aerations of both samples.

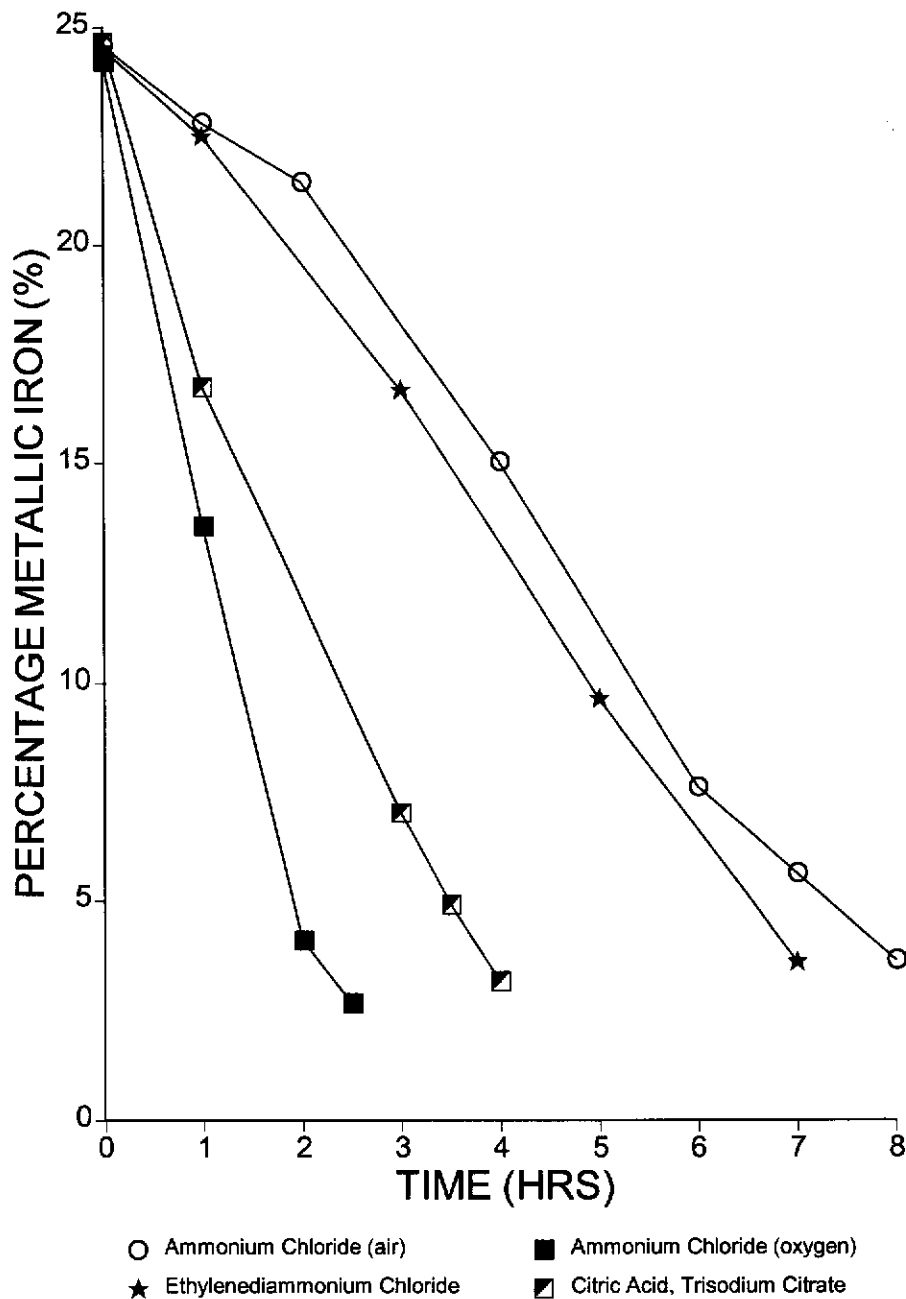


Figure 8.4: Four standard slurries using ammonium chloride with air, ethylenediammonium chloride, 0.05 M citric acid / 0.05 M sodium citrate and ammonium chloride with oxygen as aeration catalysts with reduced ilmenite sample S4.

The order of effectiveness of the various catalysts for both samples S1 and S4 of reduced ilmenite was obviously the same. That is, the ammonium chloride aeration with oxygen was the fastest, followed by the 0.05 M citric acid / 0.05 M sodium citrate aeration, then the ethylenediammonium chloride aeration and finally the slowest was the ammonium chloride aeration with air. There were

also similar time differences between the individual aerations for each sample. In all cases each of the catalysts reached a minimum level of metallic iron in the reduced ilmenites in similar times. When ammonium chloride (oxygen) was used to aerate both samples the leaching required 2.5 hours for each sample to reach the same minimum metallic iron level. In the case of the 0.05 M citric acid / 0.05 M sodium citrate used as catalysts there was only 0.5 hours separating the leaching times for samples S1 and S4. The only significant difference between these aeration trials was the level of residual metallic iron left in the upgraded reduced ilmenite structure at the completion of aeration. The S1 sample contained a residual level of 2.7 per cent while the sample S4 contained a residual level of 3.6 per cent. This difference in the residual iron level could be attributed several factors: S4 may have a slightly less porous structure than S1 thereby allowing more access to the grains of S1 and therefore a faster leaching time, or sample S4 simply having more bound iron could have taken longer to leach, or S4 may have a more effective passivating iron oxide film than S1.

8.2.2 Direct comparison between the four different reduced ilmenite under four different sets of aeration conditions

To further examine and compare these different reduced ilmenite samples the individual trials for each set of leaching conditions were grouped together. This enabled a direct comparison between all of the reduced ilmenite samples. The first trial, ammonium chloride catalyst with an air gas flow, is shown in Figure 8.5.

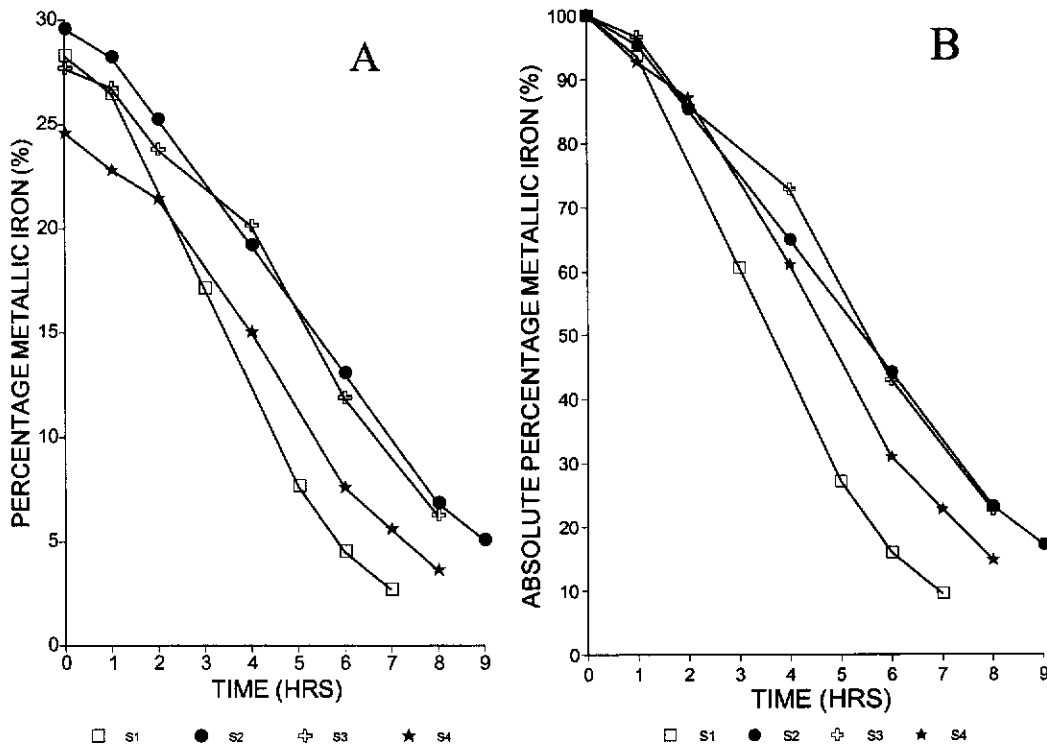


Figure 8.5: Four different reduced ilmenite samples all aerated with an ammonium chloride catalyst with an air gas flow. Graph A shows percentage metallic iron vs time While graph B shows absolute percentage metallic iron vs time.

The purpose of redrawing graph A in Figure 8.5 in terms of absolute percentage metallic iron was to allow for the fact that the different reduced ilmenites have a different starting content of metallic iron. This representation is one way to normalise the initial metallic iron contents so any differences observed can be attributed to variations in the individual reduced ilmenites aeration characteristics. It must be considered, however, that perhaps a fixed rate of removal of metallic iron (eg grams per hour) may result rather than a constant relative rate. The following three Figures show the comparison of the reduced ilmenites using citric acid / sodium citrate, ethylenediammonium chloride and ammonium chloride with an oxygen gas flow respectively.

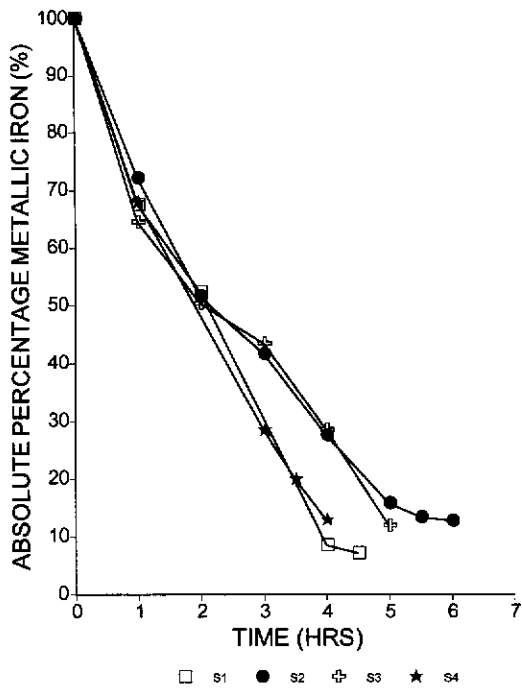


Figure 8.6: Four different reduced ilmenite samples all aerated with a 0.05 M citric acid / 0.05 M sodium citrate catalyst with an air gas flow

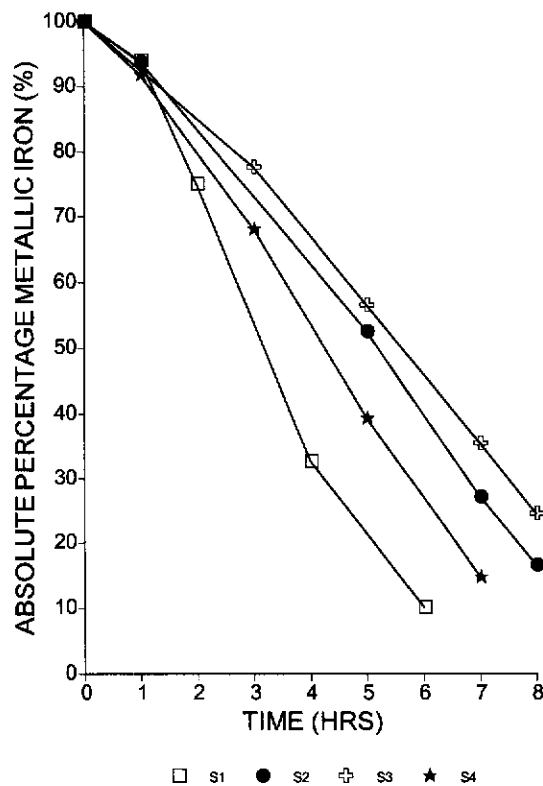


Figure 8.7: Four different reduced ilmenite samples all aerated with an ethylene diammonium chloride catalyst with an air gas flow

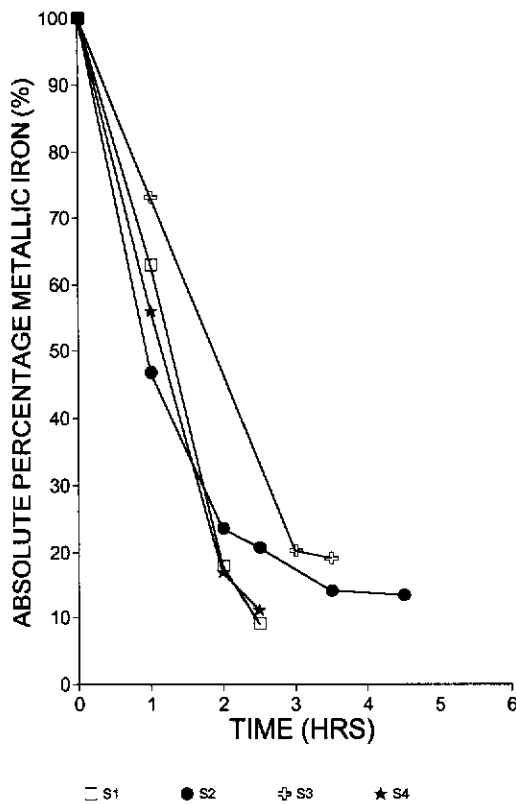


Figure 8.8: Four different reduced ilmenite samples all aerated with an ammonium chloride catalyst with an oxygen gas flow

The overall trend found in Figures 8.5 to 8.8 shows that in every case sample S1 had the fastest leaching of metallic iron. In two of the experiments, sample S4 had very similar leaching rates to sample S1 while in the other cases it required an additional hour, after sample S1 had finished, to remove all the available metallic iron from the S4 matrix. The two slower reduced ilmenite samples, S2 and S3, usually required 1.5 to 2 hours more leaching than S1 to complete their aerations.

8.3 Conclusions

When comparisons were made between different samples of reduced ilmenite it was found that the use of different reduced ilmenites could change the aeration times significantly. These same tests also showed that for almost all

cases the order of relative leaching rates for given catalysts and conditions was the same.

The major cause of the differences experienced in the aeration rate for the different samples of reduced ilmenite was likely the different surface characteristics of each sample. The factors causing variations in the surface characteristics were differing thicknesses of passivating iron oxide films created and possibly levels of porosity in the reduced ilmenite. These factors therefore controlled the access to the metallic iron for leaching.

From these findings it is reasonable to assume that any general conclusions made on the effectiveness of a catalytic system using S1 should apply to reduced ilmenite from other sources, although there may be some slight differences in the specific leaching rates for the different reduced ilmenite samples.

Chapter Nine

The products from acid washing of reduced ilmenite after aeration

9.1 Introduction

The main concern of this thesis has been centred around the ability of a catalysed aeration to remove metallic iron from the reduced ilmenite grain in the fastest and most complete manner possible. In this chapter the final acid wash in the processing route of the upgraded ilmenite will be examined to ensure the use of these different catalysts has left the upgraded ilmenite in a state acceptable for acid washing.

The purpose of the acid wash is to remove any remaining iron, in either metallic or oxide form, any accessible manganese, and any other acid soluble impurities. As acid is consumed in this stage it is desirable to only treat upgraded ilmenite with as much of the impurities removed as possible during the aeration step.

From all of the previous work carried out in this thesis a selection of aeration catalysts that aerate the fastest and most completely was chosen to find out if they could then produce the pure synthetic rutile after the acid leaching.

9.2 Removal of impurities from the upgraded ilmenite by acid leaching

A series of acid digests was completed on six products from previous aerations. The six different aerations chosen involved the use of different catalysts or different gas flows. The aeration products were all produced using a slurry of 300 grams of reduced ilmenite, 1.8 litres of water and held at a temperature between 70 and 80 degrees Celsius. The six aerations were completed by using:

- (1), 0.093 M ammonium chloride with an air gas flow,
- (2), 0.093 M ammonium chloride with a oxygen gas flow,
- (3), 0.093 M p-nitroaniline hydrochloride with an air gas flow,
- (4), 0.068 M ethylenediammonium chloride with an air gas flow,
- (5), 0.068 M ethylenediammonium chloride with a oxygen gas flow and
- (6), 0.05 M trisodium citrate with 0.05 M citric acid and an air gas flow.

These six experiments were chosen for their ability to complete the aeration of the reduced ilmenite sample in a 7.0 hour period or less. The listed order of the experiments is only an indication of the order they have previously been examined in this thesis. From each of these aeration products two 10.0 gram samples were split out and added to separate conical flasks. To one of these conical flasks 50 millilitres of 3.0 M hydrochloric acid were added and 50 millilitres of 3.0 M sulfuric acid added to the other flask. These 12 flasks were then stirred and heated at a temperature of 65 degrees for 2.0 hours. The resulting solids were separated from the liquor, washed and dried. The products plus a head sample from each aeration were then analysed for their metallic iron, total iron and manganese content.

9.3 Iron removal by acid leaching

For all the aeration products the analysis of the total iron and metallic iron contents were conducted by two separate titrimetric methods. The results of these analyses are shown in Table 9.1 and Table 9.2.

Table 9.1: The metallic iron (Fe(m)) and total iron (Fe(t)) content of six aerated samples before and after acid leaching with hydrochloric acid.

Sample No		Head	Hydrochloric Acid Leach
(1)	Fe(m)	0.89%	0.06%
	Fe(t)	5.85%	2.36%
(2)	Fe(m)	0.18%	0.17%
	Fe(t)	6.03%	2.35%
(3)	Fe(m)	0.36%	0.28%
	Fe(t)	3.59%	2.41%
(4)	Fe(m)	0.17%	0.18%
	Fe(t)	4.21%	2.73%
(5)	Fe(m)	0.12%	0.46%
	Fe(t)	3.08%	2.43%
(6)	Fe(m)	0.54%	0.36%
	Fe(t)	3.83%	2.36%

Of the samples that underwent acid washing with hydrochloric acid the experiment number 1 had clearly shown the best removal of iron from its matrix. This sample was aerated with air, in a standard ammonium chloride concentration. The other samples that had similar iron removal were aerated by ethylenediammonium hydrochloride (experiment 4), with air, and the ammonium chloride test with oxygen (experiment 2). Experiments 3, 5 and 6 were found to give a product containing considerably more iron and therefore were considered to have failed in comparison to the ammonium chloride catalyst used in industry.

Table 9.2: The metallic iron (Fe(m)) and total iron (Fe(t)) content of six aerated samples before and after acid leaching with sulfuric acid.

Sample No		Head	Sulfuric Acid Leach
(1)	Fe(m)	0.89%	0.30%
	Fe(t)	5.85%	2.41%
(2)	Fe(m)	0.18%	0.59%
	Fe(t)	6.03%	2.46%
(3)	Fe(m)	0.36%	0.41%
	Fe(t)	3.59%	2.66%
(4)	Fe(m)	0.17%	0.17%
	Fe(t)	4.21%	2.34%
(5)	Fe(m)	0.12%	0.06%
	Fe(t)	3.08%	2.64%
(6)	Fe(m)	0.54%	0.43%
	Fe(t)	3.83%	2.16%

Of the samples that underwent acid washing with sulfuric acid the experiment number 5 had clearly shown the best removal of iron from the matrix. This sample was catalysed by ethylenediammonium chloride and was aerated with oxygen. Other experiments to reach similar iron levels were aerated in ethylenediammonium chloride with an air flow (experiment 4) and in ammonium chloride with an air flow (experiment 1). As the residual iron contents from the other three tests were considerably higher they were regarded as unsatisfactory leaching.

Of the two acids hydrochloric acid appeared to have slightly better iron removal characteristics than sulfuric acid because of the lower levels of total and metallic iron in most of the samples.

9.4 Manganese removal by acid leaching

The removal of the manganese impurities from the upgraded ilmenite is important because a large amount of manganese in the synthetic rutile product makes it extremely undesirable as a feedstock to the pigment grade conversion process. As most of the manganese was in the form of manganese sulfide most of the available manganese should be removed by acid leaching (Rolfe, 1973). The

presence of manganese in the acid leached product was analysed by fusing sodium borate with each of the samples. The borate glass was then dissolved and analysed against standards with a ICP spectrometer. The results are shown in Table 9.3 and Table 9.4.

Table 9.3: The manganese (Mn) content of six aerated samples before and after acid leaching with hydrochloric acid.

Sample No	Head	Hydrochloric Acid Leach
(1) Mn	10300 ppm	7240 ppm
(2) Mn	9330 ppm	6680 ppm
(3) Mn	10700 ppm	7320 ppm
(4) Mn	9150 ppm	7440 ppm
(5) Mn	9070 ppm	6940 ppm
(6) Mn	10600 ppm	6860 ppm

Of the samples that underwent acid washing with hydrochloric acid (Table 9.3) the one that had the most effective removal of manganese was experiment 6. This sample was aerated in a citric acid / trisodium citrate catalyst with an air gas flow. The greatest removal of manganese achieved after experiment 6 was experiment 3, which was aerated in p-nitroaniline hydrochloride, and then experiment 1, which was aerated in ammonium chloride with an air gas flow. The other three experiments had significantly less amounts of manganese removed.

The actual lowest residual manganese concentration, from the hydrochloric acid leaching, was experiment 2, followed by experiment 6 and then experiment 5. These results are an indication of the combination of the catalysed aeration followed by the acid leaching. So although experiment 2 may not have had the most efficient manganese leaching in the hydrochloric acid, sufficient amounts of manganese were removed during the catalysed aeration. This is particularly important in light of the fact that experiments 2 and 5 were only aerated for 2.5 and 2 hours respectively compared with the other experiments that had in excess of 6 hours aeration.

Table 9.4: The manganese (Mn) content of six aerated samples before and after acid leaching with sulfuric acid.

Sample No	Head	Sulfuric Acid Leach
(1) Mn	10300 ppm	7140 ppm
(2) Mn	9330 ppm	7260 ppm
(3) Mn	10700 ppm	6680 ppm
(4) Mn	9150 ppm	6840 ppm
(5) Mn	9070 ppm	6060 ppm
(6) Mn	10600 ppm	6300 ppm

Of the experiments that underwent acid washing with sulfuric acid (Table 9.4) the one with the most effective removal of manganese from the acid leach was experiment 6. This particular slurry employed the use of a citric acid / trisodium citrate as the catalyst with an air gas flow. This sample was followed in effectiveness by experiments 3, the p-nitroaniline hydrochloride catalyst and then 1, the ammonium chloride catalyst, with an air gas flow.

The better acid for removal of manganese was found to be sulfuric acid because of the higher amounts of manganese removed in five out of the six experiments when compared to the hydrochloric acid results.

9.5 Conclusions

As acid washing is currently used in the Becher process any data collected on acid leaching in these conditions need to be compared to the acid leach of a sample that has been aerated by ammonium chloride with an air gas flow, representing the current industry practice (experiment 1). In the case of iron removal the standard ammonium chloride aeration sample gave the best results but the results for the ethylenediammonium chloride aeration with an air gas flow rate (experiment 4) and the aeration with ammonium chloride with oxygen as the gas flow (experiment 2) are very close and must be considered to have a similar response to washing with hydrochloric acid. While using sulfuric acid more iron was removed from an ethylenediammonium chloride aeration sample than from the standard ammonium chloride aeration sample.

Again, using the standard ammonium chloride aeration sample as the bench mark for manganese removal during hydrochloric acid leaching, it has been demonstrated that the use of ammonium chloride catalyst with an oxygen gas flow can produce a sample of upgraded ilmenite that will leach more completely. Samples generated from a 0.05 M citric acid 0.05 M sodium citrate aeration (experiment 6) and p-nitroaniline hydrochloride (experiment 3) slurries can be lowered in manganese content more than the standard ammonium chloride aeration sample using hydrochloric acid.

Finally when removing manganese with a sulfuric acid leach sample produced from a 0.05 M citric acid 0.05 M sodium citrate slurry (experiment 6) and a p-nitroaniline hydrochloride(experiment 3) slurry have a more complete manganese removal that the standard ammonium chloride slurry.

Chapter Ten

Summary and further work

10.1 Concluding Summary

This thesis has looked at several different reagents to act as catalysts in the aeration of reduced ilmenite. The accepted industrial catalyst in the Becher process is ammonium chloride, so extensive studies were carried out with ammonium chloride to find its characteristics and limitations in the test reactors. The results of the ammonium chloride aerations were then used to compare all other catalysts and as a basis for improvements to the aeration system.

Aeration studies of reduced ilmenite, conducted with ammonium chloride as the catalyst, have shown that the aeration rate can be significantly increased by changing the aeration gas from air to pure oxygen. The change from air, at approximately 20 per cent oxygen, to a pure oxygen flow reduced the aeration time from 7.0 hours to 2.5 hours. In addition the pure oxygen flow resulted in lower residual magnetic species levels.

Examinations carried out on partially aerated reduced ilmenite and fully aerated reduced ilmenite products with a scanning electron microscope have demonstrated that the metallic iron was removed from the outer edges of the reduced ilmenite grain first. The remaining iron was then progressively removed until only the iron in the centre of the grain was left to be oxidised and complexed. The porosity of a grain also influenced the speed at which the iron was removed. This meant that the more porous a reduced ilmenite grain the more access the dissolved oxygen had to the metallic iron surfaces, so oxidation and complexation to the ammonia present could occur more readily.

The use of other inorganic compounds as substitutes for the ammonium chloride as a catalyst showed that ammonium ion was required if any reasonable reaction rate was to be reached, the exception being the use of sea water. The presence of the ammonium ion was critical because of its ability to buffer the solution and its ability to complex the iron (II) ions. This was shown when all the ammonium compounds caused greater aeration rates than their sodium compound counterparts. In addition ammonium sulfate used as catalyst could produce a similar aeration rate to ammonium chloride, these being the fastest aeration results. This infers that the presence of chloride and sulfate ions must also play an important role in the mechanism to iron removal. The presence of nitrate ion was found to inhibit the removal of iron from the reduced ilmenite matrix.

Sea water was also found to be a reasonable catalyst. This was thought to be due to a combination of factors such as the higher chloride ion concentration and the presence of other ions such as magnesium (Farrow and Ritchie, 1985) and calcium.

Through the use of compounds with similar characteristics to ammonium chloride it was found that by examining the pK_a values of the compounds a relationship with the leaching rates could be found. That is the lower the pK_a the faster the leaching rate. Another factor found to dramatically effect the leaching rate was the effect of steric hindrance of the amine group in these compounds. The result of this finding indicated that the amine group in these compounds does actually interact and complex with the iron (II) ions to transport them out of the reduced ilmenite grain.

By looking at one particular compound, ethylenediammonium chloride, with many similarities to ammonium chloride, but with more reactive ammonium sites it was shown that faster aeration times were observed. The ethylenediammonium chloride completed a standard aeration in 6.0 hours compared to the standard ammonium chloride aeration of 7.0 hours. In addition the ethylenediammonium chloride used a lower concentration of 0.0698 M to achieve the 6.0 hour aeration. When this ethylenediammonium chloride was tested, as a catalyst, with a pure

oxygen aeration gas it reduced its aeration time with air threefold, that is, down from 6.0 hours to 2.0 hours.

Compounds with reactive sites other than amines showed some very promising results. Citric acid in combination with equal molar proportions of trisodium citrate proved able to almost halve the aeration time of the ammonium chloride catalyst. The success of the citric acid / trisodium citrate was found to be due to its ability to buffer the system and form complex ions with iron (II) ion.

Accurate reproduction of these results was found to be possible when more of the same reduced ilmenite sample was used. However, due to the heterogenous nature of reduced ilmenite when different samples from other sources were aerated under similar conditions, slightly different aeration times were observed. When four different reduced ilmenites were tested in a series of different aeration conditions the results showed the aerations followed the same reaction order for the use of different catalysts in almost all cases.

10.2 Suggestions for further work

This study has by no means considered all the possible catalysts that could be of use in this field. Of the experiments that met with success, further work needs to be conducted on a larger scale, possibly plant scale, aerations to evaluate the effects of these new catalysts on the aeration rate, reagent costs, catalyst usage and waste treatment costs.

Further research with the citric acid / trisodium citrate catalyst needs to be carried out to find a method to complete the difficult separation of the ultra fine iron oxide from the solution while maintaining the citrate ion concentration in the solution.

More extensive test work could be carried out on amine and / or other compounds following the relationship of pK_a with aeration times.

A final area that needs more examination is the reduced ilmenite morphology. The size and other characteristics of each type of reduced ilmenite from different sources can result in significantly different aeration times. So far this has been attributed to the different amounts, size and integrity of the passivating iron oxide film built up on the metallic iron surface but other factors such as grain porosity may also contribute to aeration rate differences.

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