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GAS PHASE EXTRACTION OF METALS FROM OXIDES USING THE LIGAND ACETYLACETONE

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A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Master of Science in Engineering

Johannesburg, 2010

DECLARATION

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

……

(Epiphania Rumbidzai Memoraine Mariba)

……day of……year……

day *month* *year*

ABSTRACT

Gas phase extraction using organic ligands has been gaining interest because it eliminates many of the problems encountered in conventional mineral processing methods. This process was successfully used to extract iron using the ligand acetylacetone from Fe_2O_3 in a fluidized bed reactor, with above 80% extraction being achieved after four hours for some experimental conditions. The extraction was shown to be dependent on temperature, ligand flow rate and the surface area available for reaction, with extraction increasing as each of the variables was increased. Chrome could not be extracted successfully, with only a maximum of 12% extraction being achieved after four hours. It was shown that the process could be used to successfully separate mixtures containing both iron and chrome oxides by extracting iron and leaving chrome in the solid phase. Classic shrinking core reaction models were tested on data obtained to evaluate their fit of experimental data with theoretical predictions. The chemical reaction limiting shrinking core model was suggested to be the one that predominantly described the experimental data. There is need however to develop a model which takes into account the influence of all the variables identified as affecting the extraction. There is also need to identify ligands which will react selectively with other metal oxides and not iron in order to the see if the other metals can also be successfully extracted. Further work should be done on this promising technology.

DEDICATION

For my family

Past, present & future

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LIST OF SYMBOLS

C_{AO} - initial concentration of gaseous reactant

d_p – diameter of a particle

E_a – activation energy for the reaction

F_g – shape factor for a grain

I – intensity of incident light

I_0 – intensity of transmitted light

k – reaction rate constant

k_0 – pre-exponential factor in Arrhenius' equation

R – ideal gas constant

r – rate of chemical reaction

u_{mf} – velocity at minimum fluidization

u_o – superficial velocity

x – fractional conversion of a reaction

Greek symbols

ρ_g – density of gas/fluid

ρ_s – density of a solid

η – effectiveness factor

μ - viscosity of a fluid

ε – voidage of a solid

NOMENCLATURE

acac – acetyl acetone anion

acacH- acetyl acetone

MS – metal sulphide

MO – metal oxide

1 INTRODUCTION

1.1 Background

Conventional methods for the extraction of metals from low grade sources follow either a hydrometallurgical or a pyrometallurgical route (Cox *et al*., 1985). However, these conventional methods have proven to be quite complex, with a number of problems associated with each method. Both routes produce by-products that are harmful to the environment, e.g. the production of large volumes of SO_2 in pyrometallurgical processing, and the production of acid fumes in the hydrometallurgical processes. In addition, both processes produce large volumes of solid waste as by-products (slags and sludge), which are normally dumped at slag dumps. These slags themselves are an environmental hazard, since the low concentrations of metals found in the slags can potentially be leached into the ground, e.g. chromium, mercury and cadmium from landfill wastes; polluting the soil and underground water resources (Groot & Pistorius, 2008). Additionally, fly ash produced from the production of electric power or waste incineration is also a source of metals that can find their way into the environment thus polluting the environment (Allimann-Lecourt *et al.*, 2002). Worldwide and locally, pressure to focus on recycling of the waste produced by base metal production is increasing, with sustainability of current practices and the environment becoming important topical issues (Groot & Pistorius, 2008).

The problems associated with conventional methods of extraction have necessitated the improvement of current practices, by the design of novel processes that try to eliminate the problems of current practices. The extraction of metals in the gas phase in fluidised bed reactors using organic chelating compounds is a process that will be investigated as an alternative extraction route (Kunii & Levenspiel, 1991).

The gas phase extraction of metals using ligands is a relatively new field, with limited work done on the subject so far. Gas phase extraction using ligands takes advantage of the chelating properties of ligands, and the relatively low volatilization temperatures of the complexes formed when the ligand reacts with the source of metal. Ligands of the β-diketone family have been found to be particularly useful in forming compounds that have the properties required for gas phase extraction. A wide variety of metals in many matrices can be converted into volatile, thermally stable metal β-diketonate complexes for various uses such as chromatographic separation and analysis (Sievers & Sadlowski, 1978).

When a ligand is brought into contact with a solid matrix containing metal, for example a metal oxide or a metal sulphide, it will form a complex with the metal which stabilises the metal. The process can be illustrated by the equation

$$Ext_{gas} + M(Matrix)_{solid} \rightarrow M(Ext)_{gas} + Matrix_{solid} \qquad \textbf{(1-1)}$$

Extraction of metals in the gas phase has been demonstrated in the SERVO process where Nickel and Vanadium where successfully extracted using tetra-iso-propyldithiophosphoramides (prps), bis(pentane-2,4-dionato)popan-1,2-diimine (pnaa) and acetyl acetone, with prps producing the highest extraction (Allimann-Lecourt *et al.*, 2002). Potgieter *et al.* (2005) have successfully extracted Aluminium, Iron, Chromium and Vanadium in the gas phase using acetylacetone, a β-diketone. This work will also use the ligand acetylacetone for the extraction of metals.

Previous work carried out on gas phase extraction of metals has been mainly concerned with preliminary feasibility of the process. Except for the effect of reaction temperature, no work has been done to date which shows how other variables affect the extraction. This work shows how additional variables such as ligand flow rate and concentration of metal in the solid matrix affect gas phase extraction.

1.2 Problem Statement

The different variables that affect gas phase extraction are not known; temperature being the only variable that has been investigated to date. Preliminary work has been carried out, which has shown that it is possible to extract metals in a fluidized bed reactor using acetylacetone ligand by carrying out extractions at different temperatures (Potgieter *et al.*, 2005). This project will aim to determine how other

variables affect gas phase extraction. Additionally the project will seek to investigate the kinetics of the process which is not well understood.

1.3 Aim of the project

The aims of the project include:

- To predict the operating ranges of gas phase extraction, i.e. the temperatures that produce reasonable extraction
- To determine how several variables such as temperature, ligand flow rate and metal concentration in the bed affects gas phase extraction
- To determine the time need to achieve economic extraction using gas phase extraction
- To determine how different variables affect the kinetics of gas phase extraction
- To model the kinetics of gas phase extraction

1.4 Hypothesis

In addition to temperature the process of gas phase extraction is affected by a number of several other variables such as ligand flow rate and concentration of metal oxide. Once the effect of the variables is known it should be possible to develop a kinetic

model that can be used to predict gas phase extraction of metals by ligands in fluidized beds from a variety of materials, such as low grade ores, slags and fly ash.

1.5 Dissertation lay-out

This dissertation constitutes further chapters as follows: Chapter 2 is a literature review which presents some of the work utilising ligand extraction, current practices for extraction and the problems they present together with the advantages of utilising fluidized bed reactors. Chapter 3 presents the experimental procedures and describes the experimental setup and the equipment used. In Chapter 4 the results of the experimental investigation are given and discussed, whilst in Chapter 5 a model that predicts gas phase extraction will be developed. Chapter 6 will summarize the conclusions and the recommendations for future work to be carried out. A list of references and appendices are given at the end of the dissertation.

2 LITERATURE REVIEW

This chapter begins by identifying the different sources of low grade ores that can be used for gas phase extraction and the conventional methods used to treat these low grade ores. Some of the problems associated with these conventional processes are identified, together with emerging technologies regarding the processing of low grade ores. The next section identifies previous work that has used ligand extraction in processing different materials. The choice of fluidized beds for the extraction is discussed by listing the advantages of using fluidized beds, and by showing some industrial applications of fluidized beds.

2.1 Sources of low grade ores

The primary source of ores used in metallurgical refining comes from underground ore bodies which are mined and undergo physical liberation processes before being taken for refining. However, as ore deposits become exhausted, other sources of low grade ores are becoming more and more important. Most resources required for the manufacture of electrical and electronic equipment, as well as the generation of electrical power are non-renewable, e.g. copper, steel, aluminium and other metals, hence the need to recycle the available resources (Groot & Pistorius, 2008). Some of the main alternative sources of metals that have been identified include slag, scrap

metals and fly ash from smelters (Allimann-Lecourt *et al.*, 2002). Metal concentrations in process residues (e.g. tailings, slag and fly ash) can exceed metal concentrations in natural ores and may therefore present opportunities for by-product recovery. In the USA, the copper, lead, and zinc commodity sectors (i.e. the non-ferrous industry) generate between 23.3 million and 24 million metric tons per year of process residues (Berry *et al.*, 2002). The iron and steel industry also produces large volumes of process residue, mainly in the form of slag. A selected example of the volume of slag produced annually in New Zealand and Australia from the iron and steel making industry is shown Table 2-1:

Table 2-1: Total slag production in Australia and New Zealand in the year 2000 (Dippenaar, 2004)

Origin	Blast furnace		Basic oxygen furnace	Electric-arc furnace	Other
	Air cooled slag	Granulated slag			
Mass Produced (ton)	1050000	700000	800000	155000	360000
% Produced	34	23	26	5	12

Some of the residues which have been found to contain metals that can be recovered include:

- Dust, fine particles and tailings - these are produced during the beneficiation of the ore in the processes of grinding, flotation, etc.

- Slag waste - smelting of the ores produces two immiscible phases; a heavier sulphide phase containing the metal being extracted, the matte; and an oxide phase, the slag. The slag is normally tapped off and dumped, but offers a viable opportunity for recovering the metal oxides in it.
- Gas cleaning sludge – waste gases from a smelting operation carry with them fine dust particles which can potentially contain metals. These are collected during gas cleaning operations (e.g. passing through venturi scrubbers and hydrocyclones,) as sludge, which can be used as a source of metals for recovery (Berry *et al.*, 2002).

The compositions of some non-ferrous slags are given in Table 2-2:

Table 2-2: Typical composition of non-ferrous slag (%)

Element	Reverberatory copper slag	Nickel slag	Phosphorus slag	Lead slag	Lead-Zinc slag
SiO_2	36.6	29.0	41.3	35.0	17.6
Al_3O_2	8.1	Trace	8.8	-	6.1
Fe_3O_2	-	53.06	-	-	-
CaO	2.0	3.96	44.1	22.2	19.5
MgO	-	1.56	-	-	1.3
FeO	35.3	-	-	28.7	-
K_2O	-	-	1.2	-	-

As can be seen in Table 2-2 non-ferrous slags provide a potential source of metal oxides which can be used for the extraction of the metals.

Traditionally, process residue has been used in the construction industry, e.g. in the manufacture of cement and concrete (Mototsugu *et al.*, 2005), and as insulation material. The various uses of different process residues in India are shown in Table 2-3:

Table 2-3: Production and use of industrial slag in India (Rai & Roa, 2005)

Waste	Annual production (millions of tonnes)	Potential uses
Blast furnace slag	11	Portland cement, super sulphated cement, oil well cement, aggregate, ceramics
Ferro-alloys slag	3.5	Masonry cement, blended cement, ceramics, aggregate
Fly ash	95	Cement, Portland slag cement, concrete, cellular concrete, lightweight aggregate, calcium silicate bricks, clay fly ash bricks
By-product gypsum	4.0	Cement additive, plaster, building-blocks and fibrous gypsum boards, special cement
Red mud	3.5	Cement raw material, bricks and tiles, sintered aggregate
Mine tailings (zinc, copper gold and iron)	17	Filler in concrete, calcium silicate bricks, cellular concrete, clay bricks and cement

The construction industry however, does not consume all the process residues, and large volumes still remain (Allimann-Lecourt *et al.*, 2002). Different types of process residues (slags) have different properties which can be used for the construction industry. Some residues require further processing before they can be used in the construction industry, e.g. laterite waste, building rubble, steel slag, etc. (Rai and Rao, 2005).

It is beneficial to use the process residues as raw materials for metal processing since they can contain higher concentrations of metals than ore bodies, as shown by the high compositions of Al_2O_3 and Fe_2O_3 in Table 2-2. Additionally, using the process residues as raw materials, also partly solves the disposal problems associated with the residues, since after processing, lower volumes of residues are left to dispose.

2.2 Treatment of low grade ores

2.2.1 Conventional treatment methods

The processing of non-ferrous metals provides a significant fraction of the metal processing industry. Conventional methods for the extraction of metals from low grade sources (sulphides, oxides and slags) follow either a hydrometallurgical or a pyrometallurgical route (Cox *et al.*, 1985). The approximate total annual production of major non-ferrous metals in 2007 is shown in the Figure 2-1:

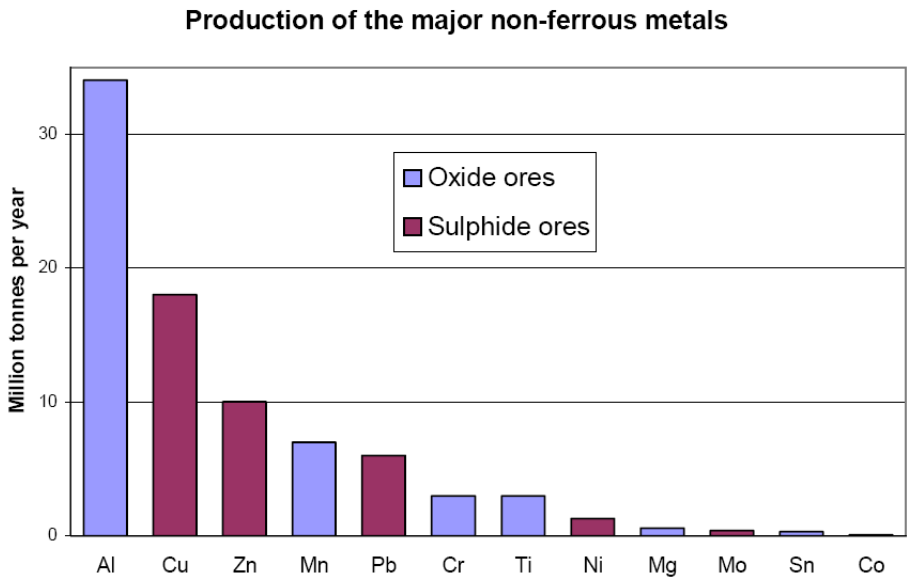


Figure 2-1 Annual production of major non-ferrous metals, showing the type of ore mainly used in the production of the metal (Sahyoun & Mason, 2007)

The first step in the processing of minerals is the liberation of the mineral from the ore body, which is normally achieved by grinding. Next is the pre-concentrating step, which produces a higher grade of metal to enter the processing step. Pre-concentration is achieved by flotation, using appropriate flotation techniques (Wesley, 1985).

2.2.1.1 Pyrometallurgical treatment

Pyrometallurgical extraction of metals involves subjecting the ore concentrates to high temperatures, either in a blast furnace or sinter plant (Wesley, 1985). During

heat treatment, the ores (sulphide and oxide) are treated under different conditions to form pure metals. Initially the sulphides are oxidised to pure metals according to the following reaction

$$MS_{(s)} + O_{2(g)} \rightarrow M_{(s)} + SO_{2(g)} \qquad \textbf{(2-1)}$$

In addition to the formation of pure metals, oxides of the metals are also formed. These are reduced to pure metal by reacting with the coke that acts as the reducing agent. The following reaction occurs

$$2MO_{(s)} + C_{(s)} \rightarrow 2M_{(s)} + CO_{2(g)} \qquad \textbf{(2-2)}$$

2.2.1.2 Hydrometallurgical treatment

Hydrometallurgical treatment of metals is the more commonly used process for the extraction of metals from their ores. It involves processing the metal ores in liquid/fluid media. Hydrometallurgy normally involves first dissolving the metals into solution, achieved by leaching. This is followed by removing the metals from solution, which can be achieved by electrowinning. Leaching can be grouped into two main categories:

i. Sulphate based process

These are more widely used because they reduce the corrosion on the equipment as compared to the other hydrometallurgical processes. In sulphate

based processes, the sulphate ion (SO_4^{2-}) forms a complex with the metal ion from the ore. The sulphate ion is not a strongly complexing ion, hence it will selectively complex some metal ions whilst leaving some, which results in the separation of different metal ions from the ore. The reaction occurring in leaching using sulphate lixiviant is as follows:

$$MO_{(s)} + H_2SO_{4(aq)} \rightarrow MSO_{4(aq)} + H_2O_{(aq)} \qquad \textbf{(2-3)}$$

The result of reaction of the metal with the acid is the dissolution of the metal into solution.

ii. Chloride based processes

These either use hydrochloric acid, ferric chloride or brine as lixiviant depending on the best pH, redox potential or chloride concentration required for the process (Wesley, 1985). The metals react to form soluble chlorides, which can then be further processed to produce pure metal. Chloride solutions are quite corrosive however; they often dissolve the reactor walls of most metal reactors.

iii. Other leaching processes

Nitric or organic based systems can also be used as lixiviants.

Once the metals have been dissolved into solution, they are removed from solution by passing an electric current through the solution in the process of electrowinning. The reactions in electrowinning are:

At the anode: $M^{2+}_{(aq)} + 2e^- \rightarrow M_{(s)}$ **(2-4)**

At the cathode: $H_2O \rightarrow \frac{1}{2}O_{2_{(g)}} + 2H^+_{(aq)} + 2e^-$ **(2-5)**

2.2.2 Problems associated with conventional methods

The conventional methods used for extraction of metal ores have proven to be quite problematic.

- There are usually a number of complex processes that have to be done before the final ore is produced, for example, pyrometallurgical treatment is rarely just one simple step.
- The energy costs of pyrometallurgical processes are very high; the process is very energy intensive.
- Pyrometallurgical processes usually have waste streams that are harmful to the environment, e.g. the large volumes of sulphur dioxide gas produced in smelters. Table 2-4 shows the volumes of sulphur dioxide produced from 2001 to 2005 years by the metal processing industry:

Table 2-4: World sulphur production from the metal industry (thousand metric tonnes) (Sahyoun & Mason, 2007)

	2001	2002	2003	2004	2005
Australia	817	899	863	865	950
Canada	1124	1109	992	1089	1057
Chile	1160	1275	1430	1510	1660
China	2000	2200	2400	2600	2800
Finland	227	308	305	301	300
Germany	684	754	701	591	600
India	458	458	539	539	580
Iran	50	50	50	60	60
Italy	203	142	127	113	115
Japan	1319	1326	1281	1263	1330
Kazakhstan	310	260	325	325	325
Korea, Repulic of	665	737	797	796	800
Mexico	572	588	539	703	700
Netherlands	126	124	131	137	135
Poland	227	276	294	290	600
Russia	460	500	520	570	600
South Africa	**265**	**179**	**174**	**180**	**250**
Spain	461	544	560	488	475
United States	982	772	683	739	711
Uzbekistan	160	170	170	170	170
Other	1260	1320	1380	1350	1350
Metallurgy Total	**13530**	**13991**	**14261**	**14679**	**15248**
Grand Total	**61400**	**62600**	**64200**	**66000**	**66000**

Table 2-4 shows that the amount of sulphur formed from metallurgical processes has been increasing steadily over the years. This is despite some decreases in emissions from some of the countries in line with global agreements for the minimization of emissions. Additionally, it has been forecasted that the annual sulphur production will go up if current practices continue to be used without the development of new processes which minimize the amount of sulphur being released into the atmosphere (Anthony *et al.*, 2004), as shown in Table 2-5:

Table 2-5: Net sulphur production for production of selected metals, 2005 and 2010

Metal	2005, ktpa S	2010, ktpa S
Copper	6070	7280
Zinc	6090	7000
Lead	550	570
Nickel	180	-300
Others	470	540
Pyrites	4000	4400
TOTAL	**17360**	**19490**

- The processes for leaching are very sensitive, requiring fine control to achieve high rates of leaching.
- In the electrowinning section, hydrogen fumes are normally produced if the lixiviant contains acid. This makes the process harmful to those working in the electrowinning section.

- Impurities in the lixiviant entering the electrowinning section disrupt the production of pure metal, resulting in undesirable elements being plated onto the metal cathode. The process needs proper control for production of pure metal.

2.2.3 Emerging technologies

Most of the emerging technologies in the processing of sulphide and oxide ores are aimed at improving the current hydrometallurgical and pyrometallurgical processes. Some of the improvements made to date include:

- Copper continues to be dominated by hydrometallurgical and pyrometallurgical techniques. Continued environmental pressures are ensuring that the pyrometallurgical techniques used are as 'clean' as possible. The same environmental pressures are ensuring that more research into hydrometallurgical treatment is carried out (Cramer, 2003). In addition prices for copper are ensuring that optimization of current processes is carried out in order to lower the production costs of the metal.

- In nickel processing, bacterial leaching is receiving marked interest. BHP-Billiton has successfully pilot tested a BioNic process that has been designed for low process temperature mesophilic bacteria, or for high temperature thermophile bacteria to treat nickel sulphides. However, no commercially sized operation has been commissioned as yet (Cramer, 2003).

- The process of extracting the metals with organic complexing agents, which will be carried out in this research, is still being studied, with preliminary work having being carried out in the processing of fly ash using the Servo process (Allimann-Lecourt *et al.*, 2002), and work having been carried out in investigating the feasibility of recovery of some metals from their ores in a fluidized bed reactor (Potgieter *et al.*, 2005).

Despite all the new methods for the processing mentioned above, more still needs to be done in order to address future needs for cleaner and greener production processes.

2.3 Extraction of metals using ligands

2.3.1 Description of ligands

A ligand is an ion, atom or molecule that donates one of its electron pairs through a coordinate covalent bond to one or more central atoms or ions to form a larger complex. These complexes formed, known as co-ordination compounds, arise when a metal cation is bonded to one or more anions through coordinate covalent bonds (Siedle, 1987). Ligands have in the past found extensive use in industry, and an example of this is the use of EDTA (ethylene diamine tetra acetic acid ligand) for the binding of heavy metals in water purification and in the textile industry (Chaudhary

et al., 2000). Other ligands are found as building blocks for catalysts, e.g. diphosphine ligand (BINAP) is used in the catalytic hydrogenation of rhodium or ruthenium; and also for the catalytic isomerisation of olefins and allyic alkylation reactions (Pretorius, 2004).

Acetylacetone

The ligand chosen for the extraction of metals in the gas phase from their oxides was the β-diketone acetylacetone (2-4-pentanedione) which is abbreviated as acacH. β-diketone ligands are chelating ligands, i.e. they have more than one lone pair of electrons which they can use for binding with metals. Acetylacetone is an example of a bidentate (bi-two, dent-teeth) ligand, since it can bond to a metal via both oxygen atoms. The outer part of the complex formed when the metal and ligand bind consists of organic groups, making most metal acetylacetonates hydrophobic, and insoluble in water (Szafran *et al.,* 1991). The potential for use of β-diketones as complexing agents for the spectrophotometric determination of metallic ions in dilute solution, and in chromatographic separations has long since been realised by several research groups (Pettinari *et al.,* 2004). Additionally, complexes formed with β-diketones have been shown to be highly volatile, forming gaseous complexes at relatively low temperatures compared to other metal compounds (Seivers & Sadlowski, 1978).

Acetylacetone (acacH) exists as an equilibrium mixture of tautomeric keto and enol forms. In basic solution, it is deprotonated to the acetyl acetonate anion (acac) as shown in Figure 2-2 (Seco, 1989):

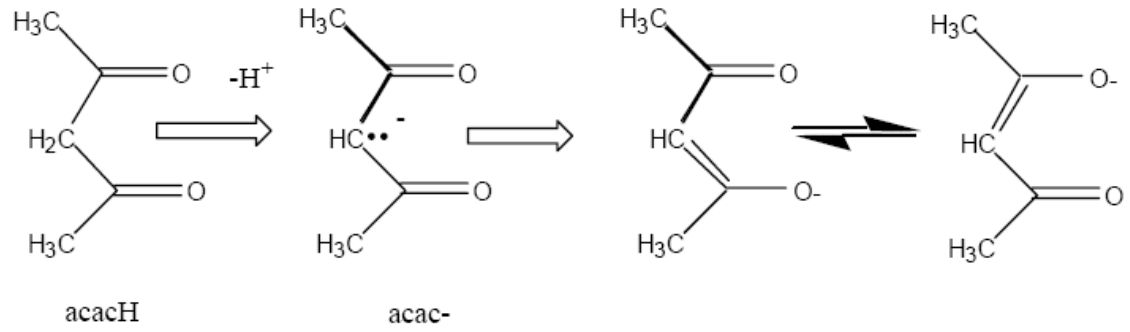


Figure 2-2 The inter-conversion between the keto and enolic form of the acac anion

Under appropriate conditions the enolic hydrogen atom of the acetylacetone may be replaced by a metal cation to produce a six membered metallocycle, thereby shifting the keto–enol equilibrium in favour of the chelated enolate anion form in metal acetylacetonate complexes (Bai *et al.,* 2007).

The reaction which occurs when the ligand acac reacts with a metal oxide is of the form

$$M_2O_n + 2nHacac \rightarrow 2M(acac)_n + nH_2O \qquad \textbf{(2-6)}$$

where

M is the metal to be extracted

2.3.2 Previous work involving the use of ligands for metal extraction

The use of ligands for extraction has found widespread application. Ligands have been used to selectively extract organic bonded metals in soils (Hamblin & Posner, 1979). Ligands have been used in solvent extraction for the removal of metals from solution (Kondo et al, 1978; Moffett & Zika, 1987). Several researchers have used ligands to extract metals from both the solid phase (Kersch *et al.*, 2000; Ozel *et al.,* 2000; Takeshita *et al.,* 2000) and the liquid phase(Galand & Wipff, 2005) using supercritical fluid extraction (SFE) with CO_2 as the fluid. Ligand extraction has also been carried out in the gas phase to extract metals from solid residues including fly ash (Allimann-Lecourt *et al.*, 1999; Allimann-Lecourt *et al.*, 2002; Cox *et al*., 1985; Potgieter *et al.*, 2005).

2.3.2.1 Solvent extraction using organic ligands

Solvent extraction of metals from industrial effluent has been carried out by sequestering the metals using organic compounds which form complexes with the metals forming a separate phase from the rest of the industrial waste (Chaudhary *et al.,* 2000). Moffett & Zika (1987) have demonstrated the use of acetylacetone for ligand exchange/solvent extraction resulting in the formation of Cu(II) complexes with acetylacetone in the presence of competing natural chelators. In some cases, the

solvent extraction of metals can also be coupled with the use of appropriate liquid surfactant membranes as shown by Kondo *et al.* (1978).

2.3.2.2 Supercritical fluid extraction using organic ligands

In SFE, the ligand mixed with the supercritical fluid (CO_2) has been extensively used for most extractions because it dissolves in the fluid. The mixture of the supercritical fluid and the ligand easily diffuses through the sample to be extracted; and the metal complex formed is carried away in the supercritical fluid since most complexes formed dissolve in the supercritical fluid. SFE-CO_2 with acac and hfacac has been successfully used to extract cobalt from a model matrix (Burford et al., 1999). Galand and Wipff (2005) have studied the effect of β-diketone ligand fluorination on the SFE-CO_2 extraction of uranyl and they have also shown that SFE-CO_2 can be used for the complixation of Fe^{3+}. Takeshita *et al.* (2000) have also shown that acac SFE-CO_2 can be used to extract Cu from contaminated wood.

The solubilites of complexes in supercritical CO_2 have been studied for different ligands by, amongst others, Aschenbrenner *et al.* (2007) and Cross & Akgerman (1996). Ozel *et al.* (2000) have also studied the extraction, solubility and stability of metal complexes in SFE-CO_2.

2.3.2.3 Gas phase extraction using organic ligands

Extraction and recovery using volatile organic compounds is an emerging technology developed during the 1970s. The process extracts heavy metal contaminants from matrices such as low grade ore, soil, sediment, used catalysts, or industrial wastes; by using volatile organic reagents which pass through the heated feed material and reacts selectively with the metal to be extracted (Cox *et al.,* 1985; Allimann-Lecourt *et al.,* 1999). Products of the reaction are volatile metal complexes which can be removed from the residual solids by a carrier gas. These complexes can then be reduced in the vapor phase to produce a metal product and regenerate the organic reagent for recycling; or treated by dilute mineral acid to decompose the complex and following separation of the liquid phase both the metal and organic extractant can be recovered by appropriate techniques (Allimann-Lecourt et al., 2002).

The organic compounds that are used for gas phase extraction are those that form compounds that generally exhibit high volatility. β-diketones and their derivates (fluorinated derivatives) are typical examples of such compounds. Allimann-Lecourt *et al.* (1999, 2002) have used β-diketones, β-diketodiimines and tetra-iso-propyldithiophosphoramides to successfully extract metals from the oxide phase of metals in fly ash and from different sediments. They have shown that by changing the source of a ligand used one can selectively extract some metals whilst others remain in the solid matrix. This selectivity of the ligand has also been shown by Cox *et al.* (1985) who have shown that it is possible to extract copper, but not iron, using

different derivatives of β-diketodimines. Potgieter *et al.* (2005) have used acac to extract metals from the oxides of iron, chromium, aluminium and vanadium.

The process flow sheet for the gas phase extraction of metals that has been proposed by Potgieter *et al.* (2005) and Allimann-Lecourt *et al.* (2002) is shown in Figure 2-3

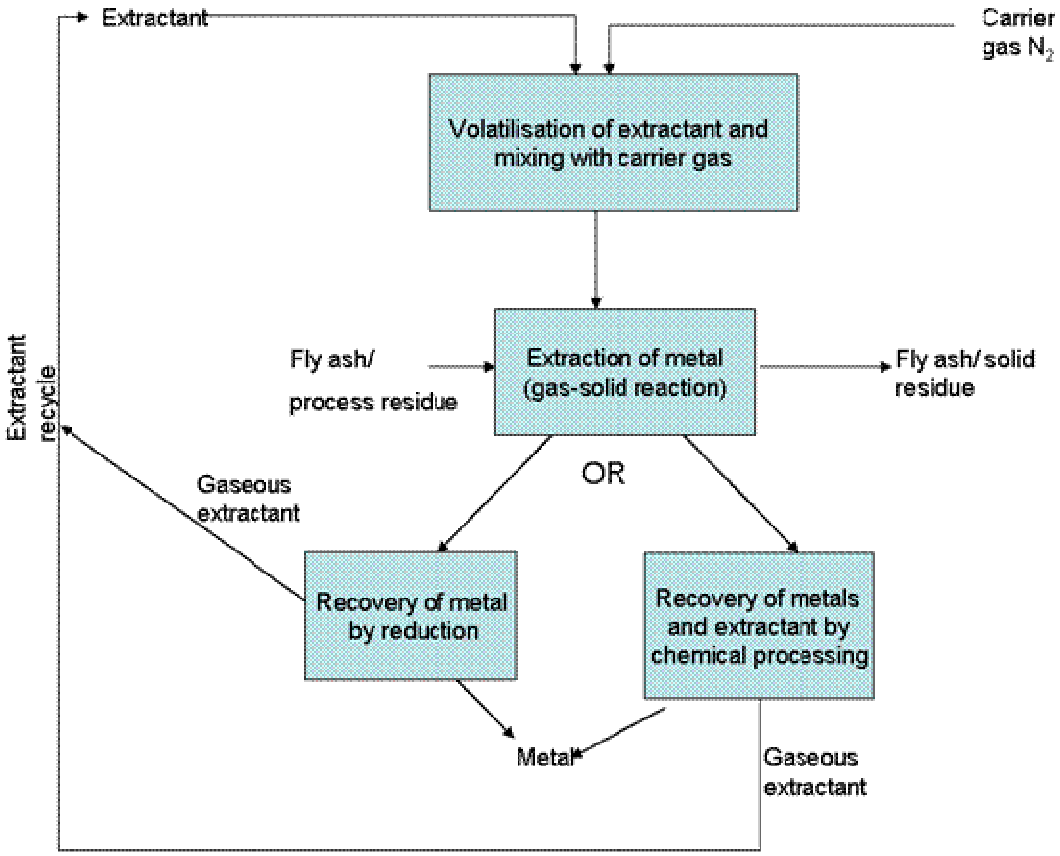


Figure 2-3 Process flow sheet for the gas phase extraction of solid residues

Although the possibility of extracting metals in the gas phase from different solid matrices has been demonstrated by different research groups, most of the work published just shows that the process is feasible. No work to date has been published that investigates how different variables affect the extraction process.

2.3.3 Recovery of the ligands

Once the volatile metal complexes are formed, it is possible to separate the metal from the ligand with subsequent recovery of the ligands. For a well designed process it is therefore theoretically possible to recycle the ligand back to the extraction process. The following processes have been proposed as potential ways of separating the metal from the ligand and for recycling purposes.

2.3.3.1 Recovery by hydrogen reduction

Production of pure metal by precipitation from a loaded chelating agent has been investigated as a way of separating metal from ligands. Demopoulos and Distin (1985) have investigated the possibility of separating a chelate loaded with copper by direct reduction with hydrogen in an autoclave. The desired metal is loaded conventionally and instead of acid stripping followed by metal recovery *(e.g.* electrowinning), the metal is precipitated in a powder form from the organic solvent by the action of hydrogen under pressure while the original organic is regenerated (Cox, 1985).

Successful application of pressure hydrogen stripping has been shown to depend on the following conditions being satisfied:

i. Ability to recycle the stripped organic

ii. Reproducible stripping rates with acceptable kinetics.

iii. Production of metal free of organic contamination, and in powder rather than plated form.

2.3.3.2 Recovery by reacting with mineral acid

In organic systems, the regeneration of extractants requires an acidic aqueous strip phase. This strip phase de-complexes the metal–extractant complex by:

1. Regeneration (reprotonation) of the extractant and
2. Dissolution of the metal cation in the acid (Kersch *et al.,* 2005).

The regeneration of the ligand is possible if the ligand has a high acid dissociation constant (pKa) that promotes the formation of a neutral complex HX and reduces consumption of a regeneration acid. Kersch *et al.* (2005) used a packed counter-current column to recover metal and regenerate ligand from an organo-metallic complex. Metal recovery of Cu, Zn, Ni, and Co from supercritical CO_2 into nitric acid was achieved by decomplexation from both a β-diketone (acetylacetone) compound and an organophosphorus compound (Cyanex 272). In another report the regeneration of hfacac from $Cu(hfacac)_2$ via ligand protonation with concentrated H_2SO_4 was

described, with a ligand recovery yield of 89% of the theoretical value. The purity of the recovered ligand was determined to be 99.98% by GC assay.

2.3.3.3 Recovery by electrochemical separation

This process has been carried out in a photolytic cell for the recovery of copper from copper ethylenediaminetetra-acetic acid (EDTA) in effluent industrial waste (Chaudhary *et al.,* 2000). In this process, copper is recovered at the cathode whilst the ligand is destroyed at the anode.

2.3.4 Uses of the metal complexes

Although it is possible to separate the metal complexes and recover the ligand and metal in pure form, metal acetylacetonates are valuable in themselves. Metal acetylacetonates are highly efficient catalysts for a wide variety of organic transformations, e.g. oligomerization, polymerization, hydrogenation, isomerisation, couplings etc. They are also used in rubber technology for vulcanization, for extraction and separation of metals, as NMR shift reagents, in microelectronic devices, for synthesis of high quality semiconductor materials for optoelectronic devices, for separation of enantiomers, as a source of metal or metal oxides for controlled deposition, as fungicides, in pigments as colour stabilizers, as carbon

scavengers for diesel fuels, as combustion control catalysts for rocket fuels, and in laser technology.

Metal acetylacetonates have also been used in the production of transition metal oxide nanoparticles, which themselves are used as catalysts (Willis *et al.*, 2007). The production of metal oxides from their acetylacetonates occurs by chemical vapour deposition (CVD) where the complexes act as the precursors, and has been demonstrated for the acac complexes of Fe^{3+}, Al^{3+}, Cr^{3+}, Mn^{3+} and Ni^{2+} (Pal & Sharon, 2000; Siddiqi *et al.*, 2007). The oxides produced by CVD have been found to be of high purity, hence the process of gas phase extraction can be an advantageous way for the production of pure metal oxides, since it will extract the metals from sources with a low purity (as low as 1% content used in this study). The complexes thus produced could be used in the production of pure metal oxides (>99%).

2.4 Fluidization

2.4.1 Fluidization theory

If a fluid is passed through a bed of fine particles it percolates through the void spaces of the stationary particles. As the velocity of the gas is increased, a point is reached where the particles are suspended by the up-flowing fluid. The bed is considered to be just fluidized and is referred to as a bed at minimum fluidization (Kunii and

Levenspiel, 1991). The velocity of the fluid at this point is known as the velocity at minimum fluidisation u_{mf}, and can be found by the equation

$$\frac{1.75}{\varepsilon_{mf}^3}\left(\frac{d_{mf}\rho_g}{\mu}\right)^2+\frac{150(1-\varepsilon_{mf})}{\varepsilon_{mf}^3}\left(\frac{d_p u_{mf}\rho_g}{\mu}\right)=\frac{d_p^3\rho_g(\rho_s-\rho_g)g}{\mu^2} \qquad \textbf{(2-7)}$$

In the case for very small particles, i.e., particles with $Re_{p,\ mf}$ <20, equation (4) simplifies to

$$u_{mf}=\frac{d_p^2(\rho_s-\rho_g)g}{150\mu}\frac{\varepsilon_{mf}^3}{1-\varepsilon_{mf}} \qquad \textbf{(2-8)}$$

where the subscript $_{mf}$ detonates parameters at minimum fluidizing conditions

When the voidage at minimum fluidization is not know, Wen and YU recommended the following expression for calculating u_{mf}

$$\mathrm{Re},_{mf}=\left[(33.7)^2+0.0494Ar\right]^{1/2}-33.7 \qquad \textbf{(2-9)}$$

where

$$\mathrm{Re},_{mf}=\frac{d_p u_{mf}\rho_g}{\mu} \qquad \text{and} \qquad Ar=\frac{d_p^3\rho_g(\rho_p-\rho_g)g}{\mu^2} \qquad \textbf{(2-10)}$$

The behaviour of a bed of solids at the point of fluidization is shown in the Figure 2-4

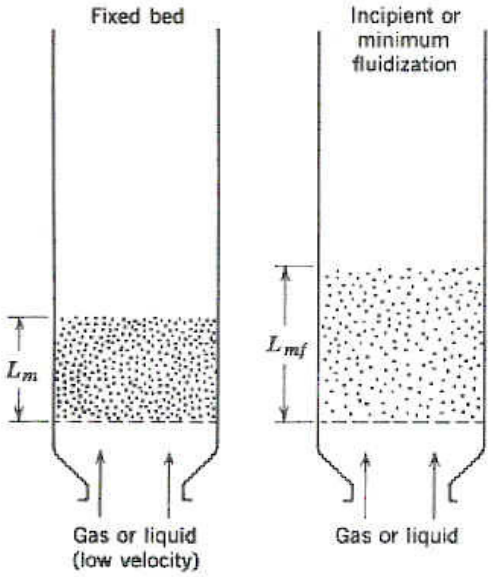


Figure 2-4 Behaviour of a packed before and at minimum fluidization velocity

Above the minimum fluidization velocity the particles are touching each other most of the time, but the inter-particle friction is so small in non-cohesive particles that the fluid/solid assembly behaves like a liquid having a density equal to the bulk density of the powder (Geldart, 1986).

Types of fluidization behaviours

Figure 2-5 shows the behaviour of particles as a packed bed, at minimum fluidization, and at velocities above minimum fluidization velocity. For gas-solid systems, an increase in gas flow rate beyond u_{mf} results in large instabilities in the bed with channelling being observed.

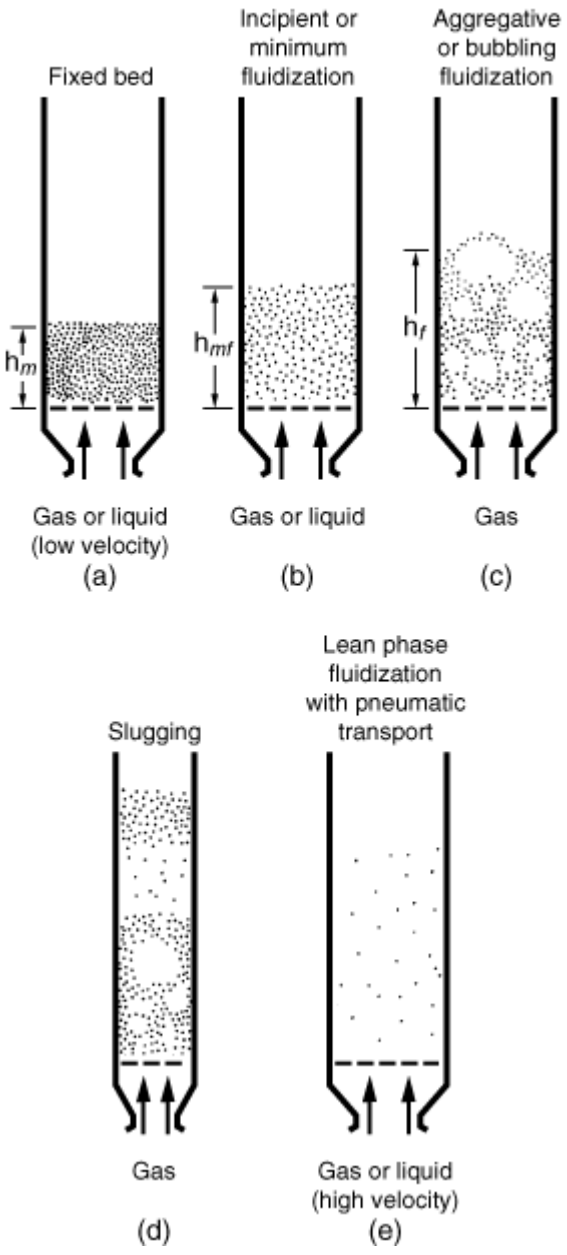


Figure 2-5 Behaviour of particles at various stages of fluidization

The behaviour of the fluidized bed will depend on the velocity of the fluidizing gas with the following behaviours typically observed (Kunii and Levenspiel, 1991):

- Aggregate fluidized bed – which is characterised by violent movement of the solids within the bed. The bed does not expand much beyond its volume at minimum fluidization.

- Slugging fluidized bed – which is normally encountered in long narrow fluidized beds. In this case as the gas bubbles rise up through the bed they coalesce and grow; and may become large enough to spread across the whole bed. As the gas rises, the solid particles, in the case of fine particles, will flow smoothly down the walls of the fluidized bed around the void of rising gas.

- Turbulent fluidized bed – which occurs when the terminal velocity of the solids is exceeded. The upper surface of the bed disappears, with some of the solid particles being entrained. Instead of bubbles in the bed, there are solid clusters and voids of gas of differing size and shape.

- Lean phase fluidization – in which the velocity of the gas is so high that solids are carried out of the bed together with the gas. This is the range of operation that is carried out in the pneumatic transportation of solids.

Gas velocity is not the only parameter that influences fluidization. Additionally, fluidization will be influenced by the particle size of the solids being fluidized. This is because particle size and superficial gas velocity together determine the major hydrodynamic characteristics of fluidized beds. Geldart came up with four

recognisable types of particle behaviour by observing the fluidization of different sizes and types of particles (Kunii and Levenspiel, 1991). Geldart has grouped the particles from the smallest particles in diameter to the largest diameters. This grouping of particles is shown in Figure 2-6.

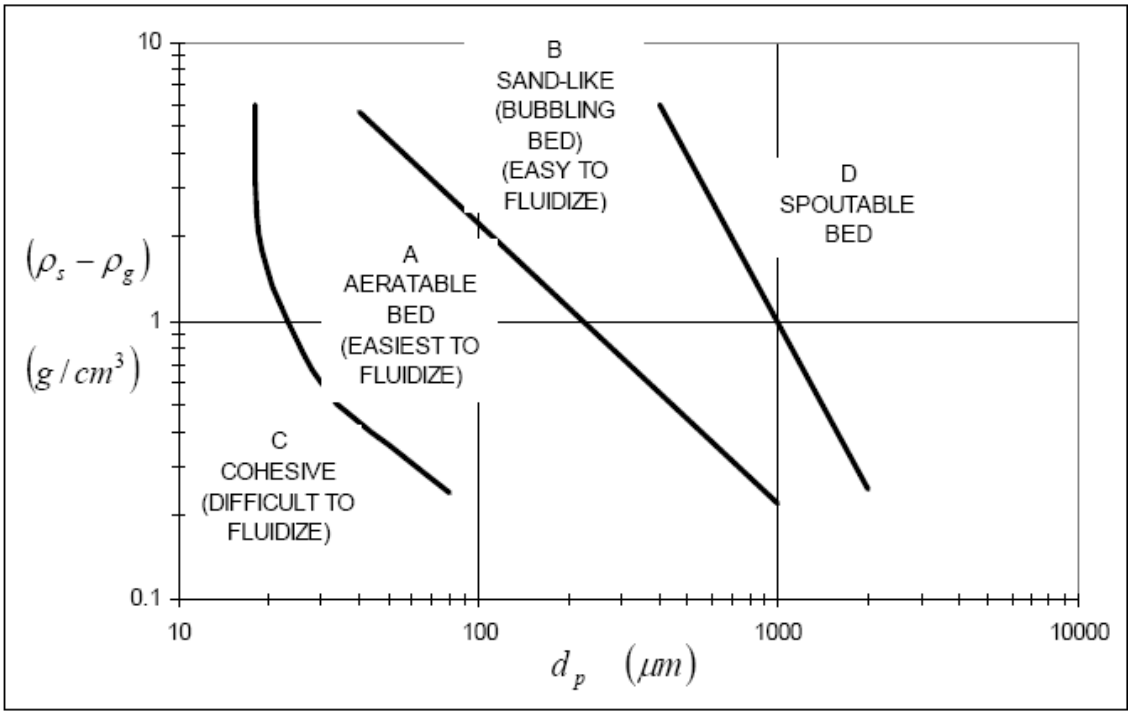


Figure 2-6 Geldart's fluidization classification of powders (Geldart, 1986)

Geldart (1986) has observed the following characteristics for the particles:

1. Group C – these comprise very fine cohesive powders which are difficult to fluidize. They are cohesive because the interparticle forces (van der Waals) are larger than the gravitational forces, causing the particles to be attracted to each other and to clump together (Knowlton, 2002). Such particles rise as a plug of solids, and in larger beds channels of gas form through the particles.

Group C particles generally have a particle diameter less than 30μm. Typical solids in this group include flour, starch and face powder.

2. Group A – these comprise particles having small mean particle size (typically 30μm-100μm) and/or low particle density which are aeratable. Inter-particle forces in these particles are not as large as those for Group C particles, and these particles fluidize well. On fluidization these particles give a region of non-bubbling fluidization at u_{mf}, followed by bubbling fluidization as the velocity of the gas is increased. Examples in this group include FCC catalyst.

3. Group B – these particles comprise particles in the range $100\mu m<d_p<1000\mu m$ and density $1.4<\rho_s<4.5 g/cm^3$. These solids easily fluidize with vigorous bubbling action and bubbles that grow large. Examples include sand and table salt.

4. Group D - these comprise large and/or dense particles. Deep beds of these particles are difficult to fluidize, producing large exploding bubbles, or severe channelling. Sprouting may also result if gas is not evenly distributed. Examples include grain, coffee beans, gasifying coals and some metal roasting ores.

2.4.2 Advantages and disadvantages of fluidized bed reactors

Fluidized bed reactors have been used because they offer the following advantages:

- **Uniform Particle Mixing:** Due to the intrinsic fluid-like behaviour of the solid material, fluidized beds do not experience poor mixing as in packed beds. This complete mixing allows for a uniform product that can often be hard to achieve in other reactor designs.
- **Uniform Temperature Gradients:** Many chemical reactions produce or require the addition of heat. Local hot or cold spots within the reaction bed, often a problem in packed beds, are avoided in a fluidized situation such as a FBR. Because of the uniform temperature gradients in a FBR, the system reacts slowly to abrupt changes in operating conditions, giving a large margin of safety in avoiding temperature runaways for highly exothermic reactions (Grace, 1986).
- **Ability to Operate Reactor in Continuous State:** The fluidized bed nature of these reactors allows for the ability to continuously withdraw product and introduce new reactants into the reaction vessel (Kunii and Levenspiel, 1991).
- **Rate of heat transfer between a fluidized bed and an immersed object is high:** This then means that the heat exchangers within a fluidized bed require relatively small surface areas (Grace, 1986).

Despite all these advantages, the fluidized bed reactor has some disadvantages which include:

- **Backmixing of both solids and gases:** This leads to non-uniform residence time in the reactor, and for continuous treatment of solids leads to non-

uniform product and lower conversions as compared to other types of reactors (Grace, 1986; Kunii and Levenspiel, 1985).

- **Pumping Requirements and Pressure Drop:** The requirement for the fluid to suspend the solid material necessitates that a high fluid velocity is attained in the reactor. In order to achieve this, more pumping power and thus higher energy costs are incurred. In addition, the pressure drop associated with deep beds also requires additional pumping power.
- **Particle Entrainment:** The high gas velocities present in this style of reactor often result in fine particles becoming entrained in the fluid. These captured particles are then carried out of the reactor with the fluid, where they must be separated. This can be a very difficult and expensive problem to address depending on the design and function of the reactor. This may often continue to be a problem even with other entrainment reducing technologies (Grace, 1986).
- **Erosion of Internal Components:** The fluid-like behaviour of the fine solid particles within the bed eventually results in the wear of the reactor vessel. This can require expensive maintenance and upkeep for the reaction vessel and pipes (Grace, 1986; Kunii and Levenspiel, 1985).

Despite the disadvantages listed above, the compelling advantage of overall economy of fluidized contacting has been responsible for its successful use in industrial operations (Kunii and Levenspiel, 1991). Additionally, some of the limitations can be overcome by modification in design of the fluidized bed reactor, e.g., backmixing of

solids can be reduced by using stages of fluidized bed reactors in series (Grace, 1986).

2.4.3 Industrial applications of fluidized bed reactors

2.4.3.1 Early uses of fluidized bed reactors

One of the pioneer uses of the fluidized bed reactor was for coal gasification in the Winkler coal gasifier in 1926(Kunii and Levenspiel, 1991). The fluidized bed reactor was also used as a catalytic cracking unit to separate oil fractions in the petroleum industry. In the 1940s, the fluidized bed reactor was used in the Fischer-Tropsch reaction to produce high grade gasoline from natural gas but it was discontinued in 1957 due to rising natural gas costs and low conversion rates in the reactor. The fluidized bed reactor also found numerous uses in catalytic synthesis reactions due to the temperature uniformity in the reactors. Fluidization has also been used in fields outside the petrochemical industry, e.g. for the roasting of sulphide ores in the FluoSolids system; and in other roasters based on the Winkler gas producer.

2.4.3.2 Physical applications of the fluidization process

The physical characteristics of the fluidization process have been exploited in industry. The following properties of the fluidization process have been used:

- Heat exchange – because fluidized beds can rapidly transport heat and maintain a uniform temperature, they have been use as heat exchangers.

- Drying of solids – a fluidized bed reactor is used where a wet solid is contacted with and fluidized using hot gas, thereby drying the solid.

- Coating of objects – a fluidized bed reactor has been used for coating metals with plastic, where the metals at a temperature above the melting point of the plastic is contacted with fine particles fluidized in air. On contact, the plastic melts and fuses with the metal. Fluidization has also been used to grow particles in size.

- Adsorption – multistage fluidized beds have been used to adsorb dilute components from carrier gas. Adsorption in fluidized reactors has been carried out for removal of trace pollutants, e.g., methylene chloride, ethyl acetate and acetone from flue gas.

2.4.3.3 Synthesis reactions of fluidized bed reactors

Fluidized bed reactors have been used in synthesis reactions involving catalysts. Fluidized bed reactors have been preferred over fixed bed reactors because of the need for strict temperature control in catalytic reactions. Catalytic reactions often need strict temperature control for some catalysts because products are very sensitive to fluctuations in temperature or the catalyst might deteriorate if there is no strict

temperature control and hot spots develop during the processing. Synthetic reactions which have used fluidized bed reactors include the Fischer-Tropsch synthesis of hydrocarbons, and polymerization of olefins.

2.4.3.4 Use of the fluidized bed reactor in hydrocarbon cracking

The catalytic cracking of hydrocarbons is an endothermic process. Fluid catalytic cracking (FCC) reactors have been designed, where the catalyst regeneration step supplies the heat required for the cracking of the hydrocarbons into smaller fractions. These reactors are two unit reactors: in the 1st reactor vaporized petroleum feed cracks on contact with hot catalyst, after which the compounds formed are transported to a regenerator where the carbon deposit on the catalyst is reduced by burning in air. The heated particles, i.e. the catalyst, are returned to the 1st reactor. Other processes which also separate fractions include the fluid coking and flexi-coking processes (separate gas oil from coke particles), and the thermal cracking processes (separate petroleum fraction to produce ethylene and propylene).

2.4.3.5 Use of the fluidized bed reactor in combustion and incineration

Fluidized bed combustion (FBC) was first researched in the early 1960s in an effort to find a combustion process suitable for low grade coal and oil shale fines. In the

FBC, limestone or dolomite particles are fluidized by air, and then small coal particles are injected into the bed.

A fluidized bed reactor was therefore chosen as the reactor for gas phase extraction of metals because of the advantages offered in the discussion above. Use of a fluidized bed reactor ensures that temperature gradients are minimized and that adequate particle mixing to ensure reaction with the ligand is achieved.

3 EXPERIMENTAL PROCEDURE

The process of extraction of metals from their oxides by acetylacetone was carried out in a fluidized bed reactor. The oxides used were iron(III) oxide and chromium(III) oxide. The parameters which were investigated for their effect on the rate of the reaction are:

- Concentration of the metal oxide in the fluidized bed - The concentrations used where chosen to represent concentrations found in different types of low grade ores. Variations of low, medium and high concentrations were used.
- Effect of bed temperature in the fluidized bed reactor on the extraction of metals by acetylacetone - This involved varying the operating temperature from 190˚C to 250˚C.
- Effect of concentration of the acetylacetone – The concentration was varied at low and medium flow rates (1ml/min and 3ml/min respectively) for the experiments where high and medium metal oxide concentration was used.
- Effect of time on the reaction - This involved, for each of the different temperatures, collecting and analyzing the product formed at 15-30 minute intervals for up to 4 hours of reaction. This was to allow for sufficient time for the reaction.

The experimental setup was therefore designed to achieve the requirements of the experimental objectives mentioned above.

3.1 Experimental setup

3.1.1 Process flow chart

The process flow sheet for the extraction of metals from their oxides by acetylacetone into the gas phase is shown in Figure 3-1

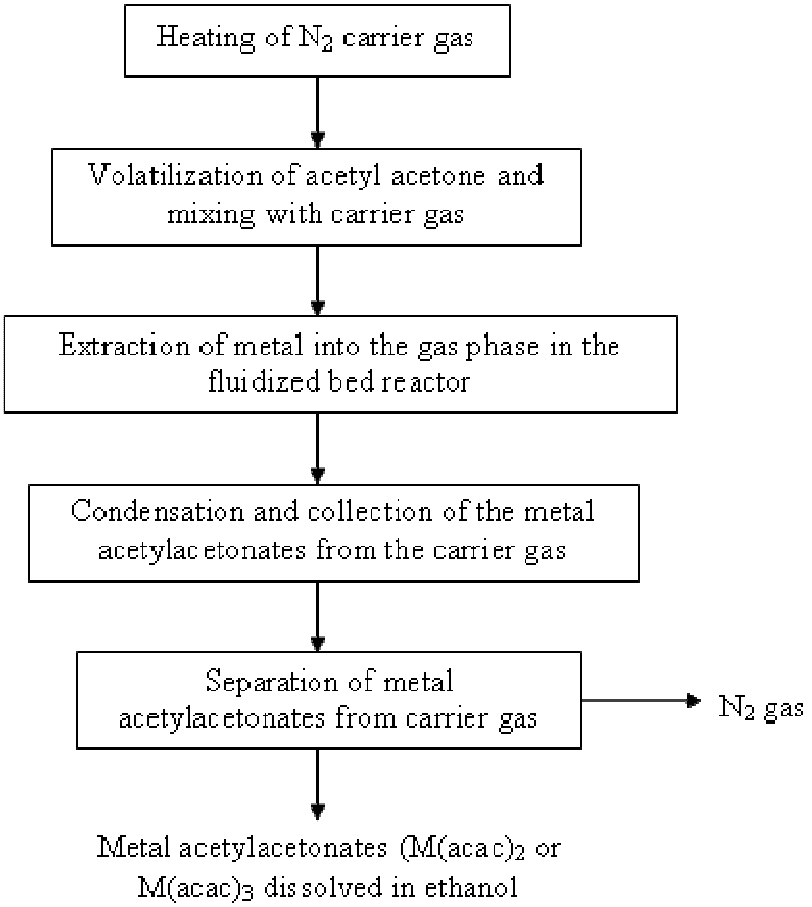


Figure 3-1 Process flow sheet for metal extraction in a fluidized bed reactor

It is possible after extraction of the metal to separate the metal from the ligand, thereby recovering the ligand for possible recycling. However, that is not the purpose

of the present research and consequently the metal acetylacetonate is recovered for analysis. Additionally, the use of a carrier gas is optional, since at the temperatures used for gas phase extraction both the ligand and metal complex formed are gasified.

3.1.2 Apparatus

The process of gas phase extraction was carried out in a fluidized bed reactor (FBR). The fluidized bed reactor consisted of a cylindrical Pyrex glass column 50 mm long and 15 mm in diameter which is tapered at both of its ends. Midway along the length of the FBR a thermocouple was inserted into the FBR, whose function was to measure the temperature in the FBR during the course of the gas phase extraction. Heating tape was coiled around the length of the FBR and connected to a temperature controller. This controller, together with the thermocouple in the FBR, kept the temperature close to the set point by regulating the amount of heat provided by the heating tape. The FBR and heating tape were wrapped with ceramic wool which served as an insulator and minimized heat loss. The fluidized bed was connected to a round bottomed flask through its bottom taper, through which the ligand and carrier gas were fed to the bed. The round bottomed flask was heated by sitting it on a heating mantle which provided the heat to vaporize the ligand. The list of major equipment used is as follows:

- Two N_2 gas flow meters; gas flow range 0-50 ml
- Heating mantle to heat the acetylacetone to above 140°C i.e. its boiling point

- 1/8 inch stainless steel tubing, through which N_2 passes to the flask containing the ligand
- Type K thermocouples, used to measure the temperature in the heating mantle and in the fluidized bed reactor.
- Temperature readout to record the temperature from the thermocouples (in the round bottomed flask)
- Temperature controller to regulate the temperature along in the fluidized bed
- Flow control valves including an open/close valve, a three way ball valve and a check valve to control direction of gas flow.
- Pressure regulator to regulate the pressure of the N_2 carrier gas as it leaves the gas cylinder.
- Peristaltic pump to control the flow rate of the ligand into the flask.

The general schematic diagram of the apparatus is shown in Figure 3-2:

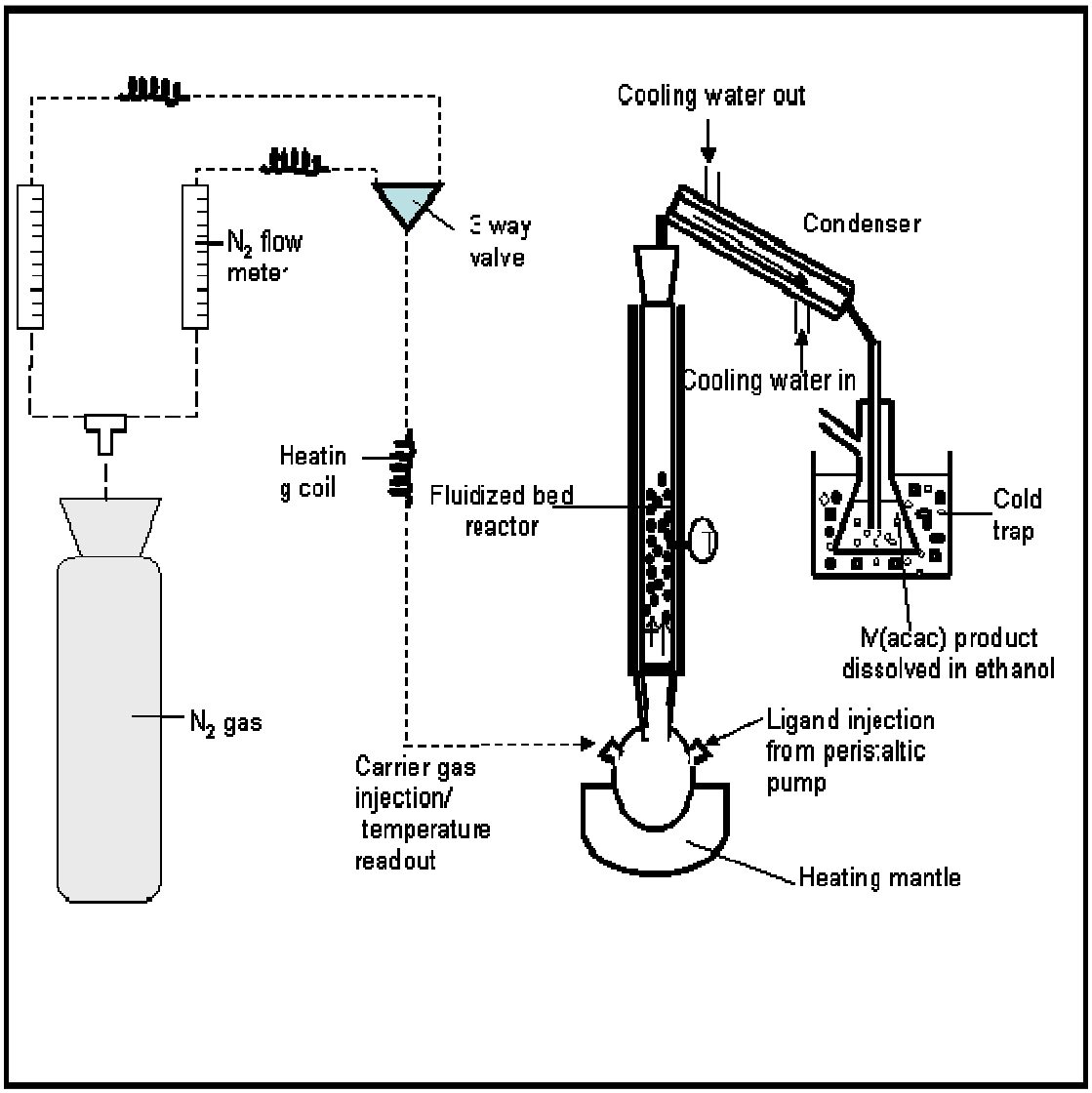


Figure 3-2 Schematic diagram of gas phase extraction

The experimental setup shown in Figure 3-2 was finally arrived at as a modification of the one proposed by Kabemba (2005). The one proposed was discarded because once volatilised the ligand expanded both into the fluidized bed and into the tubing supplying the carrier gas. It was observed that the ligand reacted with the stainless

steel tubing. As a result the setup finally used in this work comprised of only glass and silicon tubing which are both inert to the ligand.

3.2 Materials Description

The main chemicals used for the process of gas phase extraction included the metal oxides (Fe_2O_3 & Cr_2O_3), the ligand acetylacetone, and the solvent ethanol. The material safety data sheets for these chemicals are given in Appendix B. The properties of the metal oxides and are shown in Table 3-1:

Table 3-1 Properties of Fe_2O_3 and Cr_2O_3

	Fe_2O_3	Cr_2O_3
Chemical purity	97%	99%
Formula weight	159.69	151.99
Density	5.12g/cm^3	5.21g/cm^3
Melting point	1538°C	2435°C

The melting points of the two oxides show that throughout the process of gas phase extraction the oxides remain in the solid state and hence the reaction between the ligand and the oxide is a gas-solid reaction. The properties of the ligand, and the solvent used for dissolving the metal complexes formed are shown in Table 3-2:

Table 3-2 Properties of acetylacetone and ethanol

	Acetylacetone	Ethanol
Chemical formula	$C_5H_8O_2$	C_2H_6O
Purity	99%	99.8%
Boiling point	136-138°C	78-80°C
Vapour pressure(20°C)	800Pa	5950Pa

To simulate low grade ores and slags the metal oxides were mixed together with sand. The composition of the sand is shown in Table 3-3:

Table 3-3 Composition of the silica sand used

	% Composition
SiO_2	98.01
Al_2O_3	0.3
Fe_2O_3	0.6
ZnO	0.001
CaO	<0.01
MgO	<0.001
L.I.O	0.12
Average Uniformity coefficient	<1.4
Friability	<0.7°

3.3 Experimental design

The reaction of the metal oxide with the ligand is a gas-solid reaction and it is assumed that the reaction is either limited by the diffusion of the gas through the film surrounding the solid particle or the chemical reaction between the solid particle and the ligand. To test which of the resistances limit the reaction, different experimental conditions have to be used in order to limit the effect of the various resistances.

3.3.1 Gas film diffusion controlling

Gas film control can be checked by reacting similarly sized particles using different gas velocities because the mass transfer coefficient in a reaction is dependent on the linear velocity of the gas passing the particle (Szekely *et al*., 1976). If similarly sized particles are reacted at the same temperature at different gas velocities and it is noticed that the extent of reaction is different for the different gas velocities, the reaction is influenced by diffusion of the gas through the gas film surrounding the particle. Once it has been established that a reaction is mass transfer controlled, mass transfer effects can be minimized by operating the gas-solid reaction system at sufficiently high gas velocities, so that any further increase in the gas velocity does not produce an increase in the overall reaction rate (Szekely *et al.*, 1976). This will then enable one to check if there are other resistances which limit the rate of the reaction.

3.3.2 Chemical reaction control

Chemical reaction control can be checked by the determination of the kinetic parameters for the chemical reaction. Kinetic parameters cannot be predicted or estimated, they can only be determined experimentally. Kinetic parameters can be measured by carrying out experiments under otherwise fixed conditions with small but varying particle size of the oxide, i.e. at fixed gas velocities and temperatures so that the effect of gas film diffusion control are minimized. This will enable one to calculate the value of the rate constant *k* (Szekely *et al.,* 1976). Conducting similar experiments at different temperatures can be used to calculate the activation energy associated with that rate constant.

3.4 Experimental method

1. The fluidized bed reactor was charged with the feed, which consisted of a mixture of sand and metal oxide. In all cases the total mass charged was 50g; with the metal oxide concentration varying at 1wt%, 3wt% and 10wt%.
2. Once the FBR was charged all the equipment was connected and the FBR preheated to the required reaction temperature, i.e. 190°C, 210°C, 230°C and 250°C for the different experimental runs. The heating mantle was also switched on.
3. Once the required set temperature in the FBR was reached, the reaction was started by switching on the pump and pumping the ligand into the heating

mantle at the appropriate ligand flow rate. The ligand flow rate was varied, with flow rates of 1 and 3ml/min being used.

4. After each time interval (0-15min, 15-30min, thereafter 30 min intervals up to 120 min followed by 60min intervals up to 240min) the ligand supply pump was switched off and the system was left to stand for a period of about 5minutes. During this time any remaining product within the reaction zone was allowed to evaporate and be carried away to the collection beaker.
5. The sample was collected and fresh solvent put into the collection flask and the flask reconnected to the equipment. The pump was then started for the next interval in the reaction.

3.5 Experimental conditions

The major variables investigated included the effect on metal oxide concentration, ligand concentration and time on the process of gas phase extraction. The effect of carrier gas on the amount of metal recovered was also investigated. A summary of the conditions used to test the effect of the variables is given in Table 3-4:

Table 3-4 Values of the experimental variables used

Metal oxide concentration (wt%)	Temperature (°C)	Ligand flow rate (ml/min)	Time (hrs)
1, 3, 10	190, 210, 230, 250	1, 3	2, 4

3.6 Analysis of the product

The previous groups that have studied extraction in the gas phase have analysed their samples using UV spectrometry (Allimann-Lecourt *et al.,* (2002); Potgieter *et al.,* (2005)). Initially both UV and AAS were used, but AAS was finally chosen as the best analytic technique because it has now become one of the most efficient and sensitive approaches to determining metals in organometallic compounds (Hassan, 1984).

3.6.1 Atomic Absorption Spectrometry

Atomic Absorption Spectrometry is the measurement of the absorption of optical radiation by atoms in the gas phase (Welz, 1984). AAS is a flame method of analysis which uses flames to convert samples and standards into appropriate media which can produce measurable absorption i.e. the active entities (Ramirez-Munoz, 1969). The entities then absorb radiation at characteristic wavelengths, whose intensity can be related to the concentration of the absorbing entities.

The source of radiation in AAS is provided by a hollow cathode lamp, whose cathode is either made up of the analyte metal, or filled with it; whilst the anode is either tungsten or nickel (Welz, 1984). The hollow lamp also contains pressured inert gas (carrier gas) which generates positive ions that release atoms of the cathode on collision. Once the atoms from the cathode meet with the excited noble gas their spectral lines are radiated.

The emission spectrum from the radiation source is then passed through an absorption cell where a portion of the radiation is absorbed by the atoms from the sample whose concentration is to be determined. The atoms are produced by spraying the sample into the flame by means of a pneumatic nebulizer (Welz, 1985; Ramirez-Munoz, 1969). The nebulizer produces a stable time-dependent signal whose height is proportional to the concentration of the analyte material.

After analysis and collection of the experimental data the results were analyzed. The results and discussion of results follow in the next chapter.

4 RESULTS AND DISCUSSIONS

Gas phase extraction was carried out on two different metal oxides, iron(III) oxide and chromium(III) oxide. Iron(III) oxide was chosen partly because it is known that it readily reacts with acetylacetone (Cox, 1985), and because there is a large volume of waste (slag, tailings, etc) that contains iron oxides. Chromium(III) was chosen because it has the same oxidation state as iron(III) oxide which readily reacts with acetylacetone; and it was expected it would undergo similar reactions as the iron(III) oxide. The results of the iron and chrome extraction experiments are presented and discussed in this chapter.

4.1 Extraction of Iron

The extraction of iron from Fe_2O_3 using acac in the gas phase occurs according to the stoichiometric reaction

$$Fe_2O_{3(s)} + 6Hacac_{(g)} \rightarrow 2Fe(acac)_{3(g)} + 3H_2O_{(g)} \qquad \textbf{(4-1)}$$

The extraction was investigated and the results obtained are described in this chapter. The influence of various parameters, such as temperature, concentration of the reactant and flow rate of the ligand were evaluated and determined. The cumulative extraction in the graphs to follow is defined as a percentage of the total mass of metal extracted divided by the amount of metal initially present in the charge. For all the experiments carried out, the total amount of ligand passing through the system was in

large excess compared to the stoicheometric reaction amount required. The calculation of the amount of ligand required for complete reaction for the different charges of metal oxide used is given in Appendix C.

The reaction of Fe_2O_3 with acac produces a metal complex which is red in colour. For most of the experiments, the progression of the reaction could be followed by observing the colour of the product stream; the reaction proceeding rapidly in the initial stages, shown by the intense red colour of the product; then gradually slowing down as more time elapsed. For the preliminary experiments the reaction was assumed to have gone to completion when the colour of the product stream was off-white (yellowish); which is the colour of the acac when it has been heated up.

4.1.1 Effect of temperature on extraction

Gas phase extraction of iron from the metal oxide at different temperatures for different metal oxide feeds (1wt%, 3wt% & 10wt %) was carried out at a constant ligand flow rate (1ml/min). This resulted in different extraction rates as shown in Figure 4-1.to Figure 4-3

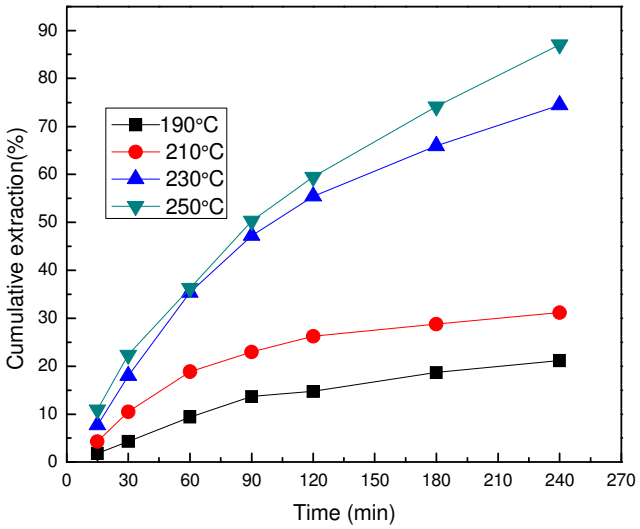


Figure 4-1 Effect of temperature on extraction for a 1wt% Fe_2O_3 mixture

The extraction is clearly dependent on the reaction temperature as can be seen from Figure 4-1. Extraction is higher at higher temperatures; with an increase in temperature from 190°C to 250°C resulting in the amount of iron extracted increasing. For all four temperatures investigated, the reaction is initially rapid before it slows down, indicated by a flattening of the graphs. The difference in extraction between 210°C and 230°C is distinctly visible in Figure 4-1, with the extraction after 4hrs more than double i.e. 31% compared to 74%. This increase in extraction suggests that between the two temperatures there is a potential energy barrier required for the extraction to occur. This barrier is achieved by more atoms at higher temperatures than is achieved at the lower temperatures of 190°C and 210°C. The increase in extraction with an increase in temperature implies a chemically controlled

process because such processes are known to be highly dependent on the operating temperature.

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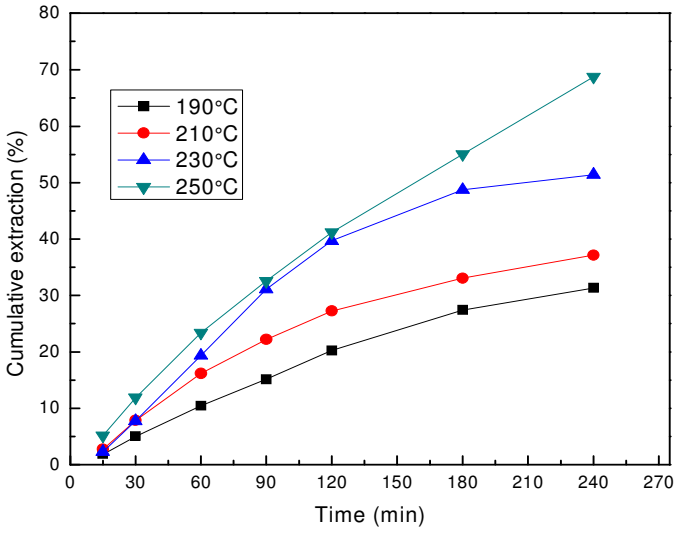


Figure 4-2 Effect of temperature on extraction for a 3wt% Fe_3O_2 mixture

For the 3wt% metal oxide mixture, the graphs are similar to those for extraction with 1wt%, with higher extraction occurring at higher temperatures. The graphs are also divided into two distinct regions, with the extraction almost doubling for the higher temperatures as compared to the lower temperatures. The total extraction however, is not as high as for the low iron(III) oxide charge (1wt%). This decrease in extraction at high charge feed implies that some other variable rather than temperature becomes limiting as the concentration of iron in the charge is increased.

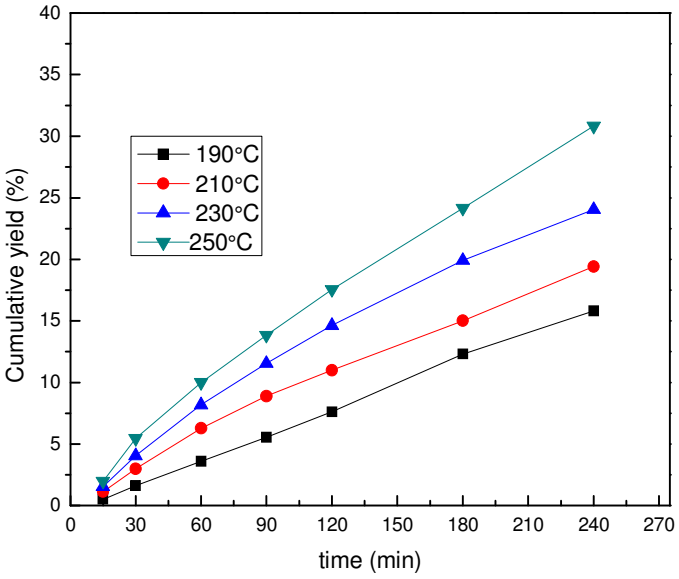


Figure 4-3 Effect of temperature on extraction for a 10wt% Fe_2O_3 mixture

Gas phase extraction of the 10wt% charge results in a maximum extraction of about 35% at 250°C after 4hours which is very low compared with the extraction for the low concentration charge mixtures. At this charge, the two distinct regions that were obvious before are not visible. The initial rate of reaction is not very fast as observed before, and none of the graphs start to flatten out as was previously observed. Rather, all the graphs appear linear and approach straight line functions.

Because of the low extraction observed for the high metal oxide charges, it was suspected that in addition to the extraction being influenced by the temperature it was also influenced by the ligand flow rate. Additionally, at high charge concentrations

more iron was extracted after 4hrs i.e. the actual mass/amounts extracted. The actual mass of iron extracted for the different charges is shown in Table 4-1

Table 4-1 Mass of iron extracted (g) after 4hrs for different charges at 1ml/min ligand flow rate

	1wt%	3wt%	10wt%
190°C	0.122	0.399	0.588
210°C	0.179	0.473	0.722
230°C	0.428	0.655	0.821
250°C	0.501	0.769	1.107

Table 4-1 shows that more iron is extracted when the amount of iron initially available in the feed is higher (in terms of total mass extracted). This can be explained by the fact that when there is more mass of Fe in the charge, the surface of Fe that is available for reaction with the ligand is more at a given ligand flow rate. Because the amount of surface available for reaction is more, more Fe will be extracted even when the flow rate of the ligand is kept constant.

The extraction of Fe from its oxide in the gas phase has been shown to be directly proportional to the temperature for all the different charges investigated. This temperature dependence has been shown in Figure 4-1 to Figure 4-3, where it was shown that the extraction of Fe generally increases as the temperature is increased. This temperature dependence can be expressed mathematically as

$$r \alpha T \qquad \textbf{(4-2)}$$

4.1.2 Effect of ligand flow rate on extraction

Once it was noticed that the flow rate of the ligand became limiting when the charge contained a higher concentration of metal, further experiments were carried out at higher ligand flow rates for the higher concentration charges (3wt% and 10wt%). The experiments were carried out at 250°C since this temperature is the one that produced the best extraction for the range of temperatures investigated. The effect of ligand flow rate is shown in Figure 4-4 and Figure 4-5

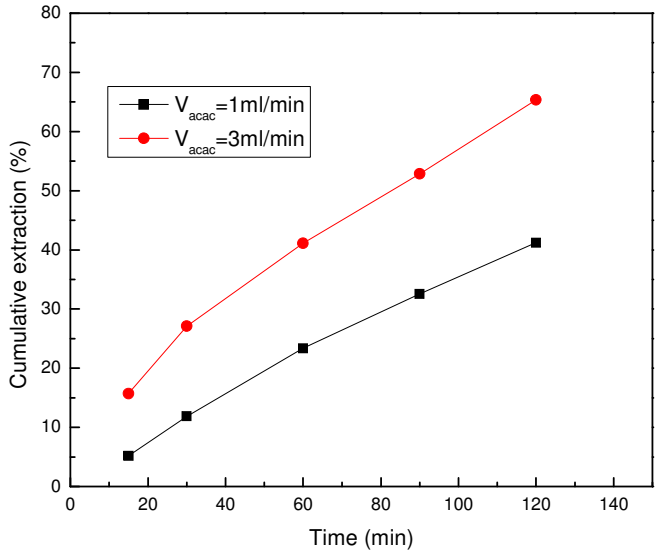


Figure 4-4 Effect of ligand flow rate on the extraction for a 3wt% mixture at 250°C

Gas phase extraction of iron at 3ml/min ligand flow rate results in the extraction increasing from about 38% to 65% after only 2hrs. At this higher ligand flow rate of

3ml/min, the initial rate of extraction is higher as compared to that at the low flow rate of 1ml/min as shown by the steeper gradient in the initial stages of the reaction.

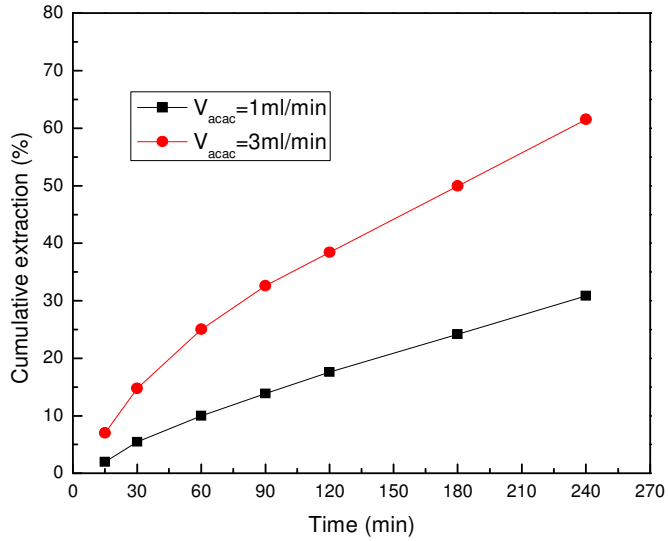


Figure 4-5 Effect of ligand flow rate on extraction for a 10wt% mixture at 250°C

Figure 4-5 also shows an increase in the initial rate of reaction when the flow rate of ligand is increased. The increase in extraction and rate of reaction when the ligand flow rate is increased can be explained by the fact that an increase in ligand flow rate means that there is more ligand available to come into contact with the solid oxide particles. At the lower ligand flow rate, although the ligand is present in excess, it probably quickly passes through the FBR reactor without having enough time to react with the oxide i.e. the residence time is insufficient for the reaction to occur. At high

flow rates the problem of residence time is partially solved since now there is more ligand available for it to react with the metal oxide.

Gas phase extraction of iron has been shown to depend on the concentration of the gas phase extractant acac. This concentration dependence has been shown in Figure 4-4 and Figure 4-5 where it was shown that by keeping the temperature and amount of metal oxide initially available constant and only changing the concentration of the ligand, the extraction of iron changed significantly after a given amount of time. The gas phase concentration dependence is summarised in Figure 4-6 where the effect of ligand concentration on the three feed masses is combined.

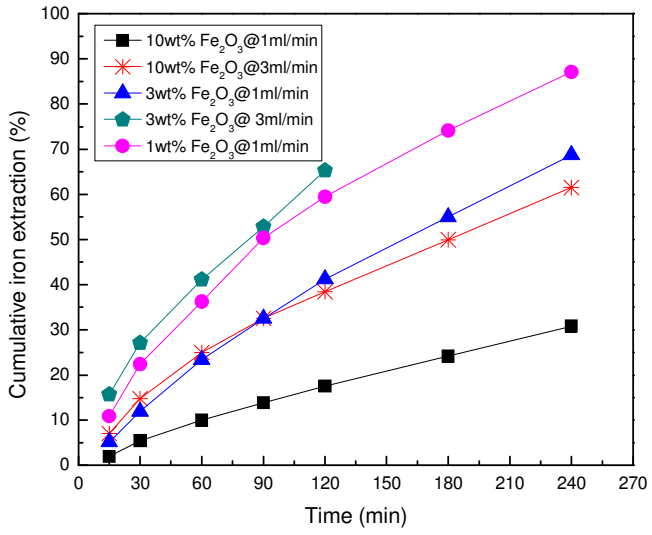


Figure 4-6 Effect of ligand concentration on extraction at 1wt%, 3wt% and 10wt% at 250°C

The increase in extraction when the ligand flow rate is increased implies a diffusion controlled process as hypothesized by Habashi (1969) who stated that a diffusion

controlled process is dependent on the gaseous reactant.The mathematical representation of the ligand concentration on the extraction can be expressed as

$$r \alpha C_{gas} \qquad \textbf{(4-3)}$$

4.1.3 Effect of carrier gas flow rate on extraction

Preliminary experiments were carried out with a carrier. No significant increase in the extraction of Fe occurred when the flow rate of the carrier gas was changed from 20 ml/min to 132 ml/min (Table 4-2). It was consequently decided to run the experiments without a carrier gas. After slight adjustments to the experimental setup the extraction of iron at the same reaction conditions using no carrier gas increased to 1.62%.

Table 4-2 Effect of carrier gas on extraction of Fe

N_2 flow rate	% extraction after 30mins
20ml/min	0.92
40ml/min	1.12
132ml/min	1.22

4.1.4 Effect of mass of oxide on extraction

The mass of the oxide was already shown to affect the extraction in Figure 4-1 to Figure 4-3 where the extraction was shown to decrease when the mass of oxide was increased. The effect of mass of metal oxide is shown in Figure 4-7

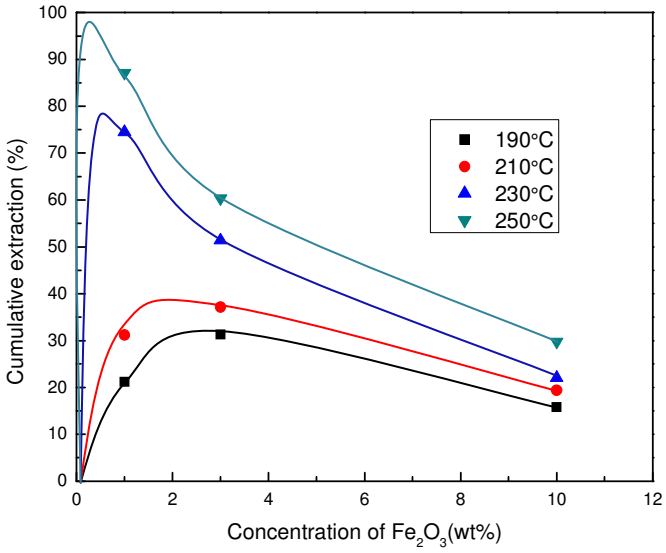


Figure 4-7 Effect of metal oxide concentration on extraction at 1ml/min flow rate after 4hrs

Figure 4-7 shows that as the concentration of iron in the charge is increased, the extraction of iron generally decreases. It appears that at the temperatures investigated, there is an optimum metal concentration in the feed that results in a maximum extraction being reached after which a further increase in metal oxide results in the extraction decreasing. After this optimum feed concentration, the extraction decreases linearly for all the temperatures investigated. Figure 4-7 shows that this optimum feed

concentration is very low, which implies that gas phase extraction will be particularly useful for the extraction of metals containing very low metal concentrations as compared to feeds containing high metal concentrations.

4.1.5 Surface area effect

The effect of surface area can be investigated by either:

i. Increasing the amount of Fe_2O_3 present in the charge and keeping all other experimental variables constant, or

ii. Carrying out experiments on the same mass of Fe_2O_3 in the charge, but with different particle sizes.

Gas phase extraction has already been shown to depend on the surface area available in Table 4-1 where it was shown that the mass of Fe extracted increases when the initial amount of Fe in the charge is increased and all other variables kept constant.

Experiments were also carried on two sets of particle size fractions to confirm the dependence of the reaction on surface area. The extraction was carried out on a mixture of sand and hematite. The hematite had a wide particle size range, which was classified into smaller size fractions by dry sieving. Extraction using different particle sizes is shown in Figure 4-8 and Figure 4-9.

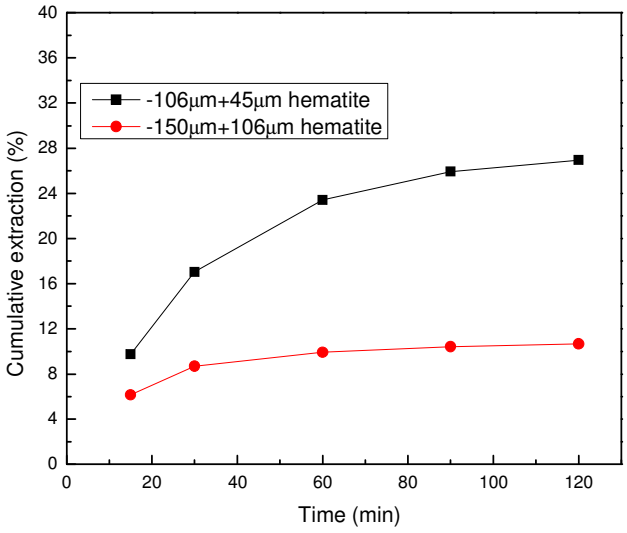


Figure 4-8 Effect of particle size on extraction at 3ml/min on a 3wt% mixture at 230°C

Figure 4-8 shows that when the particle size is decreased more of the Fe is extracted. More extraction occurs for the smaller sized particles (28%) as compared to the larger sized particles (10%) in the same amount of time This is because decreasing the particle size for the same mass results in an increase in the number of particles, and hence an increase in surface area, which allows for the ligand to come into contact with more surface of the particles to be extracted, resulting in an increase in extraction.

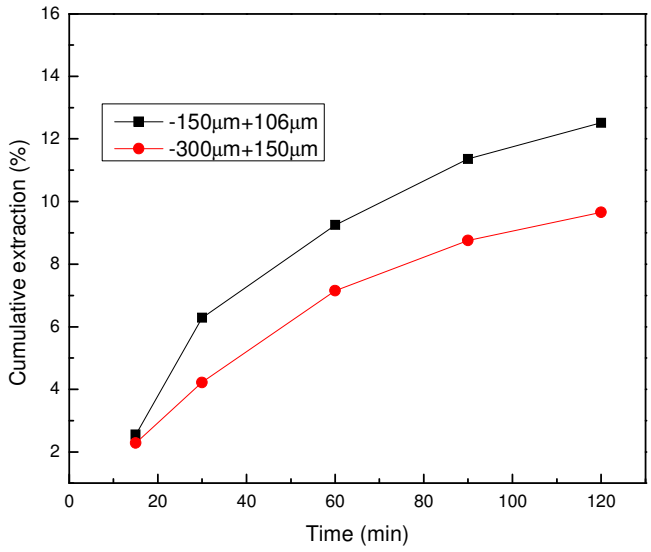


Figure 4-9 Effect of particle size on extraction at 3ml/min on a 3wt% mixture at 210°C

Figure 4-9 also shows that decreasing the particle size results in an increase in extraction (13% for -150µm+106µm as compared to 9% for 130µm+150µm). Additionally when comparing Figure 4-8 and Figure 4-9 the temperature effect on extraction can be clearly seen; with a higher extraction for the same particle size at higher temperatures.

Chemical reaction controlled processes are sensitive to a change in particle size (Szekely, 1976). The dependence of the reaction rate on the surface area available can be described mathematically as

$$r \alpha S_{ex} \qquad \textbf{(4-4)}$$

From the above discussion where the experimental observations are discussed, it is clearly evident that the gas phase extraction of iron is not controlled by only one variable. In order to come up with a kinetic model that accurately describes the process, all the variables that have an effect should be taken into account in the model.

It can be seen from the results presented that the time required to obtain reasonable extraction using gas phase extraction is much shorter than previously reported. Allimann-Lecourt *et al*. (1999) carried out experiments for 25hrs, whilst Hamblin and Posner (1979) carried out experiments for up to 8 days as compared to 4hrs in this study.

The development of a model for the extraction, together with testing some conventional models will be carried out in the next chapter.

4.2 Extraction of Chrome

Experiments were carried out for mixtures which contained 3wt% Cr_2O_3 at 3ml/min acac flow rate and two different temperatures 210°C and 250°C. These conditions were similar to the optimum conditions (3wt% Cr_2O_3, 6ml/min and 210°C) suggested

by Potgieter *et al.* (2005) for the extraction of chrome. The results are shown in Figure 4-10

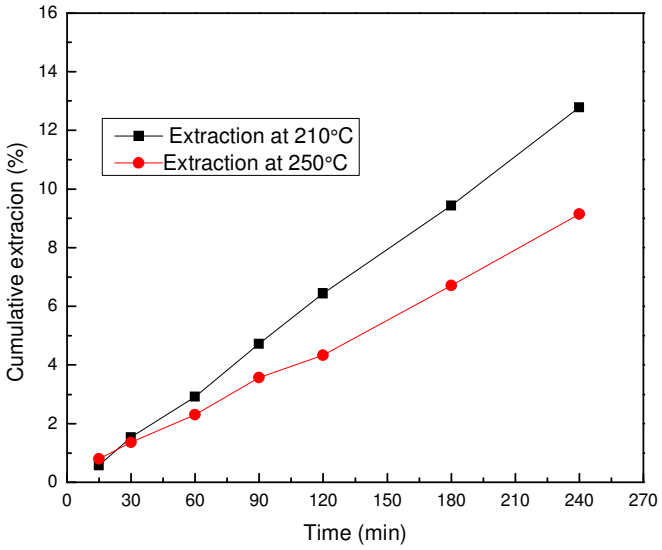


Figure 4-10 Extraction from a mixture containing 3wt% Cr_2O_3 at 3ml/min

Figure 4-10 shows that the extraction decreases when the temperature is increased from 210°C to 250°C. The lower extraction at the higher temperature could be because some of the $Cr(acac)_3$ product starts to dissociate at the higher temperature. The trend observed is in agreement to the one identified by Kabemba (2005), who showed that above 210°C, the extraction did not increase as compared to the lower temperatures he investigated, but instead the extraction appeared to be decreasing. From the figure it seems as though the extraction of chrome from chrome(III) oxide is a linear function of time for both temperatures. The results presented here are not in agreement with Potgieter *et al.* (2005) who obtained much higher extraction of

chrome, 48% after 150min at 210°C. No plausible explanation can be given for this deviation in results.

The extraction of chrome with acetylacetone produces results which might not be viable due to the low extraction amounts (12% at 210˚C and 9% at 250˚C after 4hrs). It is therefore suggested that an alternative ligand for Cr extraction be identified in future research. The results also suggested that it might be possible to preferentially extract Fe from a Fe_2O_3/ Cr_2O_3 mixture using acetylacetone. Consequently some experiments were performed using mixtures of Fe_2O_3 and Cr_2O_3.

4.3 Extraction from mixtures with chromium and iron

Gas phase extraction was also carried out using a charge that contained both iron(III) oxide and chromium(III) oxide. A constant concentration of Fe_2O_3 (5wt%) was used, whilst the concentration of Cr_2O_3 was varied. The results of this extraction are shown in Figure 4-11

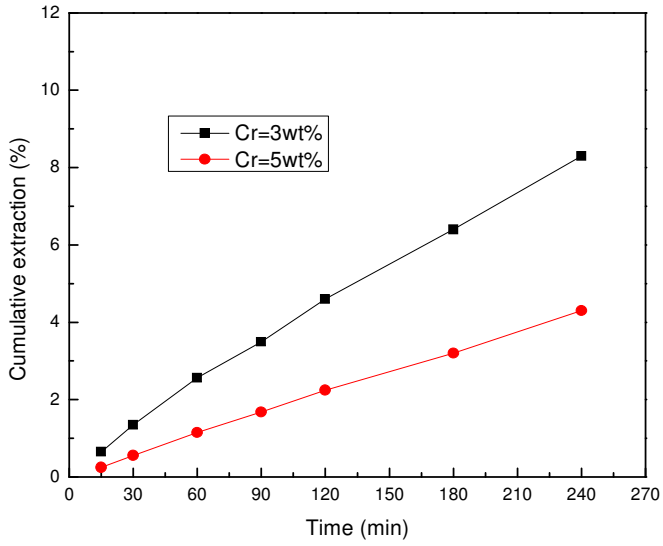


Figure 4-11 Extraction of Cr from a mixture containing Cr_2O_3 and 5wt% Fe_2O_3 at 3ml/min & 210°C

Figure 4-11 shows that the extraction of Cr is very low, with only a maximum of 8.3% extraction being achieved after 4hrs. However, this result agrees with the results shown previously for iron, where the extraction decreases as the amount of metal oxide in the charge is increased. The results confirm the trend already identified that the extraction decreases when the amount of metal oxide initially present in the charge is increased.

When comparing Figure 4-10 and Figure 4-11, the extraction at 210°C decreases from about 13% to 8% when iron(III) is introduced to the feed. This is because the acetylacetone is now reacting preferentially with the iron, resulting in less of it being available to react with the chrome.

The amount of iron and chrome extracted for this experiment is shown in and the actual mass extracted is shown in Appendix C.

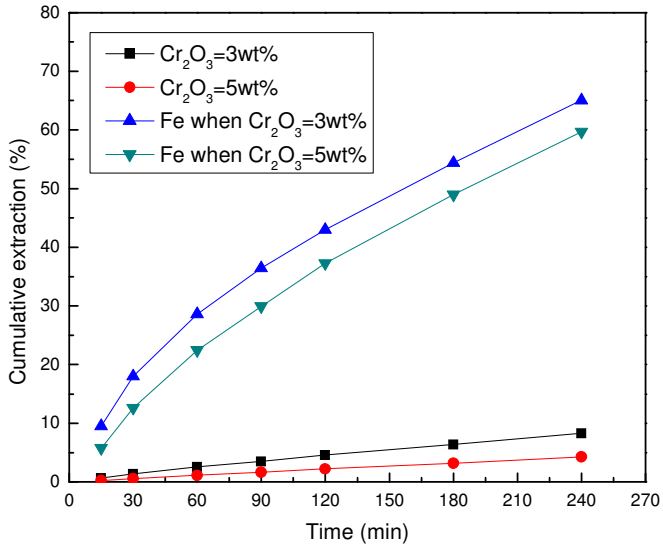


Figure 4-12 Extraction of Fe and Cr from mixtures containing Cr_2O_3 & 5wt% Fe_2O_3 at 3ml/min & 210°C

Fe_2O_3 mixed with Cr_2O_3 at 3ml/min ligand flow rate reacted preferentially, resulting in quite a high extraction of iron at 210°C (max 65% after 4hrs). In Figure 4-12 the amount of iron extracted decreases when the amount of chrome in the feed is increased, i.e. there is more extraction at 3wt% Cr_2O_3 compared with at 5wt% Cr_2O_3. This result suggests that although Fe will be extracted preferentially from Fe_2O_3/ Cr_2O_3 mixtures, higher extraction will be expected to occur in mixtures containing lower amounts of Cr.

Additionally iron was extracted from mixtures where initially there was no Fe_2O_3 added. This extraction was attributed to the fact that the sand used in the charge contained small amounts of Fe_2O_3 (0.6%) and the iron was being extracted from this sand. This extraction at very low Fe_2O_3 is in agreement with previous work which shows that when using the ligand acac iron will be preferentially extracted even from charges that contain very low iron (Cox *et al*., 1985).

5 KINETIC MODELLING OF THE EXTRACTION OF IRON

Several reaction models have been proposed for gas-solid reactions, including the classic shrinking core model. In addition, several models have also been proposed that take into account the equipment being used. Khani *et al.* (2007) carried out fluorination of uranium in a fluidized bed reactor, and they postulated that the fluid in the fluidized bed could behave as either a fluid in plug flow or in a continuous stirred tank reactor. Some of the classic models given in literature, together with those that take into account the equipment; will be tested for their fit on the experimental data obtained in the gas phase extraction of iron. The data used to model the extraction was that obtained at 1wt% Fe_2O_3 because those experiments neared completion as compared to those at other Fe_2O_3 concentrations.

5.1 General rate equation

The rate of a chemical reaction is the rate of change in concentration of a reactant or a product, i.e.

$$rate = \frac{-d[\text{reactant}]}{dt} = \frac{d[\text{product}]}{dt}$$

The rate law in general may be written as

$$\frac{dX}{dt} = k(B_g, T) f(X) \qquad \textbf{(5-1)}$$

where

k is the apparent rate constant which takes into account the effect of temperature and gas phase reactant

$f(X)$ describes changes in physical or chemical properties of the sample as the reaction proceeds

The rate constant is dependent on the temperature and is given as

$$k = k_0 e^{E_a/RT} \qquad \textbf{(5-2)}$$

where

k_0 is a pre-exponential factor

E_a is the energy of activation

R is the gas constant

T is the absolute temperature

This equation gives the temperature dependence of the rate constant, hence of the chemical reaction.

The reaction between a solid and a gas is a heterogeneous reaction which could be any one of three types

$$aA(fluid) + bB(solid) \rightarrow fluid\ products$$
$$\rightarrow solid\ products$$
$$\rightarrow fluid\ and\ solid\ products$$

In the case of reaction of metals with ligands, the solid product is formed if the metals/solids contain some foreign particles that do not form complexes with the ligand being used. It is assumed the soil matrix contains no metals that can react with the ligand hence the reaction only takes place with the metal oxide.

In the development of a model for the gas solid reaction, the model chosen must be able to interpret experimental kinetics, provide indications of the rate controlling mechanisms, and predict the kinetics of conversion under different operating conditions (Patisson & Ablitzer, 2000).

The major models that have been developed for non-catalytic fluid–solid reactions are the shrinking core, shrinking particle, homogeneous and grain models. The shrinking core model (SCM) is applicable to an initially non-porous particle, which reacts with a reagent leaving a reacted layer around the unreacted core. The shrinking particle model is similar to the SCM except that no product layer is left around the unreacted core. The homogeneous model is applicable to a solid with a homogeneous distribution of pores, where diffusional gradients may exist within the pores (Doraiswamy & Sharma, 1984)). The grain model is applicable to a solid consisting of individual dense grains compacted together. Among these models, the SCM has

been widely used in the area of hydrometallurgy to model leaching systems (Gbor and Jia, 2003).

5.1.1 The shrinking core model for chemical reactions

Traditionally, reactions involving solids and fluids have been modelled using the shrinking core models for chemical reactions developed by Levenspiel. The shrinking core model envisions a chemical reaction of the form

$$A_{(g)} + bB_{(s)} \rightarrow cC_{(g)} + dD_{(s)}$$

The model assumes that during the course of the reaction an ash layer is formed around a shrinking core of unreacted solid reactant. As a result, as the reaction progresses, the ash layer steadily increases inward towards the shrinking core, until all of the reactant solid is reacted. It is envisioned the major resistance to the reactions are as follows:

i. The diffusion of the reactant gas A to the surface of the solid through the gas film surrounding the particle
ii. The diffusion of the reactant gas through the solid ash layer to the reaction surface at the unreacted core
iii. Reaction of the gaseous reaction A at the reaction surface of the unreacted core with solid B
iv. Diffusion of the gaseous product from the surface of the unreacted core through the ash layer back to the outer part of the ash layer

v. Diffusion of the gaseous product through the gaseous film surrounding the particle.

Depending on the reaction occurring, one, or a combination of the resistances mentioned above will control the reaction, and hence can be used to develop a model that will predict how that particular chemical process will proceed with time.

In the gas phase extraction of metal oxides by acac ligand, the only products formed are gaseous products, hence the reaction occurring will be of the form

$$A_{(g)} + bB_{(s)} \rightarrow cC_{(g)} + dD_{(g)}$$

The reaction will be controlled by any of three possible resistance; the chemical reaction itself, diffusion through the fluid film surrounding the particle, or diffusion through the ash layer of product. Since no solid product is left behind, it will be assumed all product formed is immediately turned into the gas phase. When the *chemical reaction controls*, the process can be modelled as

$$kt = 1 - (1 - x)^{1/3} \qquad \textbf{(5-3)}$$

When diffusion through the *gas film controls*, for small particles in the Stokes regime, the process can be modelled as

$$kt = 1 - (1 - x)^{2/3} \qquad \textbf{(5-4)}$$

When *diffusion through the solid controls*, the reaction can be modelled as

$$kt = 1 - \tfrac{2}{3}x - (1 - x)^{2/3} \qquad \textbf{(5-5)}$$

where

x is the fractional conversion of the solid

When both the chemical reaction and diffusion through the gas film controls, the overall resistance can be taken as the sum of the two individual resistances since the resistances occur in series and hence can be assumed to be additive (Szekely *et al.*, 1976).

5.1.2 The grain model for chemical reactions

In many gas-solid reactions the solid is porous, allowing diffusion and chemical reaction to occur simultaneously throughout the solid resulting in the reaction occurring in a diffuse zone rather than at a sharp boundary as assumed by the shrinking core model (Szekely *et al.*, 1976). This model assumes that the particle is made up of a large number of grains, which might differ in both size and shape, through which the gas has to diffuse in order to react. Reaction of the pores with the gaseous reactant is affected by any of the following steps:

1. The gaseous reactant diffuses through a boundary layer surrounding the solid particle and enters the pores between the grains.
2. The gaseous reactant diffuses through the pores.
3. The gaseous reactant diffuses through the shell of solid product surrounding the core of unreacted solid within a grain.
4. Reaction takes place at the spherical reaction interface within the grain.

5. The gaseous product diffuses back into the bulk gas stream by the reverse of steps 1 to 3.

For a reaction where the particles have a high porosity, low specific surface area, or low pore diameters occurring at moderate temperatures, Evans *et al.* (1976) have suggested step 4 in the sequence, chemical reaction will control the process. For such a reaction, the process can be described according to the equations

$$g(x) = \frac{kC_{AO}S_A}{F_g}t$$

$$g(x) = 1-(1-x)^{1/F_g} \quad \textbf{(5-6)}$$

where

F_g is the shape factor for the grain, which is 3 for spherical particles

S_A is the specific surface area of the solid

5.1.3 Fluidized bed reactor models

Khani *et al.*, 2007 carried out the fluorination of uranium (a gas solid reaction) in a fluidized bed reactor. They derived models that take into account the type of flow occurring in the reactor in order to come up with models to predict the behavior of the fluorination.

The rate of a non-catalytic gas-solid chemical reaction can be written as

$$-r'_F = k\cdot\eta\cdot C_A = k\cdot\eta\cdot C_{A0}(1-X_A) \quad \textbf{(5-7)}$$

where

k is the reaction rate constant

C_{AO} and C_A is the initial concentration and the concentration of the gas at any given time

η is the effectiveness factor which takes diffusion effects into account

The flow of fluid in a fluidized bed reactor can be assumed be to either plug flow, or perfectly mixed as in a continuous stirred tank reactor. Assuming that the reaction is 1st order, conversion can then be modelled using the following equations:

For plug flow:
$$\tau.k.\eta = \ln\left(\frac{1}{1-X_A}\right) \qquad \textbf{(5-8)}$$

For mixed flow:
$$\tau.k.\eta = \frac{X_A}{1-X_A} \qquad \textbf{(5-9)}$$

For processes where external diffusional effects are negligible, the process will be controlled by the chemical reaction and the effectiveness factor can be taken as unity (Khani *et al.*, 2007). The above equations can then be used to calculate the rate constant (k) of the reaction for plug flow or mixed flow assuming the rate of reaction is controlled by the chemical reaction.

5.1 Modelling the extraction of iron

The gas phase extraction of iron from iron(III) oxide was modeled using the shrinking core model, assuming chemical reaction controlled or gas diffusion

controlled rate of reaction. These two models were chosen because they take into account the conversion of the solid which could be calculated using the amount of product formed and the original amount of metal in the feed. The grain model assumes that the Fe_2O_3 is porous and was therefore not considered. The fluidized bed reactor models was setup using the product (gas) concentration and therefore requires the analysis of the fluid product. The experimental setup did not have an on-line gas analyzer and could therefore not provide the data needed to fit this model.

5.1.1 Shrinking core model - Chemical reaction controlled

The experimental data points for the 1wt% Fe_2O_3 charge and 1 ml/min acac flow rate at various reaction temperatures were used to determine the reaction rate constant *k* for a chemical reaction controlled rate of reaction (equation 5.3). The value of *k* (gradient of plot) was obtained from the plot of $1-(1-x)^{1/3}$ (y-axis) vs. *t* (x-axis) using the experimental data points. The values of k as determined at various temperatures are given in Table 5-1.

Table 5-1Reaction rate constants under chemical reaction control for the shrinking core model

Temperature	190°C	210°C	230°C	250°C
k	**0.000306**	**0.000428**	**0.00148**	**0.00197**
Regression coefficient R^2	0.927	0.842	0.967	0.997

From Figure 5-1 to Figure 5-3 it can be seen how the fitted model compares to the experimental data points.

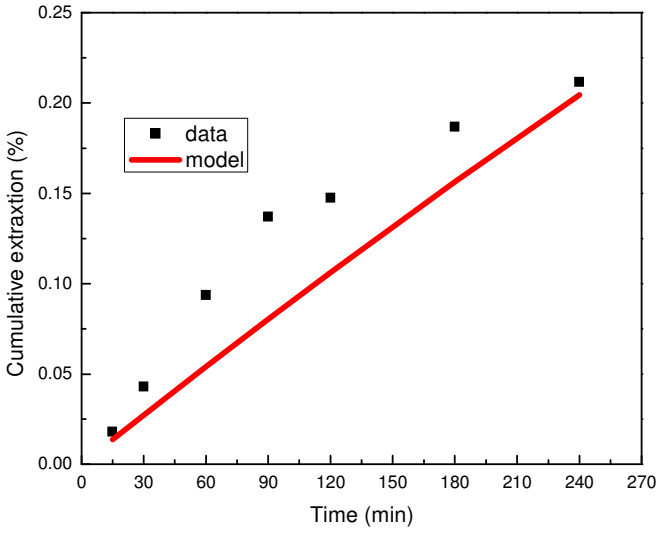


Figure 5-1Comparison of conversion predicted by chemical reaction control model with actual data obtained at 190°C

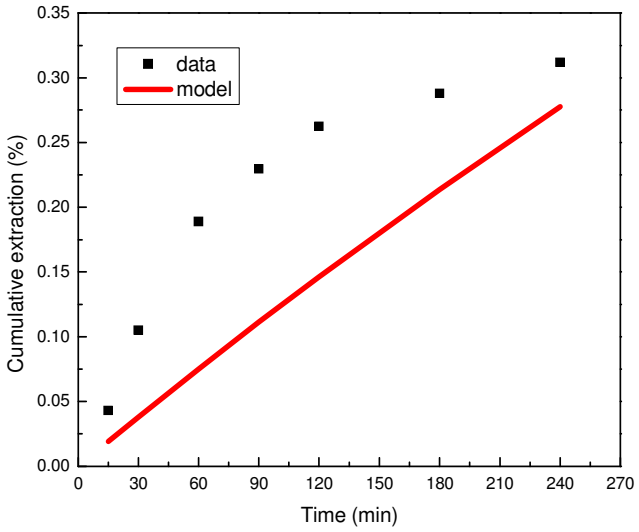


Figure 5-2 Comparison of conversion predicted by chemical reaction control model with actual data obtained at 210°C

From Figure 5-1 and Figure 5-2 it is clear that the chemical reaction model under predicts the extraction compared with what was experimentally observed. This is especially evident at 210°C where the values predicted by the model are much lower than those obtained experimentally.

For the higher temperature extraction experiments (230°C and 250°C), the chemical reaction control model appears to fit much better than for the lower temperature experiments. This is shown in Figure 5-3 and Figure 5-4

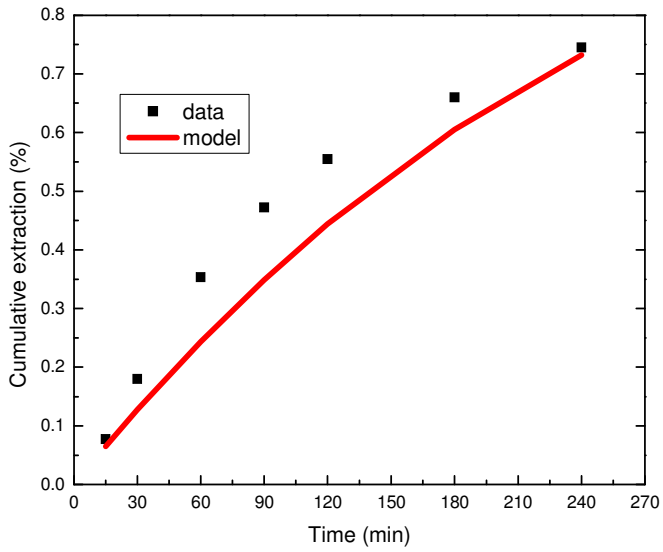


Figure 5-3 Comparison of conversion predicted by chemical reaction control model with actual data obtained at 230°C

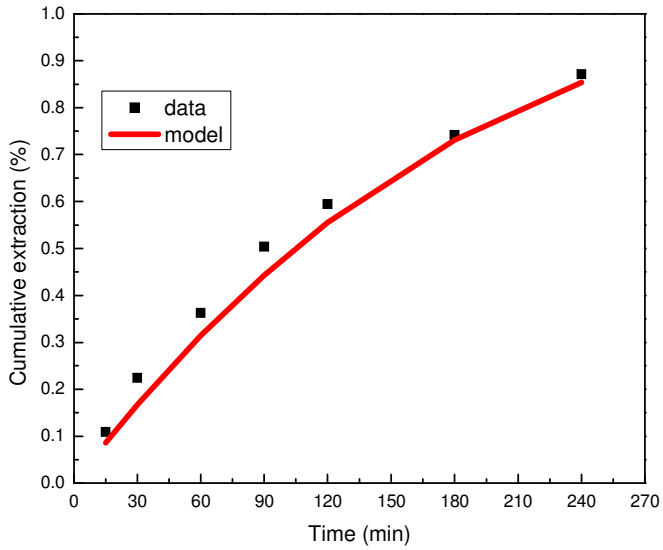


Figure 5-4 Comparison of conversion predicted by chemical reaction control model with actual data obtained at 250°C

The values of the extraction predicted by the chemical reaction control model do not differ greatly from the experimental results obtained at high temperatures.

The values of k obtained under chemical reaction control were used to calculate the activation energy of the reaction using Equation 5-2. The activation energy predicted using this equation is shown in Figure 5-5

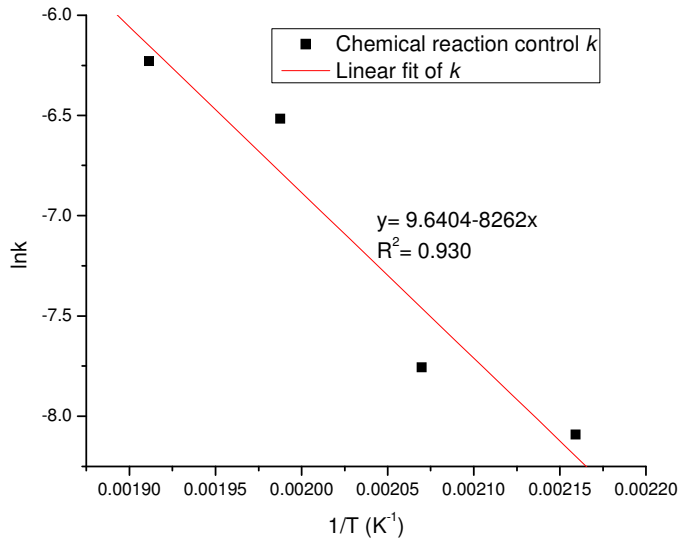


Figure 5-5 Arrhenius plot for chemical reaction control model at 1wt%Fe_2O_3 and 1ml/min ligand flow rate

The activation energy calculated using the Arrhenius plot is 68.69kJ/mol for chemical reaction controlled. The activation energy of a chemical controlled process is characteristically >41.84kJ/mol, while for a diffusion controlled reaction it is usually 4-12kJ/mol, and for an intermediate process about 20-34kJ/mol (Habashi, 1969). The activation energy control is within the range for a process controlled by the chemical reaction. Additionally, chemical control can also be assumed because chemically controlled processes are known to be highly temperature dependent (Habashi, 1969; Rosenqvist, 1974; Wen, 1968). The gas phase extraction is indeed highly temperature dependent, as was shown in Figure 4-1 to Figure 4-3.

5.1.2 Shrinking core model -Gas film diffusion controlled

The experimental data points for the 1wt% Fe_2O_3 charge and 1 ml/min acac flow rate at various reaction temperatures were also used to determine the reaction rate constant *k* for a gas diffusion controlled rate of reaction (equation 5.4). The value of *k* (gradient of plot) was obtained from the plot of $1-(1-x)^{2/3}$ (y-axis) vs. *t* (x-axis) and these values at different temperatures are given in Table 5-2

Table 5-2Reaction rate constants under gas film diffusion control for the shrinking core model

Temperature	190C	210C	230C	250C
k	0.000586	0.000787	0.00237	0.0029
Regression coefficient R^2	0.921	0.921	0.941	0.985

A similar analysis as the one carried out in the previous section was carried out and the graphs are shown in Figure 5-6 to Figure 5-9

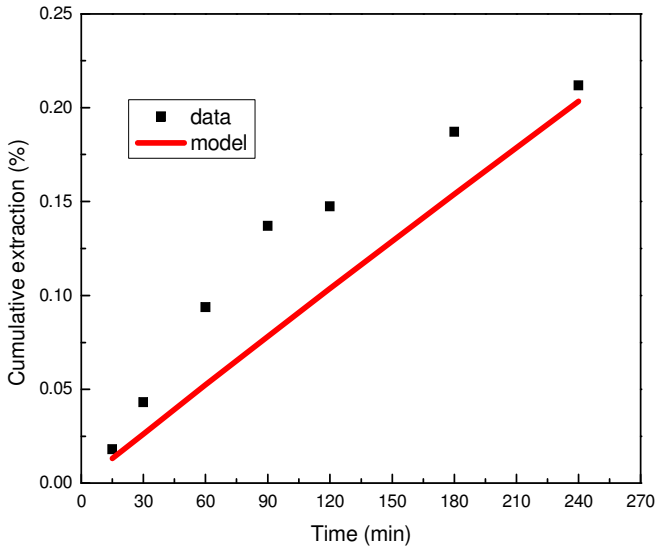


Figure 5-6 Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 190°C

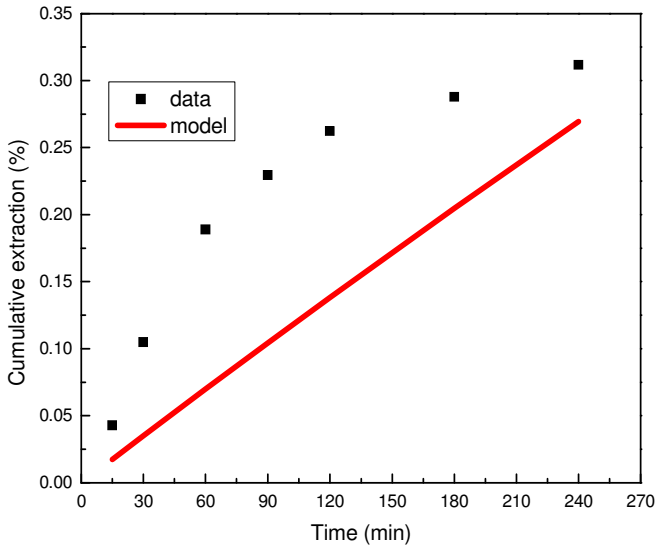


Figure 5-7 Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 210°C

It can be seen in Figure 5-6 and Figure 5-7, the experimental data obtained differs quite significantly from that predicted by the model at the lower temperatures involved. This model does not fit the data at the lower temperatures well.

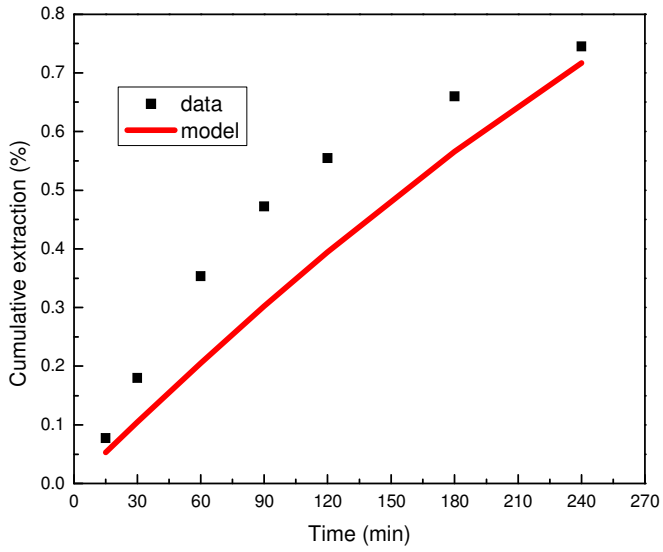


Figure 5-8 Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 230°C

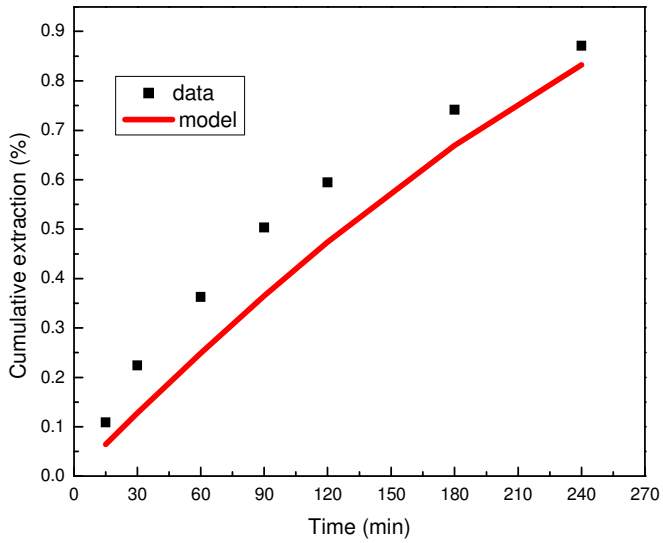


Figure 5-9 Comparison of conversion predicted by gas film diffusion control model with actual data obtained at 250°C

The gas film control model fits the experimental data better at higher temperatures as shown in Figure 5-8 and Figure 5-9. The deviation of the values predicted by the model from the experimental results is not too high. However, when comparing Figure 5-8 and Figure 5-9 with Figure 5-3 and Figure 5-4, there is a smaller deviation between the experimental data points and model values when the chemical reaction control is used. This implies that at higher temperatures the chemical reaction control model gives a better prediction of the extraction.

The Arrhenius plot obtained from gas film diffusion control model is shown in Figure 5-10

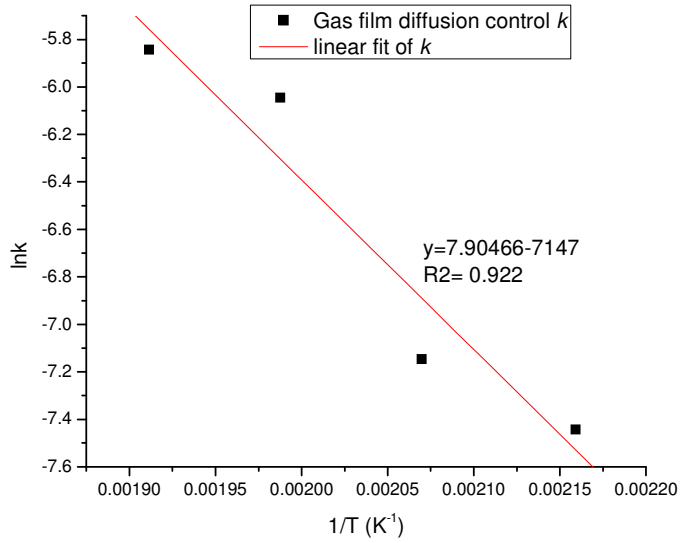


Figure 5-10 Arrhenius plot for gas film diffusion control model at 1wt%Fe_2O_3 and 1ml/min ligand flow rate

The activation energy predicted from this model is 59kK/mol Figure 5-10. This activation energy is too high for a diffusion controlled process as proposed by Habashi (1969).

From the conditions used for the modeling of the reaction, it can be concluded that chemical reaction is limiting because the reactions are highly temperature sensitive. It has been shown that the shrinking core model under chemical reaction control fits the experimental data, particularly at high temperatures.

The values for the reaction rate constant *k* and activation energy calculated from the extraction at 3wt% are shown in Appendix C. From these values the conclusion that gas phase extraction can be modeled by the shrinking core model under chemical reaction control no longer holds. When the mass of the oxide is increased, the surface area effects become more important, affecting the reaction more and the chemical reaction ceases to be the limiting factor in the reaction.

There is therefore a need to find a model that will take into account all the factors affecting the reaction which will be able to predict the extraction at any condition.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The aim of this investigation was to investigate the process of gas phase extraction with the objective of predicting the operation ranges and the kinetics of the process. Gas phase extraction of Fe showed that it is possible to extract economic yields of Fe at relatively low temperature and in a relatively short time as compared to some other conventional extraction processes. It was shown in the previous chapters that the time required to obtain reasonable extraction using gas phase extraction is much shorter than previously reported. Allimann-Lecourt *et al*. (1999) carried out experiments for 25hrs, whilst Hamblin and Posner (1979) carried out experiments for up to 8 days as compared to 4hrs in this study.

The extraction data obtained from gas phase extraction was used to test various gas-solid reaction kinetic models. The data could not be used on two models based on a fluidized bed reactor because the data needed to be used in the models requires that the gaseous product be continually measured which was not the method of analysis in the current research. The process was assumed to be a chemical controlled process at low Fe_2O_3 concentration (1wt %) because of the very strong dependence of the extraction on temperature. Gas phase extraction was shown to depend on the following variables

- Temperature - extraction increased as the temperature was increases for the extraction of iron
- Ligand flow rate – extraction increased as the ligand flow rate was increased
- Surface area available for reaction – extraction increased as the surface area available for reaction was increased

When gas phase extraction was carried out on chrome(III) oxide no appreciable extraction took place in the amount of time chosen for the reaction to take place. Extraction on a mixture of Fe_2O_3 and Cr_2O_3 only produced reasonable extraction for iron, 65% whilst the extraction of chrome was still very low 14% max, Figure 4-10). The ligand acetylacetone was shown to react preferentially with iron, resulting in iron being extracted in mixtures where even a trace amount of iron was present. Because of this preferential reaction, acac can be used for the beneficiation of chrome in mixtures where both iron and chrome oxides are present.

Gas phase extraction also holds much promise for other separations, as well as recovery of low grade metal values from ores. A further application could be to the removal of trace amounts of impurities to upgrade metal purities. This investigation has therefore proved the stated hypothesis: “The process of gas phase extraction is affected by a number of other variables such as ligand flow rate other than temperature”, absolutely correct. The additional statement that “once the effect of the variables is known it should be possible to develop a kinetic model that can be used

to predict gas phase extraction of metals by ligands in fluidized beds from a variety of materials, such as low grade ores, slags and fly ash, has also been confirmed by this work.

6.2 Recommendations

In order to better understand the process of gas phase extraction the following could still be done:

- Design a better experimental setup which will achieve better contacting for all the reactants needed to carry out gas phase extraction
- Carry out more extractions with different sized Fe_2O_3 particles in order to be able to predict a model for the extraction of iron which includes particle size effects.
- The variables that greatly affect the extraction have been identified, and the way they affect each other needs to be further investigated in order to find the optimum operating and extraction range
- There is a need to identify other ligands which can be used to extract other metals without extracting iron. This will then enable investigations into the extraction of other metal oxides, for example bivalent oxides.
- Carry out extractions on real ores and 'real samples', e.g. fly ash and tailings to check if comparable extraction will be obtained. In this study a mixture of sand and pure oxides was used for the extraction; using ores will show if the extraction can be used for practical purposes

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APPENDIX A

Parameters for the experimental setup

Minimum fluidization velocity at the reactor operating condition

The minimum fluidization for the process was calculated using Equation 2-11 and Equation 2-12 with the following parameters

d_p=64μm, ρ_p=2638kg/m3, ρ_g=1.146kg/m3, μ_g=17.81cP, g=9.81m/s

$$Ar = \frac{d_p^3 \rho_g \left(\rho_p - \rho_g\right) g}{\mu^2}$$

$$= \frac{(64*10^{-6})^3 *1.146(2638-1.146)*9.81}{(17.81*10^{-6})^2}$$

$$= 24.499$$

$$\mathrm{Re}_{,mf} = \left[(33.7)^2 + 0.0494 Ar\right]^{1/2} - 33.7$$

$$= \left[(33.7)^2 + 0.0494*24.494\right]^{1/2} - 33.7$$

$$= 0.01795$$

$$\mathrm{Re}_{,mf} = \frac{d_p u_{mf} \rho_g}{\mu} = 0.01795$$

$$\Rightarrow u_{mf} = \frac{0.01795*17.81*10^{-6}}{64*10^{-6}*1.146}$$

$$= 0.004359 m/s$$

$$= 0.4359 cm/s$$

The minimum flow rate to achieve Umf is

$$
\begin{aligned}
Q &= u_{mf} * A \\
&= 0.4359 * \pi * \left({}^{2.5}\!\!\diagup\!\!{}_{2} \right)^2 \\
&= 2.14 \, {}^{cm^3}\!\!\diagup\!\!{}_{s} \\
&= 128.4 \, {}^{cm^3}\!\!\diagup\!\!{}_{\min}
\end{aligned}
$$

It is assumed the ligand expands so much that its flow rate into the FBR is higher than the minimum fluidization velocity calculated above.

APPENDIX B

Material Safety Data Sheets

Material Safety Data Sheet IRON(III) OXIDE,

HAZARDS IDENTIFICATION

Irritating to eyes, respiratory system and skin.

COMPOSITION/INFORMATION ON INGREDIENTS

Product Name FERRIC OXIDE CAS Index NO.: 1309-37-1 215-168-2

Formula Fe_2O_3 Molecular Weight 159.69 AMU

FIRST AID MEASURES

After inhalation: If inhaled, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen.

After skin contact: In case of contact, immediately wash skin with soap and copious amounts of water.

After eye contact: In case of contact, immediately flush eyes with copious amounts of water for at least 15 minutes.

After ingestion: If swallowed, wash out mouth with water provided person is conscious. Call a physician.

FIRE FIGHTING MEASURES

Extinguishing media: Suitable: Noncombustible. Use extinguishing media appropriate to surrounding fire conditions.

Special risks: Specific Hazard(s): Emits toxic fumes under fire conditions.

Special protective equipment for firefighters: Wear self-contained breathing apparatus and protective clothing to prevent contact with skin and eyes.

ACCIDENTAL RELEASE MEASURES

Procedure of personal precaution(s): Wear respirator, chemical safety goggles, rubber boots, and heavy rubber gloves.

Methods for cleaning up: Sweep up, place in a bag and hold for waste disposal. Avoid raising dust. Ventilate area and wash spill site after material pickup is complete.

HANDLING AND STORAGE

Directions for Safe Handling: Do not breathe dust. Avoid contact with eyes, skin, and clothing. Avoid prolonged or repeated exposure.

Storage: Conditions of Storage: Keep tightly closed.

EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering controls: Safety shower and eye bath. Mechanical exhaust required.

General hygiene measures: Wash thoroughly after handling.

Respiratory Protection: Use respirators and components tested and approved under appropriate government.

Hand Protection: Compatible chemical-resistant gloves.

Eye Protection: Chemical safety goggles.

PHYSICAL AND CHEMICAL PROPERTIES

Appearance Physical State: Solid MP/MP Range 1,538 °C

SG/Density 5.12 g/cm3 Solubility in Water: Insoluble.

Other Solvents: hydrochloric acid, sulfuric acid slightly soluble

STABILITY AND REACTIVITY

Stability: Stable

Materials to Avoid: Strong acids, Peroxides, Chloroformates.

HAZARDOUS DECOMPOSITION PRODUCTS

Hazardous Decomposition Products: Nature of decomposition products not known.

Material Safety Data Sheet CHROMIUM(III) OXIDE

HAZARDS IDENTIFICATION

This substance is not classified as dangerous according to Directive 67/548/EEC.

COMPOSITION/INFORMATION ON INGREDIENTS

Formula: Cr_2O_3 Molecular Weight: 151.99 g/mol

FIRST AID MEASURES

If inhaled: If breathed in, move person into fresh air. If not breathing give artificial respiration

In case of skin contact: Wash off with soap and plenty of water.

In case of eye contact: Flush eyes with water as a precaution.

If swallowed: Never give anything by mouth to an unconscious person. Rinse mouth with water.

FIRE-FIGHTING MEASURES

Suitable extinguishing media: Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for fire-fighters: Wear self contained breathing apparatus for fire fighting if necessary.

ACCIDENTAL RELEASE MEASURES

Personal precautions: Avoid dust formation.

Methods for cleaning up: Sweep up and shovel. Keep in suitable, closed containers for disposal.

HANDLING AND STORAGE

Handling: Provide appropriate exhaust ventilation at places where dust is formed. Normal measures for preventive fire protection.

Storage: Store in cool place. Keep container tightly closed in a dry and well-ventilated place. Hygroscopic- Handle and store under inert gas.

EXPOSURE CONTROLS/PERSONAL PROTECTION

Respiratory protection: Respiratory protection is not required. Where protection from nuisance levels of dusts are desired use dust masks. Use respirators and components tested and approved under appropriate government standards

Hand protection: For prolonged or repeated contact use protective gloves.

Eye protection: Safety glasses

Hygiene measures: General industrial hygiene practice.

PHYSICAL AND CHEMICAL PROPERTIES

Density 5,210 g/cm3 Water solubility: no data available

STABILITY AND REACTIVITY

Storage stability: Stable under recommended storage conditions.

Conditions to avoid: Avoid moisture.

Materials to avoid: Strong oxidizing agents

Hazardous decomposition products: Hazardous decomposition products formed under fire conditions. - Chromium oxides

Material Safety Data Sheet ACETYLACETONE

HAZARDS IDENTIFICATION

Flammable, Harmful if swallowed.

COMPOSITION/INFORMATION ON INGREDIENTS

Product Name:2,4-PENTANEDION CAS No: 123-54-6 204-634-0 606-029-00-0

Formula $C_5H_8O_2$ Molecular Weight 100.12 AMU

FIRST AID MEASURES

After inhalation: If inhaled, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen.

After skin contact: In case of contact, immediately wash skin with soap and copious amounts of water.

After eye contact: In case of contact, immediately flush eyes with copious amounts of water for at least 15 minutes.

After ingestion: If swallowed, wash out mouth with water provided person is conscious. Call a physician.

FIRE FIGHTING MEASURES

Extinguishing media suitable: For small (incipient) fires, use media such as "alcohol" foam, dry chemical, or carbon dioxide. For large fires, apply water from as far as possible. Use very large quantities (flooding) of water applied as a mist or spray; solid streams of water may be ineffective. Cool all affected containers with flooding quantities of water.

SPECIAL RISKS

Specific Hazard(s): Vapour may travel considerable distance to source of ignition and flash back.

Explosion Hazards: Vapour may travel considerable distance tosource of ignition and flash back. Container explosion may occur under fire conditions. Forms explosive mixtures in air.

Special protective equipment for fire fighters: Wear self-contained breathing apparatus and protective clothing to prevent contact with skin and eyes.

Specific method(s) of fire fighting: Use water spray to cool fire-exposed containers.

Accidental Release Measures

Personal precaution procedures to be followed in case of leak or spill: Evacuate area. Shut off all sources of ignition.

Procedure of personal precaution(s): Wear respirator, chemical safety goggles, rubber boots, and heavy rubber gloves.

Methods for cleaning up: Absorb on sand or vermiculite and place in closed containers for disposal. Ventilate area and wash spill site after material pickup is complete.

HANDLING AND STORAGE

Handling: Directions for Safe Handling: Do not breathe vapour. Avoid contact with eyes, skin, and clothing. Avoid prolonged or repeated exposure.

Storage: Conditions of Storage: Keep tightly closed. Keep away from heat, sparks, and open flame.

EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering controls: Use only in a chemical fume hood. Safety shower and eye bath. Use non-sparking tools.

General hygiene measures: Wash thoroughly after handling.

Personal protective equipment: Respiratory Protection: Use respirators and components tested and approved under appropriate government standards. If the respirator is the sole means of protection, use a full-face supplied air respirator.

Hand Protection: Compatible chemical-resistant gloves.

Eye Protection: Chemical safety goggles.

PHYSICAL AND CHEMICAL PROPERTIES

Appearance Physical State: Liquid BP/BP Range 136.0 - 138.0 °C

Flash Point 38 °C Auto ignition Temp 350 °C

Explosion Limits Lower: 1.7 % Upper: 11.4 %

Vapour Pressure 2.96 mmHg SG/Density 0.972 g/cm3

Vapour Density 3.5 g/l Surface Tension 31.2 mN/m 20 °C

Other Solvents: alcohol, ether, chloroform, acetone

Miscible with: glacial acetic acid, benzene

STABILITY AND REACTIVITY

Stability: Stable.

Materials to Avoid: Strong oxidizing agents, Reducing agents, Strong bases, Metals.

Material Safety Data Sheet ETHANOL

HAZARDS IDENTIFICATION

Highly flammable.

COMPOSITION/INFORMATION ON INGREDIENTS

Synonyms : Ethyl alcohol CAS-No.64-17-5 200-578-6 603-002-00-5 F, R11 -

Formula : C_2H_6O Molecular Weight : 46,07 g/mol

FIRST AID MEASURES

General advice: Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled: If breathed in, move person into fresh air. If not breathing give artificial respiration Consult a physician.

In case of skin contact: Wash off with soap and plenty of water. Consult a physician.

In case of eye contact: Flush eyes with water as a precaution.

If swallowed: Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

FIRE-FIGHTING MEASURES

Suitable extinguishing media: For small (incipient) fires, use media such as "alcohol" foam, dry chemical, or carbon dioxide. For large fires, apply water from as far as possible. Use very large quantities (flooding) of water applied as a mist or spray; solid streams of water may be ineffective. Cool all affected containers with flooding quantities of water.

Special protective equipment for fire-fighters: Wear self contained breathing apparatus for fire fighting if necessary.

ACCIDENTAL RELEASE MEASURES

Personal precautions: Avoid breathing vapours, mist or gas. Ensure adequate ventilation. Remove all sources of ignition. Evacuate personnel to safe areas. Beware of vapours accumulating to form explosive concentrations.

Environmental precautions: Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

Methods for cleaning up: Contain spillage, and then collect with non-combustible absorbent material, (e.g. sand, earth, diatomaceous earth, vermiculite) and place in container for disposal according to local / national regulations

HANDLING AND STORAGE

Handling: Avoid inhalation of vapour or mist. Keep away from sources of ignition - No smoking. Take measures to prevent the build up of electrostatic charge.

Storage: Store in cool place. Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage. Hygroscopic

EXPOSURE CONTROLS/PERSONAL PROTECTION

Personal protective equipment: Respiratory protection where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multipurpose combination or respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator.

Hand protection: Handle with gloves.

Eye protection: Safety glasses

Skin and body protection: Choose body protection according to the amount and concentration of the dangerous substance at the work place.

Hygiene measures: Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

PHYSICAL AND CHEMICAL PROPERTIES

Appearance: Form liquid, clear Colour: colourless

Melting point -144,0 °C Boiling point 78,0 - 80,0 °C Flash point 14,0 °C

Ignition temp 363 °C Lower explosion limit 3,3 %(V) Upper limit 19 %(V)

Vapour pressure 59,5 hPa at 20,0 °C Density 0,79 g/cm3

Water solubility completely soluble

STABILITY AND REACTIVITY

Storage stability: Stable under recommended storage conditions. Conditions to avoid- Heat, flames and sparks. Materials to avoid- Alkali metals, Ammonia, Oxidizing agents, Peroxides

Hazardous decomposition products: Hazardous decomposition products formed under fire conditions. - None known.

APPENDIX C

Experimental results

Table C 1: Cumulative mass (g) of Fe extracted at 1wt% and 1ml/min ligand flow rate

Time (min)	Temperature (°C)			
	190	210	230	250
15	0.01	0.02	0.04	0.06
30	0.02	0.06	0.10	0.13
60	0.05	0.11	0.20	0.21
90	0.08	0.13	0.27	0.29
120	0.08	0.15	0.32	0.34
180	0.11	0.17	0.38	0.43
240	0.12	0.18	0.43	0.50

Table C 2: Percentage (%) extraction of Fe at 1wt% and 1ml/min ligand flow rate

Time (min)	Temperature (°C)			
	190	210	230	250
15	1.81	4.30	7.72	10.92
30	4.31	10.49	18.02	22.39
60	9.36	18.89	35.37	36.27
90	13.71	22.96	47.23	50.33
120	14.75	26.25	55.44	59.46
180	18.71	28.79	65.95	74.16
240	21.17	31.18	74.48	87.10

Table C 3: Cumulative mass (g) of Fe extracted at 3wt% and 1ml/min ligand flow rate

Time (min)	Temperature (°C)			
	190	210	230	250
15	0.02	0.04	0.03	0.06
30	0.06	0.10	0.10	0.14
60	0.13	0.21	0.25	0.27
90	0.19	0.28	0.40	0.38
120	0.26	0.35	0.53	0.48
180	0.35	0.42	0.62	0.62
240	0.40	0.47	0.66	0.77

Table C 4: Percentage (%) extraction of Fe at 3wt% and 1ml/min ligand flow rate

Time (min)	Temperature (°C)			
	190	210	230	250
15	1.88	2.75	2.30	4.72
30	5.05	7.85	7.78	10.98
60	10.44	16.15	19.34	21.44
90	15.17	22.19	31.12	30.01
120	20.23	27.25	41.94	37.57
180	27.43	33.04	48.72	48.87
240	31.31	37.13	51.40	60.34

Table C 5: Cumulative mass (g) of Fe extracted at 10wt% and 1ml/min ligand flow rate

Time (min)	Temperature (°C)			
	190	210	230	250
15	0.02	0.04	0.01	0.03
30	0.06	0.11	0.09	0.16
60	0.13	0.23	0.21	0.33
90	0.21	0.33	0.36	0.47
120	0.28	0.41	0.47	0.61
180	0.43	0.56	0.67	0.86
240	0.59	0.72	0.82	1.11

Table C 6: Percentage (wt%) extraction of Fe at 10wt% and 1ml/min ligand flow rate

Time (min)	Temperature (°C)			
	190	210	230	250
15	0.51	1.11	0.30	0.89
30	1.62	2.96	2.41	4.37
60	3.58	6.26	6.08	8.90
90	5.53	8.88	9.58	12.74
120	7.61	10.98	12.67	16.46
180	12.30	15.00	17.94	23.07
240	15.79	19.41	22.08	29.74

Table C 7: Extraction of Fe at 250°C and 3ml/min

Time (min)	3wt%		10wt%	
	Cum mass (g)	% extraction	Cum mass (g)	% extraction
15	0.20	15.71	0.26	7.01
30	0.35	27.14	0.55	14.76
60	0.52	41.12	0.93	25.00
90	0.67	52.85	1.21	32.58
120	0.83	65.35	1.43	38.42
180	0.83	-	1.75	47.11
240	0.83	-	2.18	58.68

Table C 8: Extraction of Cr at 210°C and 3ml/min from a mixture containing Fe & Cr oxides

Time (min)	3wt%		5wt%	
	Cum mass (g)	% extraction	Cum mass (g)	% extraction
15	0.0067	0.65	0.01	0.39
30	0.014	1.35	0.01	0.81
60	0.026	2.56	0.03	1.54
90	0.036	3.49	0.04	2.10
120	0.047	4.60	0.05	2.76
180	0.066	6.40	0.07	3.84
240	0.085	8.30	0.09	4.98

Table C 9: Extraction of Fe at 210°C and 3ml/min from a mixture containing Fe & Cr oxides

Time (min)	3wt%		5wt%	
	Cum mass (g)	% extraction	Cum mass (g)	% extraction
15	0.188	9.53	0.11	5.77
30	0.355	17.98	0.25	12.62
60	0.565	28.64	0.44	22.47
90	0.719	36.42	0.59	29.93
120	0.849	42.99	0.74	37.27
180	1.074	54.41	0.97	48.97
240	1.285	65.07	1.18	59.68

Table C 10: Extraction of Cr from a 3wt% mixture at 3ml/min ligand flow rate, no Fe_2O_3

Time (min)	210°C		250°C	
	Cum mass (g)	% extraction	Cum mass (g)	% extraction
15	0.006	0.58	0.008	0.8
30	0.016	1.54	0.014	1.36
60	0.03	2.92	0.024	2.31
90	0.049	4.73	0.037	3.57
120	0.066	6.44	0.044	4.33
180	0.097	9.44	0.069	6.71
240	0.13	12.78	0.094	9.15

Reaction models for gas phase extraction

Table C 11: Values of *k* and R^2 for the shrinking core models at 3wt%Fe_2O_3

Temp (°C)	Reaction control		Film diffusion control	
	k	R^2	*k*	R^2
190	0.000507	0.980	0.000949	0.975
210	0.000590	0.942	0.00109	0.933
230	0.000968	0.917	0.00171	0.904
250	0.00109	0.996	0.00187	0.989

Table C 12: Activation energy for shrinking core models at 3wt% Fe_2O_3

Model	Ea (kJ/mol)	ln k_0	R^2
Chemical reaction control	28	-0.33	0.972
Film diffusion control	25	-0.49	0.931

Table C 13: Values of *k* and R^2 for the shrinking core models at 10wt%Fe_2O_3

Temp (°C)	Reaction control		Film diffusion control	
	k	R^2	*k*	R^2
190	0.000243	0.998	0.000472	0.998
210	0.000284	0.992	0.000548	0.991
230	0.000352	0.991	0.000675	0.989
250	0.000467	0.996	0.000881	0.994

Table C 14: Activation energy for shrinking core models at 10wt% Fe_2O_3

Model	Ea (kJ/mol)	ln k_0	R^2
Chemical reaction control	22	-2.70	0.973
Film diffusion control	20	-2.29	0.974

Amount of ligand required for complete reaction

The reaction of Fe_2O_3 with acetylacetone occurs according to the reaction

$$Fe_2O_3 + 6C_5H_8O_2 \rightarrow 2Fe(C_5H_7O_2)_3 + 3H_2O$$

i.e. 1mol of the metal oxide produces 2 mols of $Fe(acac)_3$. For complete reaction, the amount of $Fe(acac)_3$ produced is twice the amount of Fe_2O_3. For the 3% mixture, the amount of $Fe(acac)_3$ produced is:

$$n(Fe_2O_3) = \frac{m}{Mr} = \frac{1.5g}{159.687\,{}^{g}/_{mol}} = 0.0094mol$$

The theoretical amount of $Fe(acac)_3$ formed is

$$n(Fe(acac)_3) = 2 \times n(Fe_2O_3) = 0.0188mol$$

The mass of $Fe(acac)_3$ theoretically formed is

$$m = n \times Mr = 0.0188mol \times 353.199\,{}^{g}/_{mol} = 6.64g$$

The theoretical mass of Fe^{3+} formed is

$$m(Fe^{3+}) = m(Fe(acac)_3) \times \frac{Mr(Fe^{3+})}{Mr(Fe(acac)_3)}$$

$$= 6.64g \times \frac{55.845\,{}^{g}/_{mol}}{353.199\,{}^{g}/_{mol}} = 1.05g$$

From the stoichiometric equation, 1 mol of metal oxide requires 6 mols of ligand, therefore the theoretical amount of ligand required for the 3% mixture is

$$n(HAcac) = 6 \times n(Fe_2O_3) = 0.0564mol$$

The mass of ligand supplied after 4hrs at 1ml/min ligand flow rate flow rate is:

$$m(HAcac) = \rho_{HAcac} \times Flowrate \times Time$$

$$= 0.98\,{}^{g}/_{ml} \times 1\,{}^{ml}/_{min} \times 240 min = 235.2g$$

The amount of ligand supplied after 4hrs is therefore:

$$n(HAcac) = \frac{m}{Mr} = \frac{235.2g}{100.13\,{}^{g}/_{mol}} = 2.349 mol$$

The amount of ligand supplied (2.349mol) is therefore much higher than the theoretical amount required for the reaction to proceed to completion (0.0564mol).

APPENDIX D

Contributions

The following contributions to conferences and journals have originated from this work:

VanDyk, L., Mariba, E. R. M., Chen, Y., & Potgieter, J. H. (2010) Gas Phase Extraction of Iron from its Oxide in a Fluidized Bed Reactor. *Minerals Engineering*, 23, 58-60

Mariba, E. R. M., VanDyk, L. & Potgieter, J. H., (2009) Iron extraction from iron (III) oxide using acetylacetone in the gas phase: Effect of reaction variables. Poster presented at the School of Chemical and Metallurgical Engineering Poster day, Wits University, Johannesburg, 6 Nov 2009