

**THE EXTRACTION OF ALUMINIUM FROM FLY ASH USING
ACETYLACETONE IN GASEOUS PHASE**

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DECLARATION

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

(Signature of Candidate)

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ABSTRACT

Fly ash is a coal waste produced as a result of coal combustion in coal fired power plants and it is considered as a potential source of aluminium because it contains 14.8-31 wt% aluminium(III) oxide in amorphous and mullite phases depending on the coal type. Mullite is a crystalline structure formed by aluminium(III) oxide and silicate. The extraction of aluminium from a mixture of 31 wt% aluminium(III) oxide and silica as well as from fly ash collected from Eskom, Kendal Power Station using acetylacetone has been studied. A mixture of 31 wt% aluminium(III) oxide and silica was prepared based on the aluminium(III) oxide weight percentage in the fly ash. The extraction temperature, reaction time, acetylacetone flow rate, fly ash particle size distribution and bed weight were varied. The extraction was shown to be dependent on the reaction time, temperature, bed weight and acetylacetone flow rate. The extraction increased with increasing temperature from 90 °C to 250 °C, 250 °C was chosen as maximum temperature to avoid the decomposition of aluminium(III) acetylacetonate. The extraction increased with increasing acetylacetone flow rate from 2 to 6 mL/min and stabilized at 6 mL/min and the extraction percentage increased with decreasing bed weight. A maximum of 64% of available aluminium was extracted from a 31 wt% aluminium(III) oxide and silica mixture after 600 minutes at 250 °C using 6 mL/min acetylacetone flow rate. The extraction from the fly ash stabilized at about 18% after 360 minutes at 250 °C, 6 mL/min acetylacetone flow rate. The result showed that extraction is dependent on the mineralogy of the feed material. The result also showed that the particle size distribution and the introduction of nitrogen, a carrier gas, have no significant influence on the extraction of aluminium from the fly ash. A kinetic model was developed and used to model the extraction results. The model fits the data obtained from the extraction of aluminium from a 31wt% aluminium(III) oxide and silica mixture at 250 °C and 6 mL/min acetylacetone flow rate well. When used to model extraction data of a fly ash sample at similar reaction conditions, the model fits the experimental results only up to 240 minutes extraction time. The activation energy of the reaction was found to be 11.5 kJ/mol. There is need however to develop a model which takes into account the influence of temperature and acetylacetone flow rate.

DEDICATION

In the memory of my Father

Shortie William Mpana

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TABLE OF CONTENTS

DECLARATION	i
ABSTRACT	ii
DEDICATION	iii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF FIGURES	viii
LIST OF TABLES	x
LIST OF SYMBOLS	xii
NOMENCLATURE.....	xiv
1. INTRODUCTION	1
1.1 Background and rationale	1
1.2 Gas phase extraction of aluminium from fly ash.....	2
1.3 Objectives	5
1.4 Report layout	5
2. LITERATURE REVIEW	6
2.1 Fly ash.....	6
2.1.1 Production of ash from coal	6
2.1.2 Application of coal fly ash	9
2.1.3 Potential application of coal fly ash.....	10
2.2 Aluminium.....	12
2.2.1 Industrial production of aluminium	12
2.2.2 Alternative processes for production of aluminium.....	14
2.2.3 Industrial applications of aluminium	17
2.3 Gas phase extraction process	18
2.4 Summary.....	19
2.5 Kinetic modeling of the extraction of aluminium from fly ash.....	20
2.5.1 Reaction Mechanism.....	21
2.5.2 Mathematical Model	23

3.	EXPERIMENTAL.....	26
3.1	Chemicals	26
3.2	Raw Materials.....	28
3.2.1	Fly ash	28
3.2.2	Silica sand	29
3.3	A mixture of silica and 31 wt% aluminium(III) oxide	29
3.4	Gas Phase Extraction Experimental Set up	29
3.5	Experimental Method	31
3.6	Experimental Conditions	32
3.6.1	Extraction from Al ₂ O ₃ and Silica mixture	32
3.6.2	Extraction from fly ash.....	32
3.7	Analyses.....	33
3.8	Liquid Phase Extraction of Aluminium.....	34
4.	RESULTS AND DISCUSSION.....	35
4.1	The effect of temperature on the extraction of aluminium.....	35
4.2	The effect of acetylacetone flow rate on the extraction.....	39
4.3	Introduction of a carrier gas to the system (fluidized bed).....	43
4.4	The effect of the bed weight on the extraction of aluminium from fly ash....	45
4.5	The effect of the bed weight and acetylacetone flow	46
4.6	The effect of particle size distribution on the extraction of aluminium from fly ash.....	47
4.7	Kinetic model	48
5.	CONCLUSIONS	57
6.	RECOMMENDATIONS.....	59
7.	REFERENCES	60
8.	APPENDICES	65
8.1	Appendix A: Determination of Mass Extracted	65
8.1.1	Extraction Percentage of Aluminium.....	65
8.1.2	Density of the fly ash from Kendal Power Station	66

8.1.3	Amount of acetylacetone required for complete reaction	66
8.2	Appendix B: Summary of Experimental Results	68
8.3	Appendix C: Experimental set up and standards preparation.....	82
8.3.1	Gas Phase Extraction Experimental Set up.....	82
8.3.2	Preparation of Al(acac) ₃ standards.....	84
8.4	Appendix D: Determination of aluminium(III) oxide in the mullite phase and the amorphous phase	84

LIST OF FIGURES

Figure 1: Process flowsheet for production of aluminium(III) oxide from fly ash using gas phase extraction.....	3
Figure 2: Schematic diagram of aluminium extraction (http://www.encyclopedia.farlex.com).....	13
Figure 3: Fly ash particles.....	21
Figure 4: Steps for the formation of aluminium(III) acetylacetonate from aluminium(III) oxide.....	22
Figure 5: Mechanism of formation of aluminium(III) acetylacetonate from fly ash.....	23
Figure 6: Gas phase extraction experimental set up	31
Figure 7: The effect of temperature on the extraction of aluminium at 6 mL/min acetylacetone flow rate and 50 g of a mixture of 31 wt% aluminium(III) oxide and silica.....	37
Figure 8: The effect of acetylacetone flow rate on the extraction of aluminium at 250 °C and 50 g of 31 wt% aluminium(III) oxide.....	40
Figure 9: The effect of acetylacetone flow rate on the extraction of aluminium at 250 °C and 50 g fly ash	41
Figure 10: Comparison of aluminium extraction from fly ash and a mixture of silica and 31 wt% aluminium(III) oxide.....	42
Figure 11: The effect of nitrogen flow rate on the extraction of aluminium at 250 °C, 2 mL/min and 50 g fly ash	44
Figure 12: Effect of the fluidized bed size on the extraction of aluminium from fly ash at 2 mL/min and at 220 °C.....	45
Figure 13: Effect of fluidized bed size and acetylacetone flow rate at 220 °C.....	46
Figure 14: Effect of PSD on the extraction of aluminium at 220 °C, 2 mL/min and 50 g fly ash	48
Figure 15: Comparison of the kinetic model and the experimental data obtained at 250 °C, 6 mL/min and 50 g of 31 wt% aluminium(III) oxide.....	49

Figure 16: Comparison of the kinetic model and experimental data obtained at 220 °C, 6 mL/min and 50 g mixture of silica and 31 wt% aluminium(III) oxide	50
Figure 17: Comparison of the kinetic model and experimental data obtained at 190 °C, 6 mL/min and 50 g mixture of silica and 31 wt% aluminium(III) oxide	51
Figure 18: Arrhenius plot at 6 mL/min acetylacetone flow rate and 50 g mixture of 31 wt% aluminium(III) oxide and silica	52
Figure 19: Comparison of the kinetic model, projected kinetic model and experimental data obtained at 250 °C and 50 g 31 wt% aluminium(III) oxide using 6 mL/min acetylacetone flow rate	54
Figure 20: Comparison of the kinetic model and experimental data obtained at 250 °C, 6 mL/min and 50 g fly ash	55
Figure 21: Comparison of the kinetic model and experimental data obtained at 250 °C using 2 mL/min and 9 mL/min respectively	56

LIST OF TABLES

Table 1:	Mineralogy of fly ash from Kendal Power Station	7
Table 2:	Chemical composition of fly ash from Kendal Power Station.....	8
Table 3:	Properties of acetylacetone.....	26
Table 4:	Properties of aluminium(III) acetylacetonate.....	27
Table 5:	Properties of aluminium(III) oxide	27
Table 6:	Mineralogy of Kendal Power Station fly ash	28
Table 7:	Composition of Silica.....	29
Table 8:	Variable values of experiments carried out.....	32
Table 9:	Variable values of experiment carried out on fly ash.....	33
Table 10:	Liquid phase extraction of aluminium from fly ash and 31 wt% aluminium(III) oxide at various temperatures after 360 minutes.....	36
Table 11:	Fly ash particle size distribution	47
Table 12:	Values of reaction constant and regression coefficient at different temperatures	50
Table A. 1:	Determination of fly ash density	66
Table A. 2:	Mass balance of 1 mole Al_2O_3 reacting with 6 moles acetylacetone	66
Table B. 1:	The extraction of Al from 50 g 31 wt% Al_2O_3 and silica at 200 $^{\circ}C$ and 6 mL/min acacH flow rate/.....	69
Table B. 2:	The extraction of Al from 50 g 31 wt% Al_2O_3 and silica at 200 $^{\circ}C$ and 6 mL/min acacH flow rate.....	70
Table B. 3:	The extraction of Al from 50 g 31 wt% Al_2O_3 and silica at 220 $^{\circ}C$ and 6 mL/min acacH flow rate.....	71
Table B. 4:	The extraction of Al from 50 g 31 wt% Al_2O_3 and silica at 250 $^{\circ}C$ and 6 mL/min acacH flow rate.....	72
Table B. 5:	The extraction of Al from 50 g of a mixture of 31 wt% Al_2O_3 and silica at 250 $^{\circ}C$ and 9 mL/min acacH flow rate	73
Table B. 6:	The extraction of Al from 50 g of a mixture of 31 wt% Al_2O_3 and silica at 250 $^{\circ}C$ using 2 mL/min acacH flow rate	74

Table B. 7: The extraction of Al from 50 g fly ash at 250 °C using 9 mL/min acacH flow rate.....	75
Table B. 8: The extraction of Al from 50 g fly ash at 250 °C & 6 mL/min acacH flow rate.....	76
Table B. 9: The extraction of Al from 50 g fly ash at 250 °C & 2 mL/min acacH flow rate.....	76
Table B. 10: The extraction of Al from 50 g fly ash at 220 °C & 2 mL/min acacH flow rate.....	77
Table B. 11: The extraction of Al from 30 g fly ash at 220 °C & 2 mL/min acacH flow rate.....	77
Table B. 12: The extraction of Al from 70 g fly ash at 220 °C & 2 mL/min acacH flow rate.....	78
Table B. 13: The extraction of Al from 100 g fly ash at 220 °C & 4 mL/min acacH flow rate.....	78
Table B. 14: The extraction of Al from 100 g fly ash at 220 °C & 6 mL/min acacH flow rate.....	78
Table B. 15: The extraction of Al from 50 g fly ash at 220 °C & 2 mL/min acacH flow rate and -75 µm PSD.....	79
Table B. 16: The extraction of Al from 50 g fly ash at 220 °C & 2 mL/min acacH flow rate and -150 µm +75 µm PSD.....	80
Table B. 17: The extraction of Al from 50 g fly ash at 250 °C & 2 mL/min acacH flow rate and 10 mL/min nitrogen.....	80
Table B. 18: The extraction of Al from 50 g fly ash at 250 °C & 2 mL/min acacH flow rate and 20 mL/min nitrogen.....	81

LIST OF SYMBOLS

<i>Symbols</i>	<i>Units</i>	<i>Names</i>
C_d	Ppm	Concentration of $Al(acac)_3$ in the diluted solution
C_{acacH}	$\frac{mol}{l \cdot min}$	Initial concentration of gas reactant
C_f	ppm	Concentration of the sample
k_1		Rate constant due to the reaction of acacH and aluminium(III) oxide
k_2		Rate constant due to removal of products
n	<i>mol</i>	Number of moles
M_{Al}	<i>g</i>	Mass of aluminium
M_{Al}^0	<i>g</i>	Initial mass of aluminium
$M_{fly\ ash(1-\delta)}$	<i>g</i>	Mass of aluminium(III) oxide in fly ash
$M_{fly\ ash(1-\delta)}^0$	<i>g</i>	Initial mass of aluminium(III) oxide in fly ash
R	$J/(mol \cdot K)$	Ideal gas constant
r_1		Rate of the reaction
r_2		Rate of the removal of products
r_f		Rate of the consumption of aluminium(III) oxide

S	m^2/g	Surface area
t	<i>minutes</i>	Time
u_{mf}	m/s	Velocity at minimum fluidization
Q	ml/min	Volumetric velocity
W_{Al}	g/mol	Molar mass of aluminium
$W_{Al_2O_3}$	g/mol	Molar mass of aluminium(III) oxide
X_{Al}	%	Mass fraction of aluminium

Greek symbols

α_1		Fraction of the surface area
α_2		Fraction of the surface area
μ		Amorphous factor
$1 - \delta$	%	Weight percentage of Al_2O_3 in fly ash

NOMENCLATURE

<i>Abbreviations</i>	<i>Names</i>
acacH	Acetylacetone
acac	Acetylacetonate anion
CVD	Chemical Vapour Deposition
MOCVD	Metal Organic Chemical Vapour Deposition

1. INTRODUCTION

1.1 Background and rationale

Aluminium is the third most abundant element in the earth's crust and the most common metal. It is usually alloyed with other elements such as silicon, copper or magnesium. Pure aluminium is not very strong and alloying adds to its strength. The aluminium demand has increased mostly in emerging countries, driven by greater urbanization and it was estimated at 4% global demand growth in 2010 (Novelis Inc, 2010). Bauxite is the principal ore for the production of aluminium metal via a two-stage process that involves, firstly the refining of bauxite to aluminium(III) oxide by a wet chemical caustic leach process (the Bayer process) and secondly the electrolytic reduction of aluminium(III) oxide to aluminium metal (the Hall-Heroult process) (Green, 2007).

World reserves of Bauxite were estimated at 27000 Mt in 2008 (Bray, 2009). If an annual Bauxite production growth rate of 5% is considered, the current known reserves of 27000 Mt will be exhausted within the next 20 years. One of the aluminium industry's long term targets is to recover aluminium from other sources. One such alternative resource is fly ash as it is known to contain about 14.8-31 wt% of aluminium(III) oxide (in amorphous and mullite phases) depending on the precursor coal type.

Fly ash is a predominantly inorganic residue obtained from the flue gases of boilers at coal power plants. When coal is burnt in pulverized coal boilers, the minerals contained in the coal are thermally transformed into chemical species that are reactive or could be chemically activated (Landman, 2003). Eskom, a major power utility in the Republic of South Africa, is a major producer of fly ash. Eskom produced approximately 36.7 million tonnes of fly ash in 2009 of which only 2.1 million tonnes (5.7%) were used (Vadapalli et al., 2010). In the world only 20% to 40% of the fly ash produced is used for productive purposes such as an additive in cement. The remaining amount of fly ash produced annually must either be disposed in controlled

landfills or waste containment facilities. Numerous researchers are investigating economical ways to use the higher volumes of fly ash and to convert fly ash into valuable products at low cost. One of the economical uses of fly ash is the extraction and recovery of its mineral contents. Fly ash contains elements such as aluminium, iron, silicon, calcium, chromium, magnesium, manganese and titanium. There is no commercial process for the extraction of minerals from fly ash.

The conventional Bayer process for the recovery of aluminium(III) oxide from bauxite cannot be used for the extraction of aluminium from fly ash due to the high silica content (22-61 wt%) in fly ash as compared to 4-8 wt% silica content in bauxite (Adrian and McCulloch, 1966). Due to the high silica content (22-61 wt%) in fly ash, removal of silicon species from the aluminate solution prior to the precipitation of $\text{Al}(\text{OH})_3$ is a major concern if the Bayer process is to be considered.

An alternative process therefore needs to be developed for the extraction of aluminium from fly ash. The product of such a process would be aluminium(III) oxide and the challenge would lie in the fact that aluminium smelters require iron free aluminium(III) oxide with a purity of at least 98.7 wt%. The research work presented here will focus on one such an alternative process called gas phase extraction.

1.2 Gas phase extraction of aluminium from fly ash

The process flowsheet for the recovery of aluminium(III) oxide from fly ash using acetylacetone in gaseous phase is shown in Figure 1.

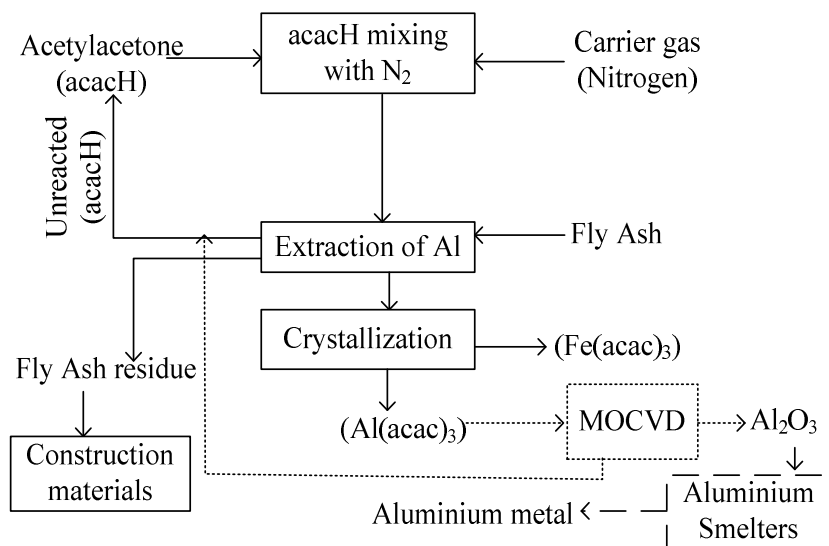
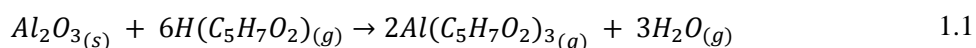


Figure 1: Process flowsheet for production of aluminium(III) oxide from fly ash using gas phase extraction.

Evaporated acetylacetone is mixed with hot nitrogen and fed to a fluidized bed reactor. A mixture is passed through a bed of fly ash at the required reaction temperature maintained. The acetylacetone reacts with the aluminium(III) oxide in the fly ash to form aluminium(III) acetylacetonate. The reaction between gaseous acetylacetone and aluminium(III) oxide can be written as follows:



The reaction is environmentally friendly as water is the only by-product and the unreacted acetylacetone can be recycled to the reactor. Nitrogen is used as carrier gas to remove volatile aluminium(III) acetylacetonate from residue gangue (Potgieter et al., 2006). Nitrogen is separated from aluminium(III) acetylacetonate and it is recycled. Iron(III) oxide is present in the fly ash and it reacts rapidly with acetylacetone (Allimann-Lecourt et al., 2001).

However, aluminium(III) acetylacetonate can be separated from iron(III) acetylacetonate through crystallization as these two complexes have different

crystallization temperatures, 190 °C and 160 °C, respectively. The recovered iron(III) acetylacetonate can be sold separately as it is used for several industrial applications, alternatively it may be converted into iron and acetylacetone by reduction with hydrogen (Potgieter et al., 2006).

After the extraction using acetylacetone the product aluminium(III) acetylacetonate can be sold separately or it can be converted to aluminium(III) oxide by metal organic chemical vapour deposition (Pflitch et al., 2007; Singh and Shivashankar, 2002 & Troester et al., 2005) as indicated by the dotted lines in Figure 1. Aluminium(III) acetylacetonate is decomposed into aluminium(III) oxide and acetylacetone in the presence of oxygen. Acetylacetone is recycled back to the extraction process. MOCVD produces an aluminium(III) oxide with a purity greater than 99% and 0% iron acceptable for use in the aluminium smelters.

As mentioned previously, the aluminium(III) acetylacetonate can also be sold to various industries for the following applications:

- Catalysis and synthesis
- Adhesive tape for sealing window flanges in automobiles (Boehm and Krupke, 2006),
- Translucent flame-retardant tapes and manufacture thereof (Kavature, 2007).
- Skin adhesive compositions for electrode patches, transdermal patches and adhesive tapes (Kamiyama and Quan, 2006).
- Aluminium(III) oxide thin films prepared by chemical vapour deposition from aluminium(III) acetylacetonate (Maruyama and Arai, 2009),
- Organometallic vapour deposition of crystalline aluminium(III) oxide films on stainless steel substrates (Pflitch et al., 2007),
- Fabrication of transparent alumina nano fibers by electrospinning (Azad, 2006).
- MOCVD of environmental barrier coatings for ceramic matrix composites (Troester et al., 2005),
- Coating materials for forming anti-reflecting transparent thin films (Hosono et al., 2007).

The main focus of this study is the extraction of aluminium as aluminium(III) acetylacetonate using acetylacetone.

1.3 Objectives

Numerous research efforts are devoted to the extraction of aluminium from Bauxite ore and other alternative sources of aluminium, such as kaolin clay and fly ash. The present study aims to extract aluminium from fly ash using acetylacetone in gaseous phase. The following objectives have been set:

- To investigate the effect of acetylacetone flow rate on the extraction of aluminium from fly ash.
- To investigate the effect of temperature on the extraction of aluminium from fly ash.
- To investigate the effect of bed size (mass) on the extraction of aluminium from fly ash.
- To investigate the effect of carrier gas (flow rate) on extraction of aluminium from fly ash.
- To derive a kinetic model for the extraction of aluminium as aluminium(III) acetylacetonate using acetylacetone in the gas phase.

1.4 Report layout

The structure of the report is as follow:

Chapter 2 is the literature review which presents the production and application of fly ash, industrial production and application of aluminium, fly ash as source of aluminium and gas phase extraction process. Chapter 3 presents the chemicals and raw materials used and describe the experimental setup and equipment used. Chapter 4 presents the experimental results and discussion, and a comparison of the data with the developed model for gas phase extraction. Chapter 5 summarized the conclusions of the study, whilst Chapter 6 gives the recommendations of the future work to be carried out. A list of references and appendices are given at the end of the report.

2. LITERATURE REVIEW

2.1 Fly ash

Fly ash is a predominantly inorganic residue obtained from the flue gases of boilers at coal power plants. When coal is burnt in pulverized coal boilers, the minerals contained in the coal are thermally transformed into chemical species that are reactive or could be chemically activated (Landman, 2003).

2.1.1 Production of ash from coal

Coal used for the generation of electricity is pulverised into a very fine dust before being fed into the boilers to ensure efficient combustion. Almost 90% of ash produced in the generation process is called fly ash or pulverised fuel ash (Eskom annual report, 2010). The larger particles of the ash are called coarse ash, which make up the rest of ash produced at the power station. Coarse ash drops down from the furnace and is collected at the bottom in the ash hopper of the boiler. The fly ash is removed from the flue gas stream by means of electrostatic precipitators. The fly ash and coarse ash are mixed and stored in the ash dams and landfills (Eskom annual report, 2010).

The characteristics of fly ash differ depending on the source of the coal used in the power plant and the method of combustion. Fly ash can be approximated as an aluminosilicate glass and can be used like other minerals. The amorphous aluminosilicate nature of fly ash makes the chemical structure of fly ash difficult to characterize, but also very versatile, since the glassy phase reacts first before the crystalline phase and also goes into solution first (Landman, 2003). The mineralogy of fly ash is closely related to the minerals contained in the coal. Different minerals within the fly ash have been identified using X-ray diffraction.

Table 1: Mineralogy of fly ash from Kendal Power Station

	% composition
Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)	30.68
Quartz (SiO_2)	13.97
Hematite (Fe_2O_3)	0.8
Magnetite (Fe_3O_4)	1.65
Amorphous	52.9

The common phases in fly ash are glass (amorphous), mullite, quartz, magnetite, hematite and anhydrite. The mullite present in fly ash is formed by the decomposition of kaolinite which is contained in the coal. Mullite is a crystalline structure formed by alumina and silicate, and it has a chemical formula $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Quartz has a chemical formula SiO_2 . Hematite is the mineral form of iron(III) oxide (Fe_2O_3). The magnetite referred to in Table 1 should be classified as ferrite, due to the different rates of substitution of ferrous and ferric ions by other ions, such as chromium, manganese, cobalt, nickel and zinc (Hulett & Weinberger, 1980). A hard glassy mineral occurring as octahedral crystals of variable color and consisting mostly of magnesium and aluminium(III) oxides, containing iron, chromium and nickel impart magnetic properties of magnetite to approximately 39% of the particles. This leads to the concentration of these elements in these fractions and makes fly ash a valuable ore for these metals (Landman, 2003).

The chemical compositions vary for different fly ash samples. Four major elements, silicon, aluminium, iron and calcium, constitute the major part of the fly ash. X-ray fluorescence is mainly used to determine the composition of fly ash. The composition of Eskom Kendal Power Station fly ash given in Table 2 was obtained experimentally.

Table 2: Chemical composition of fly ash from Kendal Power Station

Compound	wt% Composition
SiO ₂	56.14
Al ₂ O ₃	30.52
CaO	5.03
FeO	3.23
Fe ₂ O ₃	0.40
TiO ₂	1.67
MgO	1.43
P ₂ O ₅	0.60
K ₂ O	0.71
MnO	0.03
Na ₂ O	0.24
Cr ₂ O ₃	0.03
NiO	0.01
L.O.I	1.43

The major elements silicon, aluminium, iron and calcium constitutes 95.32 wt% of the total weight (Table 2). L.O.I in Table 2 is the loss of ignition. Loss on ignition measures the amount of moisture or impurities lost when the sample is ignited under conditions specified. It can be seen that fly ash contains a high silica content of 56.14 wt% for ESKOM, Kendal Power Station fly ash. It can also be seen that iron exists as both ferrous and ferric ions and it contains 30.52 wt% of aluminium(III) oxide.

When comparing fly ash with the principal source of aluminium, bauxite; fly ash is the ore that contains the second highest content of aluminium(III) oxide. The aluminium(III) oxide in fly ash differs to aluminium(III) oxide in bauxite due to the difference in the mineralogy of fly ash and bauxite.

The worldwide production of fly ash was estimated at 900 million tons in 2010 and it was anticipated to be 2000 million tons in 2020 (Izquierdo et al., 2009 & Malhotra et al., 2002). Only 20% to 40% of the fly ash produced worldwide is used for productive purposes, such as an additive in cement. The remaining amount of fly ash produced annually must either be disposed in controlled landfills or waste containment facilities. Fly ash causes environmental problems, such as ground water contamination, spills from bulk storage, etc.

2.1.2 Application of coal fly ash

Fly ash is classified as the sixth most abundant resource in the United State of America (Landman, 2003). The use of coal as the generator of electricity is increasing worldwide, thus increasing the production of fly ash. Due to the problems caused by fly ash the application of fly ash is vital. Listed below are some of the uses of fly ash.

- The most common use of fly ash is in the cement industry, where the presence of fly ash adds strength to concrete. Fly ash is used as cement extender in the manufacture of building material, such as panels and boards. In general fly ash reduces the water consumption of cement, increases the setting time, reduces the heat of hydration and add long term strength to the cement products (Landman, 2003).
- Fly ash improves corrosion protection by decreasing concrete permeability. Fly ash can reduce the rate of ingress of water and corrosive chemicals; therefore protecting steel reinforcements from corrosion.
- Fly ash fineness and spherical shape makes fly ash an effective filler in improving the rheological behaviour of fresh cementitious mixtures, increasing its workability (slump) and pumpability, while reducing the risk of bleeding and component segregation during moulding (Berry et al., 2009). Fly ash is used as a major ingredient in the manufacturing of ceramic tiles due to the mullite and quartz in the non-magnetic fraction of fly ash (Mishulovich & Evanko, 2003 and Zimmer & Bergmann, 2007).

- Fly ash is used as an adsorbent for the uptake of organic compounds from petrochemical waste effluents. The availability, inexpensiveness and its adsorption characteristic had made it an alternative media for the removal of organic compounds from aqueous solution (Bada & Potgieter-Vermaak, 2007).
- Fly ash is used as soil modifier and nutrients supplier for upgrading soil for its use in agriculture and to improve the production potential. It improves permeability status of soil, fertility, soil texture, water holding capacity and porosity, soil aeration, and reduces bulk density of soil, crust formation, and provides micro nutrients, such as iron, zinc, copper, boron, etc, and macro nutrients, such as potassium, phosphorus, calcium, magnesium, etc (Aktar, 2007; Arivazhagan et al., 2011 & Basu et al., 2009).
- Fly ash is used for the synthesis of zeolites and the zeolite formed from fly ash cover a substantial range of the known structure for zeolites (Vadapalli et al., 2010 & Landman, 2003). Mullite is the least reactive component in fly ash during the formation of zeolites, while the glass phase reacts first.

2.1.3 Potential application of coal fly ash

Due to its chemical composition, fly ash is considered as a valuable resource and research has been carried out on fly ash, in order to facilitate its application to new and innovative areas of economic interest. One of the economical uses of fly ash is the extraction and recovery of its mineral contents.

2.1.3.1 Extraction of heavy metals from fly ash

Seidel and Zimmels (1998) used sulphuric acid to extract aluminium and iron from fly ash and studied the mechanism and kinetics of the extraction of aluminium and iron. They showed that in the extraction process, particles follow the shrinking core model with respect to the formation of unreacted core that is encapsulated by a leached, porous, layer.

Allimann-Lecourt and co-workers, (2002) have used acetylacetone, bis-(pentane-2,4-dionato) propan-1,2-diimine and tetra-iso-propyldithiophosphoramidate to extract iron, vanadium, lead, nickel, copper and zinc from different fly ash samples. Prasad and Mondal (2008) extracted zinc, iron, manganese, chromium, lead, copper, nickel and chromium from Indian fly ash using sulphuric acid. They showed that the metals extraction efficiency differs with respect to the type fly ash sample used. The metal extraction was shown to increase with a decrease on pH.

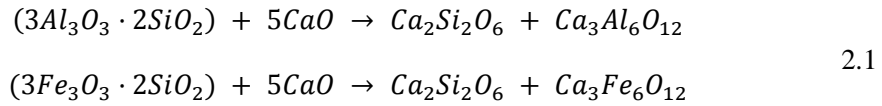
Luo and co-workers (2009) used synthetic ammonia based wet fine gas desulfurization conditions to extract iron from fly ash. They showed that extraction increased with the reaction temperature, and vibration frequency and the decrease of the pH value and liquid/solid ratio. Their results agree with the work done by Prasad and Mondal (2008). Nayak and Panda (2009) used sulphuric acid to extract aluminium, iron, calcium, titanium, potassium, sodium and magnesium from the Talcher thermal power station fly ash. They extracted a maximum of 41.30% aluminium and 53.0% iron from raw fly ash, while Matjie and co-workers (2005) achieved a limit of 24% aluminium extraction from raw fly ash generated from low rank bituminous South African coal. These results indicate that the degree of extraction of metals depends on the extractant used.

2.1.3.2 Challenges encountered when leaching fly ash

The metals in fly ash that are in the mullite phase do not readily dissolve in mineralized acids such as nitric acid, hydrochloric acid or sulphuric acid (Matjie et al., 2005). This makes fly ash a complex resource of metals. Numerous researchers have used sintering processes to overcome this challenge. Fly ash particles are pelletized before sintering at 800 °C to 1200 °C. The main purpose of sintering is to destroy the crystalline mullite phase ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) releasing free aluminium(III) oxide that is available to be leached (Matjie et al., 2005).

The aluminosilicate reacts with calcium oxide to form glassy phases such as calcium silicate ($\text{Ca}_2\text{Si}_2\text{O}_6$) and calcium aluminate ($\text{Ca}_3\text{Al}_6\text{O}_{12}$) during the calcination of the

pellets prepared with lime, fly ash and washed coal (Li et al., 2009). The reactions occurring during the sintering of pelletised fly ash at elevated temperatures are:



The extraction efficiency increases for sintered fly ash pellets. Matjie and co-workers, (2005) improved the extraction efficiency of aluminium from 20% achieved from raw fly ash to 85% achieved from sintered fly ash pellets. Li and co-workers (2009) extracted 94.60% iron and 86.50% aluminium from sintered boiler slag pellets. These results agree with work done by Matjie and co-workers (2005).

2.2 Aluminium

Aluminium is the most widely used non-ferrous metal in the world. It is usually alloyed with other elements due to its lighter density.

2.2.1 Industrial production of aluminium

The industrial process for aluminium production is given by Figure 2. It is a step by step illustration from the mining of the bauxite ore to the production of aluminium metal. Bauxite is the principal ore for the production of aluminium metal. Aluminium(III) oxide constitutes 26 to 60 wt% of bauxite (Grafe et al., 2009).

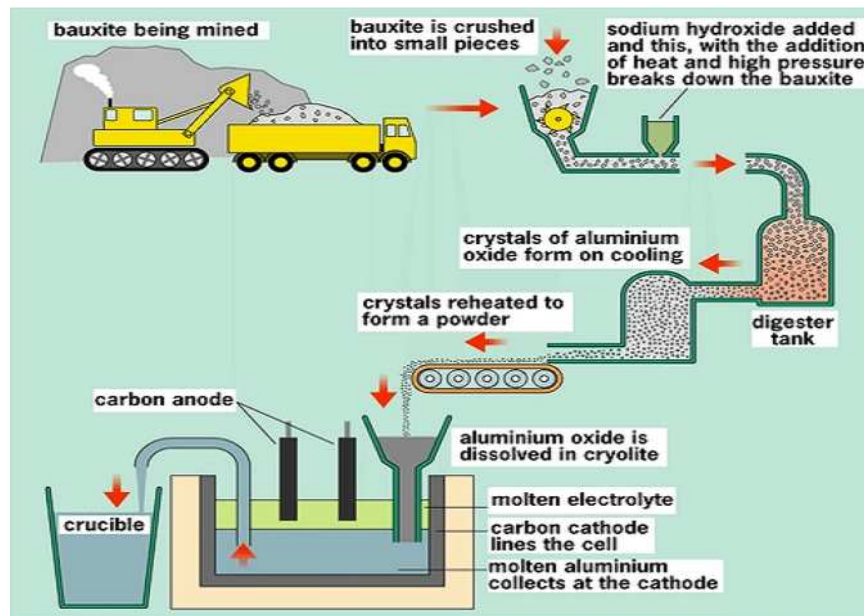


Figure 2: Schematic diagram of aluminium extraction

(<http://www.encyclopedia.farlex.com>)

Aluminium metal is industrially produced via a two-stage process that involves, firstly the refining of bauxite to aluminium(III) oxide by a wet chemical caustic leach process (the Bayer process) and secondly the electrolytic reduction of aluminium(III) oxide to aluminium metal (the Hall-Heroult process) (see Figure 2).

Bayer process

Crushed bauxite is dissolved in sodium hydroxide solution at typical temperatures ranging from 140-280 °C (Green, 2007). Alumina and silicon oxide in the bauxite dissolve in the sodium hydroxide to yield the solution of aluminium(IV) hydroxide and silicate ($Si(OH)_6^{4-}$) precipitates. This solution is clarified to remove all the impurities. The precipitated $Si(OH)_6^{4-}$ and undissolved impurities from the digestion stage are filtered and stored in the huge lagoons (Green, 2007). The clarified solution is cooled and seeded with aluminium hydroxide to form the precipitates of $Al(OH)_3$. The aluminium hydroxide precipitates are heated at temperatures above 1000 °C to yield aluminium(III) oxide. This process is called the calcination process and it must

be carefully controlled since it dictates the physical and chemical properties of the final product.

Electrolytic reduction

Approximately 90% of the aluminium(III) oxide produced is smelted in the Hall-Heroult process in order to produce aluminium metal (Meyer, 2004). The chemical bonds of aluminium(III) oxide are broken into aluminium metal and oxygen through electrolytic reduction.

Limitations of the Bayer process

The conventional Bayer process for the recovery of aluminium(III) oxide from bauxite (4-8 wt%) involves the dissolution of aluminium(III) oxide and trace amounts of silica in sodium hydroxide. Due to the high silica content (22-61 wt%) in fly ash, removal of silicon species from the aluminate solution prior to the precipitation of $\text{Al}(\text{OH})_3$ is a major concern if the Bayer process is to be considered (Adrian and McCulloch, 1966). Thus, Bayer process can only be used to recovery aluminium(III) oxide from low silica content aluminium sources.

Bauxite reserves

The current annual production of bauxite was estimated at 211 Mt in 2010. The reserves of Bauxite were estimated at 27000 Mt in 2008 (Bray, 2009). If an annual Bauxite production growth rate of 5% is considered, the current known reserves of 27000 Mt will be exhausted within the next 20 years. It is therefore important to develop new technologies for the extraction of aluminium from alternative sources such as fly ash, kaolin clay and recycled aluminium crabs (Meyer, 2004).

2.2.2 Alternative processes for production of aluminium

There are a number of research initiatives currently underway to produce aluminium from alternative sources of aluminium. These include:

2.2.2.1 Kaolinite Technology

Kaolinite technology is a process whereby aluminium is produced by the reduction of aluminium(III) chloride. The raw material used in this process is kaolin clay. Kaolin clays contain kaolinite which is composed of hydrated aluminium silicate, titanium dioxide and other materials. Green (2007) proposed that the thermodynamics of the Kaolinite process provides higher-conversion reaction with lower electrical demand as compared to the Hall Heroult and the Carbothermic processes. The kaolinite process takes place in two steps, namely carbo-chlorination and electrolytic reduction.

Carbo-chlorination

The carbo-chlorination step is a catalyzed exothermic reaction of calcined clay with chlorine and coke to produce aluminium(III) chloride. Aluminium(III) chloride must be purified for easy operation of the electrolytic reduction cells and for the final aluminium quality.

Electrolytic reduction

An aluminium(III) chloride smelting cell is used and it comprises of a stack of horizontal bipolar graphite electrodes between which the aluminium chloride is converted into high-grade aluminium and chlorine gas. Chlorine gas produced is recycled back to the carbo-chlorination step (Green, 2007).

2.2.2.2 Recycling of Aluminium

Recycling of aluminium is a major consideration in continued aluminium use, representing one of the key attributes of aluminium metal, with economic, ecological, environmental and social implications. More than a third of all the aluminium currently produced globally originates from recycling and more than half of all the aluminium currently produced in European Union originates from recycled aluminium (International Aluminium Institute, 2009).

Aluminium scraps, such as aluminium cans are collected and serves as source of aluminium. The aluminium recycling industry includes both refiners and re-melters to transform aluminium scrap into standardised aluminium. In 2007, 18 million tonnes of recycled aluminium was produced from aluminium scraps, while 38 million tonnes of aluminium was produced through electrolysis in the same year (International Aluminium Institute, 2009). Recycling aluminium scraps is less expensive and energy intensive than producing aluminium through electrolysis of aluminium(III) oxide. It requires only 5% of the energy used in the electrolysis of aluminium(III) oxide.

2.2.2.3 Extraction of aluminium from fly ash

Numerous researchers have studied the extraction of aluminium from fly ash using inorganic acids, such as sulphuric, hydrochloric and nitric acid.

Direct leaching of aluminium

The direct leaching of fly ash with sulphuric acid solution (6.12 mol dm^{-3}) at a solid to liquid ratio of 1:4 yields an extraction efficiency of 12-24% Al_2O_3 even after 6 hours of leaching under reflux (Matjie et al., 2005; Hansen et al., 1966). Matjie et al., (2005) proposed that this is due to the higher percentage of aluminium(III) oxide in fly ash consisting in the crystalline mullite phase making it inaccessible to react with the acid.

Allimann-Lecourt and co-workers, (2002) used acetylacetone, bis-(pentane-2,4-dionato) propan-1,2-diimine and tetra-iso-propyldithiophosphoramidate to successfully extract iron, vanadium, lead, nickel, copper and zinc from difference fly ashes.

Indirect leaching of aluminium

Fly ash was pelletised and sintered at elevated temperatures by Torma, (1983) and Matjie et al., (2005). The main objective of sintering step is to break the crystalline mullite phase ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) presenting free Al_2O_3 that is available for leaching. The aluminosilicate reacts with calcium oxide to form glassy calcium silicate and calcium aluminate during the calcination of the pellets prepared with calcium oxide, fly ash and fine coal (Torma, 1983; Matjie et al., 2005; Gabler & Stoll, 1982). Matjie and co-

workers, (2005) used sulphuric acid to obtain 89% aluminium extraction during the leaching of the sintered pellets (50% Fly ash: 40% fine coal: 10% CaO) with sulphuric acid at solid to liquid ratio of 1:3 and 80 °C for 8 hours from SASOL fly ash. Better aluminium extraction can be achieved from a sintered fly ash sample compared to that from raw fly ash.

2.2.3 Industrial applications of aluminium

Aluminium is used industrially for the following applications due to its properties:

- It is a very light metal with a specific weight of 2.7 g/cm³. This makes it suitable to be used in vehicles to reduce dead-weight and energy consumption while increasing load capacity. It is also used in the construction for aircraft (European Aluminium Association, EAA, 2002).
- It is strong when alloyed. Magnesium, silicon, copper and zinc are most commonly used alloying elements in aluminium which have sufficient solid solubility. High purity aluminium has a very low yield strength (7-11 MPa), but can be strengthened by solid solubility hardening. Magnesium is the most effective strengthener on a weight basis due to its high solubility (Udomphol, 2007).
- It is an excellent conductor of both heat and electricity and due to its weight is almost twice as good a conductor as copper. Thus most major power transmission lines use aluminium.
- It resists corrosion because of the strong thin layer of aluminium(III) oxide on its surface. This layer can be strengthened further by anodising the aluminium.
- It is recyclable and when recycled there is no degradation in the properties and recycling requires only ~ 5% of the input energy required to produce primary aluminium metal. Currently about seven billion pounds of aluminium are recycled annually and ceramic-based materials are used in the melting,

holding, transfer and forming of recycled aluminium in the same ways they apply to processing of shapes of primary aluminium (Richerson, 2006).

- It is non-toxic and also does not release any smell when it is in contact with other materials. This makes it suitable for use in packaging for sensitive products such as food and pharmaceuticals where it is used as foil.
- It is a good reflector of visible light as well as heat and that together with its low weight makes it an ideal material for reflectors in light fitting or rescue blankets (Green, 2007).

2.3 Gas phase extraction process

Gas phase extraction is an emerging technology for the extraction of heavy metals from matrices such as a low grade ore, soil sediment and industrial waste, by using a volatile organic reagent (Allimann-Lecourt et al., 1999). The volatile organic reagent passes through a heated feed material and reacts selectively with the metal to be extracted. The metal to be treated must be present as oxides, hydroxides or sulphides, because the organic chelating reagents are weak acids (Allimann-Lecourt et al., 2002). 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; Potgieter et al., 2006 & Van Dyk et al., 2010).

Allimann-Lecourt and co-workers (2002) used gas phase extraction to extract iron, vanadium, lead, nickel, copper and zinc from fly ashes using acetylacetone, bis-(pentane-2,4-dionato) propan-1,2-diimine and tetra-iso-propyldithiophosphoramidate. They extracted 18.7% iron, 18.6% vanadium and 13.6% chromium at 130 °C to 235 °C after 120 minutes. They also showed that by changing the ligand used one can selectively extract some metals while others remain in the solid matrix.

Potgieter and co-workers (2006) investigated the effect of temperature on the extraction of aluminium, iron, vanadium and chromium from their oxides mixed with silica using gas phase extraction and acetylacetonone as a ligand. They successfully extracted more than 60% of each metal.

Van Dyk and co-workers (2010) studied factors such as temperature, ligand flow rate, mass percentage of iron(III) oxide that affects gas phase extraction of iron on a mixture of iron(III) oxide and silica in a fluidized bed reactor. They showed that temperature, ligand flow rate and iron(III) oxide mass percentage influence the extraction of iron.

The volatile metal complexes formed can be used as catalysts in a wide variety of organic transformations, such as polymerization, hydrogenation, isomerisation. They are also used to produce the nano particles of metal oxides (Pflitch et al., 2007; Singh and Shivashankar, 2002 and Troester et al., 2005). The production of metal oxides from their acetylacetonates occurs by metal organic chemical vapour deposition (MOCVD) where the metal complexes act as the precursors, and has been demonstrated for the acetylacetonates complexes of iron(III), aluminium(III), chromium(III) and nickel(II) (Siddiqui, 2009, Pal & Sharon, 2000). The metal oxides produced by MOCVD have been found to be of high purity (>99%), thus the gas phase extraction process can be used to produce pure metal oxides.

2.4 Summary

Fly ash is a coal waste produced when coal is burnt in pulverized coal boilers. In 2010 approximately 900 million tons of fly ash was produced worldwide and only 20 to 40% of fly ash produced was used and the rest is stored in the storage dams, landfills which causes environmental and ecological problems. These problems can be solved if an industrial process which uses large volumes of fly ash can be developed. Extraction of heavy metals from fly ash can be one of the industrial processes to utilize large volumes of fly ash since fly ash contains minerals, such as aluminium, iron, silicon, calcium, chromium, magnesium, manganese and titanium.

Fly ash is an alternative source of aluminium because it contains about 14.8-31 wt% (in amorphous and mullite phases) of fly ash (depending on coal type). Thus, the extraction of aluminium from fly ash can present a new industrial use of fly ash.

Due to the high silica content in the fly ash the conventional Bayer process for the recovery of aluminium(III) oxide from bauxite cannot be used for the recovery of aluminium(III) oxide from fly ash. A new process called gas phase extraction process which is a promising emerging technology for the extraction of metals from low grade ore, soil sediment and industrial waste which includes fly ash is proposed for the extraction of aluminium from fly ash using acetylacetone as a ligand. Aluminium(III) acetylacetonate is the product of the extraction process and it can be used for the recovery of aluminium(III) oxide through metal organic chemical vapour deposition (MOCVD). Aluminium(III) oxide produced through MOCVD is of highest purity (>99%) and would be suitable for the aluminium smelters for the production of aluminium metal. Alternatively aluminium(III) acetylacetonate can be used as a catalyst, adhesive tape and for the synthesis of thin films.

2.5 Kinetic modeling of the extraction of aluminium from fly ash

Fly ash is a heterogeneous material. The extraction of aluminium depends not only on the chemical composition of fly ash, but largely on its mineralogy. XRD have showed that fly ash contains aluminium(III) oxide in both non-crystalline amorphous (Al_2O_3) and crystalline mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) phases. Figure 3 is a graphical illustration of the fly ash particles with aluminium(III) oxide being represented by the dark colour for both amorphous and mullite phases.

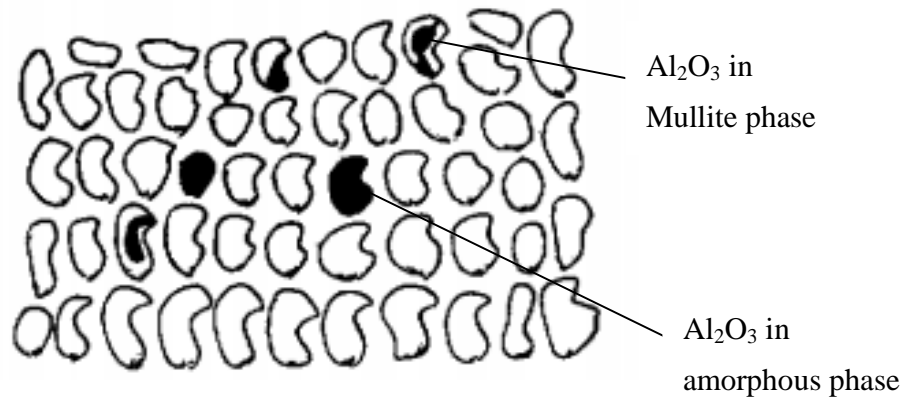


Figure 3: Fly ash particles

Aluminium(III) oxide in the mullite phase formed a crystalline structure with silicon dioxide. Matjie and co-workers (2005) suggested that aluminium(III) oxide in the mullite phase does not react with acids. Hence, it is assumed that only aluminium(III) oxide in the amorphous phase participate in the reaction.

2.5.1 Reaction Mechanism

The following steps are assumed (Szekely et al., 1976):

- Acetylacetone, from the bulk of gas stream diffuse to the gas film.
- Acetylacetone diffuse through the gas film to the surface of fly ash solid particles.
- Acetylacetone is absorbed on the surface of the fly ash.
- Acetylacetone reacts with aluminium(III) oxide in amorphous phase contained in fly ash to produce aluminium(III) acetylacetonate and water as a by product. The proposed steps for the formation of aluminium(III) acetylacetonate from fly ash is given in Figure 4.
- The products, aluminium(III) acetylacetonate and water evolve and remain in the adsorbed state on the surface of aluminium(III) oxide contained in fly ash.
- Desorption of the products, aluminium(III) acetylacetonate and water from the surface of the fly ash.

- The products diffuse through the gas film to the bulk of the product stream.

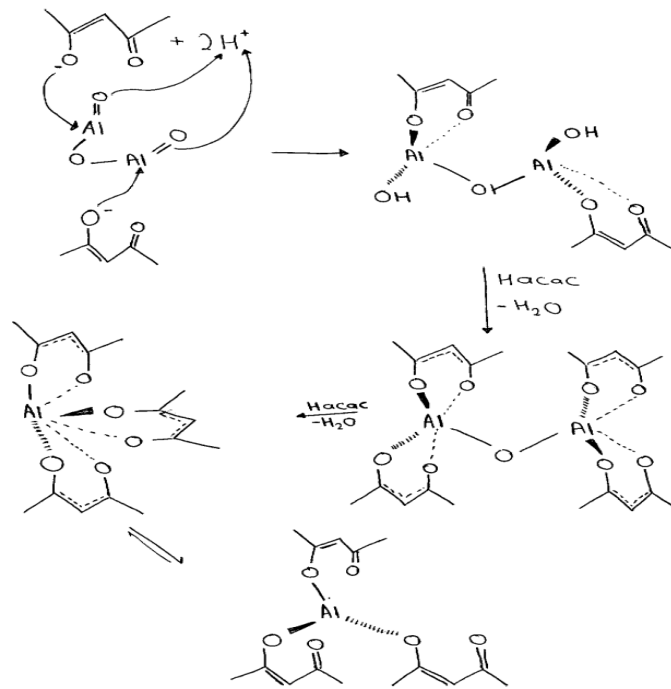


Figure 4: Steps for the formation of aluminium(III) acetylacetonate from aluminium(III) oxide

The described mechanism is shown in Figure 5.

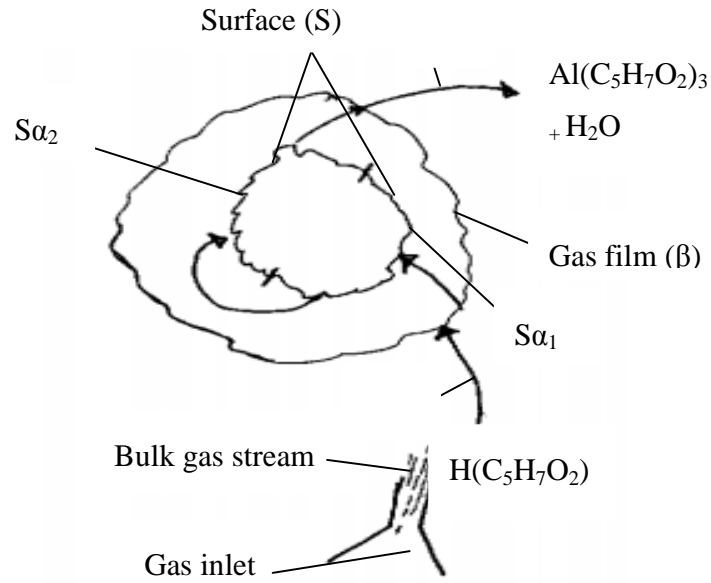


Figure 5: Mechanism of the formation of aluminium(III) acetylacetonate from fly ash

2.5.2 Mathematical Model

The concentration of acetylacetonone was high enough such that the mass transfer was negligible (Szekely et al., 1976). It is assumed that chemical reaction is the only rate limiting step and that the whole surface of the non-porous aluminium(III) oxide particle (in amorphous phase) contained in fly ash take part in the heterogeneous reaction and the reaction is assumed to be a first order reaction.

The rate of acetylacetonone reacting with aluminium(III) oxide contained in the fly ash is given by equation 2.2 (Szekely et al., 1976).

$$r_1 = Sk_1C_{Hacac} = Sk_1M_{Flyash(1-\delta)} \quad 2.2$$

Where S is the surface area of the particle, k_1 the reaction constant, $M_{fly\ ash(1-\delta)}$ the mass of the aluminium(III) oxide contained in fly ash, $1-\delta$ is the weight percentage of aluminium(III) oxide contained in fly ash, and C_{Hacac} the concentration of acetylacetonone.

The rate of the removal of the products (aluminium(III) acetylacetonate and water) is given by equation 2.3.

$$r_2 = Sk_2 \quad 2.3$$

If quasi-stationary conditions are supposed then equation 2.4 states that

$$\alpha_1 + \alpha_2 = 1 \quad 2.4$$

Where α_1 is the fractional coefficient for aluminium(III) oxide in amorphous surface area available to react with acetylacetone and α_2 is the fractional coefficient for surface area of aluminium(III) oxide in amorphous phase covered by reaction products.

And
$$r_1\alpha_1 = r_2\alpha_2 \quad 2.5$$

The rate of aluminium(III) oxide consumption (equation 2.6) from the amorphous phase contained in the fly ash is

$$r_f = r_1\alpha_1 \quad 2.6$$

$$r_f = -\frac{dM_{fly\ ash(1-\delta)}}{dt} = Sk_1\mu M_{fly\ ash(1-\delta)}$$

Combining equation 2.2 to 2.6 gives equation 2.7.

$$\frac{S}{r_f} = \frac{1}{k_1 M_{fly\ ash(1-\delta)}} + \frac{1}{k_2} \quad 2.7$$

The reaction products are formed in the gaseous phase, so the rate due to the removal of the products r_2 is assumed to be zero. Hence, equation 2.7 reduces to equation 2.8.

$$r_f = -\frac{dM_{fly\ ash(1-\delta)}}{dt} = Sk_1 M_{fly\ ash(1-\delta)} \quad 2.8$$

Integrating equation 2.8 yields:

$$M_{fly\ ash(1-\delta)} = M_{fly\ ash(1-\delta)}^0 e^{(-Sk_1t)} \quad 2.9$$

It is also assumed that only aluminium(III) oxide in the amorphous phase takes part in the reaction. By introducing a amorphous phase factor, μ , equation 2.9 can be rewritten to equation 2.10.

$$\mu M_{fly\ ash(1-\delta)} = \mu M_{fly\ ash(1-\delta)}^0 e^{(-Sk_1t)} \quad 2.10$$

The mass of aluminium(III) acetylacetonate formed at time t, is given by equation 2.11.

$$M_{A1} = \mu(M_{fly\ ash(1-\delta)}^0 - M_{fly\ ash(1-\delta)}^0 e^{(-Sk_1t)}) \frac{2 \times W_{Al}}{W_{Al_2O_3}} \quad 2.11$$

The percentage extraction (equation 2.12) X can be determined as follows:

$$X_{A1} = \frac{M_{A1}}{M_{Al}^0} \times 100\% \quad 2.12$$

The BET surface area of the fly ash used in this study (fly ash from Kendal Power Station) was found experimentally to be $0.9696 \pm 0.0053 \text{ m}^2/\text{g}$.

3. EXPERIMENTAL

3.1 Chemicals

The following chemicals were used:

- Aluminium(III) oxide, standardized for column chromatographic adsorption from Merck.
- 99% Acetylacetone reagent from Sigma-Aldrich.
- 99.8% Ethanol absolute puriss from Sigma-Aldrich.
- 99.99% aluminium(III) acetylacetonate was used to prepare standard solutions.

The properties of acetylacetone, aluminium(III) oxide and aluminium(III) acetylacetonate are given in Table 3, Table 4 and Table 5 respectively.

Table 3: Properties of acetylacetone

Acetylacetone	
Chemical Formula	C ₅ H ₈ O ₂
Chemical purity	99%
Molar mass	100.12 (g/mol)
Boiling point	136-140 °C
Density	0.975 g/cm ³

It can be seen that acetylacetone evaporates at temperatures above 136 °C, thus the evaporator's temperature should be maintained at 140 °C in order to evaporate it immediately.

Table 4: Properties of aluminium(III) acetylacetonate

Aluminium(III) acetylacetonate	
Chemical Formula	$\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ ($\text{Al}(\text{acac})_3$)
Molar mass	324.34 (g/mol)
Melting point	190 °C
Boiling point	325 °C
Volatilisation temperature	143-245 °C
Solubility in water	2% at room temperature
Soluble	Hydrocarbons and alcohols

The volatilisation temperature of aluminium(III) acetylacetonate plays a vital role in choosing the reaction temperature. Aluminium(III) acetylacetonate is formed in gaseous phase at volatilization temperature.

Table 5: Properties of aluminium(III) oxide

Aluminium(III) oxide	
Chemical Formula	Al_2O_3
Chemical purity	90%
Molar mass	101.96 (g/mol)
Melting point	2054 °C
Density	3.97 (g/cm ³)

Aluminium(III) oxide was used to prepare a mixture of aluminium(III) oxide and silica sand.

3.2 Raw Materials

3.2.1 Fly ash

A 10 kg sample of dry fly ash was collected from the Kendal Power Station for the gas phase extraction experiments. Kendal Power Station is one of Eskom's power stations in Mpumalanga, South Africa. Particle size distribution, chemical and mineralogical analyses were conducted on the sample. The particle size distribution (PSD) of fly ash was obtained by physically screening the samples using 150 and 75 μm screens. The composition of fly ash (Table 2) was determined by XRF analysis and has already been presented. From Table 2 it can be seen that Kendal Power Station fly ash contains 30.52 wt% aluminium(III) oxide.

The mineralogy was determined by the XRD (Table 6)

Table 6: Mineralogy of Kendal Power Station fly ash

	% composition
Mullite	30.7
Quartz	14.0
Hematite	0.8
Magnetite	1.7
Amorphous	52.9

Mullite is a crystalline structure formed by alumina and silicate, and it has a chemical formula $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Quartz has a chemical formula SiO_2 . Hematite is the mineral form of iron(III) oxide (Fe_2O_3). If mineral's atoms are randomly arranged it is called amorphous and the most common amorphous material is glass. Thus, 52.9 wt% of fly ash minerals exist in their pure form.

XRD and XRF shows that 72 wt% of aluminium(III) oxide contained in fly ash is in the mullite form and 28 wt% in the amorphous form. A detailed calculation is given in Appendix D.

3.2.2 Silica sand

Silica with particle size distribution, +53 to -75 μm . Chemical composition of the silica was determined with XRF shown in Table 7.

Table 7: Composition of Silica

Compounds	% Composition
SiO ₂	98.0
Fe ₂ O ₃	0.6
Al ₂ O ₃	0.3
ZnO	0.001
CaO	<0.01
MgO	<0.001
L.I.O	0.1
Friability	<0.7
Average Uniformity Coefficient	<1.4

3.3 A mixture of silica and 31 wt% aluminium(III) oxide

A mixture of silica and 31 wt% aluminium(III) oxide was prepared based on the composition of fly ash. The initial experiments were carried out on a mixture of silica and 31 wt% aluminium(III) oxide to investigate the feasibility of extracting aluminium from aluminium(III) oxide using acetylacetone.

3.4 Gas Phase Extraction Experimental Set up

Gas phase extraction of aluminium was carried out in a fluidized bed reactor (FBR). The fluidized bed reactor was chosen due to its advantages such as uniform particle mixing, uniform temperature gradient (Grace, 1986). Fluidized bed reactor consisted of an evaporator comprised of a 500 ml round bottom flask, seated in a heating mantle with adjustable temperature connected to the fluidized bed. The ligand and

carrier gas are fed into the evaporator. Fluidized bed consisted of a cylindrical pyrex glass column 50 cm long and 15 mm in diameter which served as a fluidized bed. Midway along the length of the fluidized bed reactor a thermocouple was inserted into the fluidized bed, which was used to measure the temperature of the fluidized bed during the course of the gas phase extraction. Heating wire was coiled around the length of the fluidized bed and connected to a temperature controller. This temperature controller, together with the thermocouple in the fluidized bed reactor, kept the temperature close to the set point by regulating the amount of heat provided by the heating wire. The fluidized bed reactor and heating wire were wrapped with ceramic wool which served as an insulator and minimized heat loss.

The acetylacetone flow rate was controlled and pumped into the evaporator by a peristaltic pump. The reactor also consisted of the carrier gas preheating section, which comprised of 5 meter coiled stainless steel tubing immersed in heating oil and placed into the oil bath. Nitrogen feed pressure was regulated by a pressure regulator on the cylinder and its flow rate was controlled by a nitrogen flow meter. The nitrogen flow was controlled with a two way ball valve.

The experimental set up is shown in Figure 6:

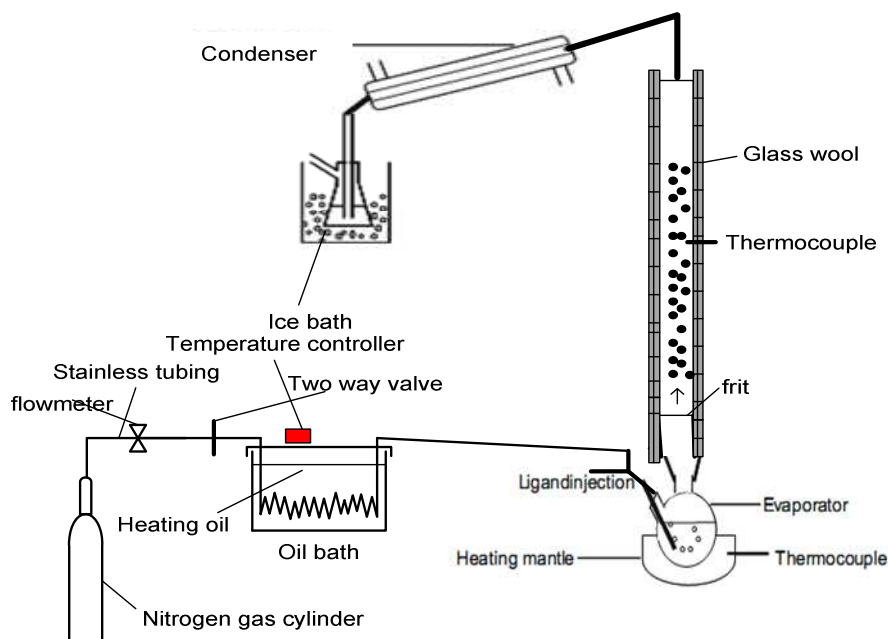


Figure 6: Gas phase extraction experimental set up

Detailed gas phase extraction set up start up, operating and shut down procedures are given in section 8.3.1 of Appendix C.

3.5 Experimental Method

The fluidized bed reactor was charged with the feed, which initially consisted of a mixture of 31 wt% aluminium(III) oxide and silica sand and during later experiments comprised of fly ash. The total mass of a mixture of 31 wt% aluminium(III) oxide and silica was 50 g and the total mass of fly ash was varied at 25 g, 30 g, 50 g, 70 g and 100 g for difference experiments. All equipment were connected after the fluidized bed reactor was charged and the fluidized bed reactor was heated to the reaction temperature, 190 °C, 200 °C, 220 °C and 250 °C for different experimental runs. The heating mantle was also switched on. Once the experimental conditions were reached, the experiment was started by switching on the peristaltic pump, and pumping the acetylacetone at the required flow rate to the evaporator. The

acetylacetone flow rate was varied from 1 mL/min, 2 mL/min, 4 mL/min, 6 mL/min to 9 mL/min.

After each time interval (0-15 minutes, 15-30 minutes, thereafter 30 minutes interval) the pump was switched off and the sample was collected and fresh solvent put into the collection flash which was then connected to the equipment. The pump was started for the next time interval.

In cases where carrier gas is introduced to the system, nitrogen was preheated before it was introduced into the fluidized bed reactor by heating the heating oil to 110 °C before opening the nitrogen regulator at required pressure and flow meter at the required nitrogen flow rate.

3.6 Experimental Conditions

3.6.1 Extraction from Al₂O₃ and Silica mixture

The effects of temperature and acetylacetone flow rate on the extraction of aluminium from aluminium(III) oxide were investigated. The experimental variables are shown in Table 8.

Table 8: Variable values of experiments carried out

Time (hours)	Temperature (°C)	Flow rate (mL/min)
6, 8, 10	190, 200, 220, 250	2, 6, 9

3.6.2 Extraction from fly ash

The effects of acetylacetone flow rate and bed size were investigated on the extraction of aluminium from fly ash. The variable values of the experiments carried out on fly ash are shown in Table 9.

Table 9: Variable values of experiment carried out on fly ash

Time (hours)	Temperature(⁰ C)	Mass (g)	Flow rate (mL/min)
6	220, 250	25, 30, 50, 70, 100	1, 2, 4, 6, 9

3.7 Analyses

The sample is collected after 0-15 minutes, 15-30 minutes, thereafter 30 minutes intervals. 10 ml of each sample is diluted to 100 ml. The diluted solution is analyzed by Ultra-Violet Visible double beam spectrophotometry to determine the concentration of aluminium(III) acetylacetonate in the solution. The measurements were carried out at the maximum absorption wavelength of the aluminium(III) acetylacetonate. The preparation of aluminium(III) acetylacetonate standards used is described in section 8.3.2 of Appendix C. The number of moles of aluminium(III) acetylacetonate was determined using equation 3.1.

$$n = C_d V_d \quad 3.1$$

The total concentration of aluminium(III) acetylacetonate in the sample was determined from the number of moles using equation 3.2.

$$C_s = n/V_s \quad 3.2$$

Where: C_d is the concentration of $Al(acac)_3$ in the diluted solutions,

C_s is the concentration of $Al(acac)_3$ in the sample,

V_d is the volume of diluted solution (100 ml),

V_s is the volume of the sample that is diluted (10 ml).

Mass of aluminium in aluminium(III) acetylacetonate is determined using the molecular formula of aluminium(III) acetylacetonate ($Al(C_5H_7O_2)_3$).

3.8 Liquid Phase Extraction of Aluminium

A batch reactor was used for the liquid phase extraction of aluminium. The required volume of acetylacetone was determined for a given mass using the reaction stoichiometry. A detailed calculation of the volume of acetylacetone theoretically required to react with 50 g fly ash is shown in section 8.1.3 of Appendix A.

Experimental method

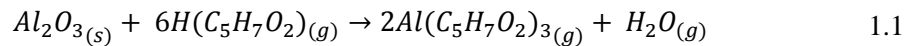
Liquid phase extraction of aluminium consisted of adding a 50 g of fly ash or a mixture of 31 wt% aluminium(III) oxide and silica sample to 93 mL of acetylacetone placed in the 500 ml measuring flask. The 500 ml measuring flask is heated with the heating plate and the temperature of the reaction is maintained at 90 °C or 130 °C for different experimental runs and the agitation speed is fixed at 1083 rpm using a magnetic stirrer. After 360 minutes or 48 hours the heating plate and the magnetic stirrer are switched off and the sample is filtered and residues are washed with 100 ml of ethanol. The volume of the collected sample is measured.

The same analyses procedure as described above is used to analyse the concentration of aluminium(III) acetylacetonate in the samples.

4. RESULTS AND DISCUSSION

The extraction of aluminium from a mixture of silica and 31 wt% aluminium(III) oxide and from fly ash were carried out using acetylacetone as a ligand. Acetylacetone was chosen because of the recent reports (publications) on the ability of acetylacetone in gaseous phase to extract metals from their oxides (Allimann-Lecourt et al., 2002; Potgieter et al., 2006 & Van Dyk et al., 2010). Fly ash was partly chosen because it contains 14.8-31 wt% aluminium(III) oxide (in mullite and amorphous form) depending on coal type, and because there is a large volume of fly ash stored in landfills, waste dumps, and large volumes are produced annually worldwide.

A mixture of silica and 31 wt% aluminium(III) oxide was prepared based on the composition of the Kendal Power Station fly ash. Experiments were carried out on a mixture of silica and 31 wt% aluminium(III) oxide to investigate the potential use of acetylacetone to extract aluminium. The reaction of acetylacetone and aluminium(III) oxide produces aluminium(III) acetylacetonate. The reaction between gaseous acetylacetone and aluminium(III) oxide can be written as follows:



The influence of various parameters, such as temperature, acetylacetone flow rate and bed weight were evaluated and determined. The percentage cumulative extraction is defined as the total amount of aluminium extracted divided by the amount of aluminium originally in the bed.

4.1 The effect of temperature on the extraction of aluminium

The liquid phase extraction of aluminium from a mixture of silica and 31 wt% aluminium(III) oxide and from fly ash at different temperatures were carried out at a constant feed (50 g) and constant acetylacetone volume (93 ml). The reaction equation (Equation 4.1) was used to determine the required acetylacetone volume to

react with 30.52 wt% aluminium(III) oxide in 50 g fly ash. The results are presented in Table 10.

Table 10: Liquid phase extraction of aluminium from fly ash and 31 wt% aluminium(III) oxide at various temperatures after 360 minutes.

Temperature (°C)	% Aluminium Extraction	
	Mixture: 31 wt% Al ₂ O ₃ and sand	Fly ash
90	3.7	1.0
130	8.9	4.1

The extraction of aluminium from both a mixture of silica and 31 wt% aluminium(III) oxide and fly ash is dependent on the reaction temperature. Increasing temperature resulted in an increase in the amount of aluminium extracted. 8.9% of available aluminium was extracted at 130 °C after 360 minutes, while only 3.7% was extracted at 90 °C at the same reaction time from a mixture of silica and 31 wt% aluminium(III) oxide. A maximum of 4.1% was extracted from fly ash at 130 °C, while only 1.0% was extracted at 90 °C.

The results showed that the reaction temperature has a substantial influence on the extraction of aluminium. The lower extraction may be due to that at lower reaction temperature the conversion rate is smaller, thus more reaction time is required to achieve higher extraction. The experiments were carried out for longer reaction time, i.e 48 hours and at 130 °C.

A maximum of 14.0% aluminium was extracted from fly ash at 130 °C after 48 hours. The results show that time has an influence on the extraction efficiency of aluminium from fly ash. Hence at low temperature the reaction rate is very slow and in order to improve extraction longer reaction time is required.

Gas phase extraction of aluminium from a mixture of silica and 31 wt% aluminium(III) oxide at different temperatures were carried out at a constant bed size

(50 g) and constant acetylacetonone flow rate (6 mL/min). A temperature of 250 °C have been chosen as the highest temperature to investigate the effect of temperature on the extraction of aluminium to prevent decomposition of aluminium(III) acetylacetonone due to the TG-DSC thermogram of aluminium(III) acetylacetonone recorded by Shirodker and co-workers (2010). The TG-DSC thermogram of aluminium(III) acetylacetonone showed a sharp endotherm accompanied by a total weight loss at 257 °C, indicating the decomposition of aluminium(III) acetylacetonone to aluminium(III) oxide (Shirodker and co-workers, 2010).

The reaction was stopped after 600 minutes due to the fact that acetylacetonone was consumed at a high rate and no recycling of the unreacted acetylacetonone was done which may be done through a fractional distillation process. The results are presented in Figure 7.

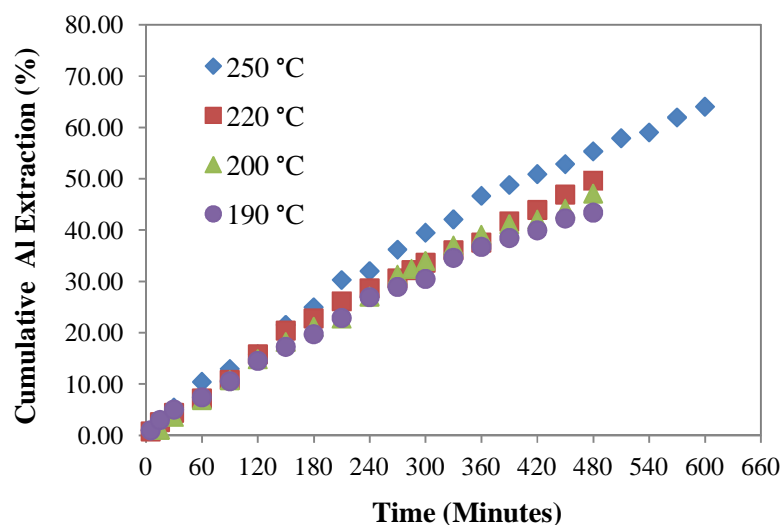


Figure 7: The effect of temperature on the extraction of aluminium at 6 mL/min acetylacetonone flow rate and 50 g of a mixture of 31 wt% aluminium(III) oxide and silica

The extraction of aluminium from a mixture of silica and 31 wt% aluminium(III) oxide is dependent on the reaction temperature. Extraction is higher at higher temperatures; increasing the temperature from 190 °C to 250 °C resulted in the

amount of aluminium extracted increasing substantially. The reaction is initially rapid (linear curve) before it slows down, indicated by flattening of the graphs which implies that the reaction rate decrease as time progress. The highest extraction of 64.0% was obtained at 250 °C after 600 minutes. Increasing temperature from 190 °C to 250 °C resulted in an increase of aluminium extraction by about 12% after 480 minutes.

The results obtained showed that an increase of temperature from 200 °C to 220 °C did not affect the extraction to any great extent; 47.1% of the available aluminium was extracted after 480 minutes of the reaction at 200 °C, while 49.6% was extracted at 220 °C in the same time. It was observed that increasing temperature by the same factor resulted in almost similar increase in extraction. Increasing temperature from 190 °C to 220 °C, increased extraction from 43.4% to 49.6%, while increasing from 220 °C to 250 °C, increased extraction from 49.6% to 55.4% after 480 minutes.

This result agrees with those obtained by Potgieter and co-workers (2006). These authors conducted experiments on the recovery of valuable metals from solid oxide compounds using gas phase extraction. The difference in extraction percentage between their work, which was 65.7% at 220 °C after 105 minutes and the values obtained in the current work, may be due to the difference in the experimental conditions and the aluminium(III) oxide weight percentage in the charge. In the current work a maximum aluminium extraction of 64.0% was obtained at a higher temperature of 250 °C, after a longer reaction time of 600 minutes, but at a much higher aluminium(III) oxide weight percentage of 31 wt% in the feed. Potgieter and co-workers, (2006) used 1 wt% aluminium(III) oxide, while the current work used 31 wt% aluminium(III).

This results shows that a higher amount of aluminium was extracted using acetylacetone in gas phase as compared to using acetylacetone in liquid phase. Increasing temperature from 130 °C (Table 10) to 190 °C (Figure 7) increased extraction from 8.9% to 36.7% after 360 minutes. This increase in extraction suggests that between the two temperatures there is a potential energy barrier required for the

reaction to occur. This barrier is achieved by more atoms at higher temperatures than is achieved at lower temperature of 130 °C. This increase in extraction might also be that the reaction is restricted by mass transfer in liquid phase extraction.

The lower extraction at 90 °C and 130 °C may be due to the solubility of aluminium(III) acetylacetonate in acetylacetone. Aluminium(III) acetylacetonate is 5% soluble in acetylacetone at ambient temperature. Thus, it might be that the product dissolves in the unreacted acetylacetone, inhibiting the reaction to continue. However, this will have to be verified by experiments.

Thus, temperature and reaction time have an influence on the extraction of aluminium from a mixture of silica and 31 wt% aluminium(III) oxide and fly ash. Increasing the reaction temperature and time resulted in an increase of the amount of aluminium extracted.

4.2 The effect of acetylacetone flow rate on the extraction

Previous work on gas phase extraction of metals from their oxides showed that the ligand flow rate has an influence on the extraction (Van Dyk et al., 2010). Gas phase extraction of aluminium from a mixture of silica and 31 wt% aluminium(III) oxide at different acetylacetone flow rate were carried out at 250 °C and at a constant bed size (50 g).

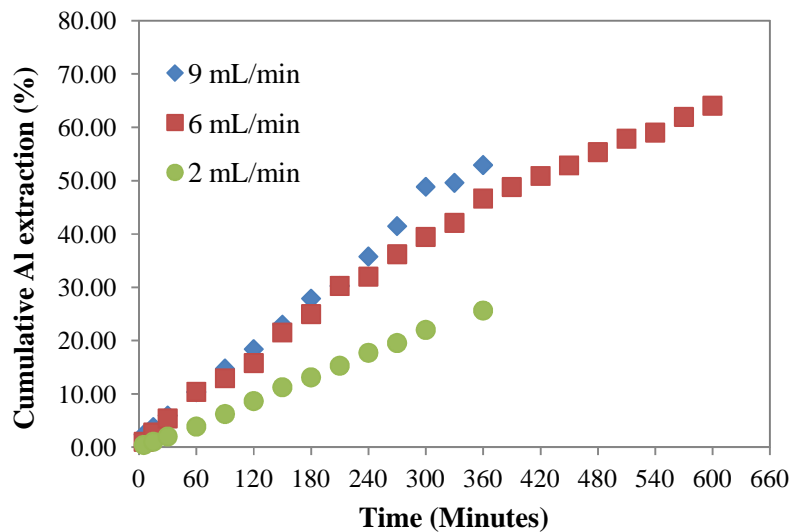


Figure 8: The effect of acetylacetone flow rate on the extraction of aluminium at 250 °C and 50 g of 31 wt% aluminium(III) oxide

The extraction of aluminium from a mixture of silica and 31 wt% aluminium(III) oxide is dependent on the acetylacetone flow rate (Figure 8). Increasing acetylacetone flow rate from 2 mL/min to 9 mL/min resulted in an increase in the amount of aluminium extracted. It can be seen that the extraction of aluminium improves substantially from 25.7% to 46.7% at 250°C after 360 minutes, when the acetylacetone flow rate increase from 2 mL/min to 6 mL/min.

It can be seen that the difference in aluminium extraction for the first 240 minutes at 250 °C using 6 mL/min and 9 mL/min acetylacetone flow rate is similar. After 240 minutes the extraction using 9 mL/min diverges from the extraction using 6 mL/min acetylacetone flow rate. A maximum of 46.7% of aluminium was extracted using 6 mL/min acetylacetone and 52.93% was extracted using 9 mL/min at 250 °C after 360 minutes. The effect of acetylacetone flow rate on the extraction of aluminium was investigated from fly ash at 250 °C and at constant fly ash bed size (50 g). The results are shown in Figure 9 below.

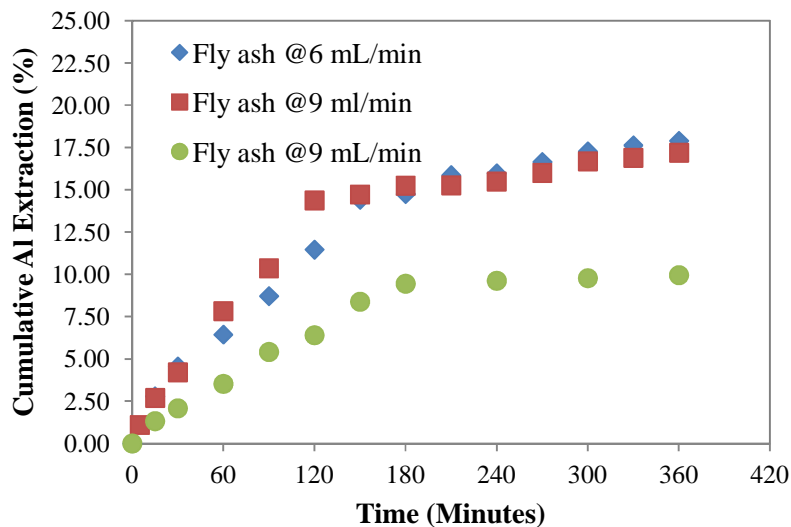


Figure 9: The effect of acetylacetone flow rate on the extraction of aluminium at 250 °C and 50 g fly ash

The similar behaviour obtained in the extraction from a mixture of silica and 31 wt% aluminium(III) oxide (Figure 8) can be seen in Figure 9. About 10.0% of the available aluminium was extracted at an acetylacetone flow rate of 2 mL/min after 360 minutes, while about 17.9% was extracted at 6 mL/min at the same reaction time. It can be seen from Figure 9 that an increase in acetylacetone flow rate from 6 mL/min to 9 mL/min has no difference on the extraction, 17.9% was extracted using 6 mL/min acetylacetone flow rate and 17.2% was extracted using 9 mL/min acetylacetone flow rate at 250 °C after 360 minutes.

This acetylacetone flow rate trend agrees with the trend found in a previous work (Van Dyk et al., 2010). Van Dyk and co-workers (2010) have shown that increasing the acetylacetone flow rate at constant iron(III) oxide charge improves the amount of iron extracted.

Similar results were also obtained to previous works (Matjie et al., 2005 & Hansen et al., 1966). Matjie and co-workers (2005) extracted aluminium from fly ash generated from a selected low ranked bituminous South African coal using sulphuric acid. They showed that 12-24% of aluminium can be extracted after 360 minutes. The 17.9%

aluminium extracted at the same reaction time in this work falls within their range. This suggest that the aluminium extraction efficiency from fly ash is in the same range independent of the extractant used.

It can be seen from Figure 8 and Figure 9 that different aluminium extractions were obtained at the same reaction conditions for what was believed to be similar aluminium(III) oxide weight percentage feed materials (a mixture of silica and 31 wt% aluminium(III) oxide and fly ash). This can be summarized in Figure 10.

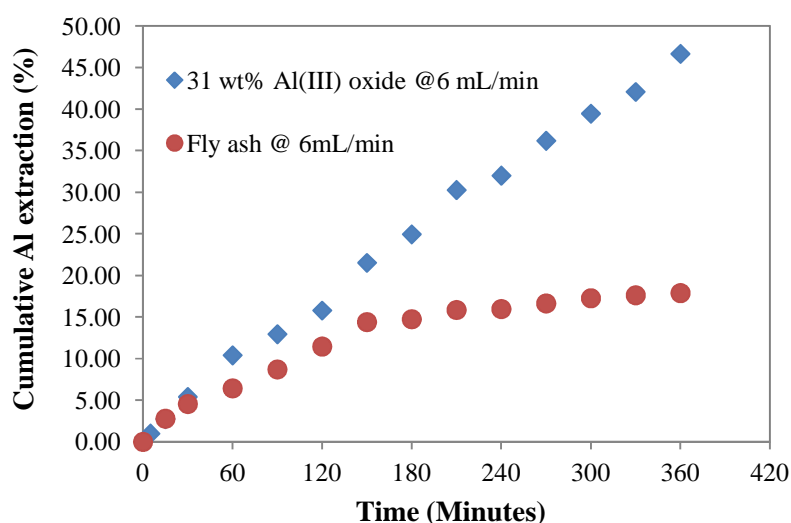


Figure 10: Comparison of aluminium extraction from fly ash and a mixture of silica and 31 wt% aluminium(III) oxide

The extraction of aluminium from a mixture of silica and 31 wt% aluminium(III) oxide and fly ash at 250 °C, 50 g feed and 6 mL/min acetylacetone is shown in Figure 10. It can be seen that the extraction is dependent on the source of aluminium (feed material) as only 17.9% of available aluminium was extracted from fly ash after 360 minutes, while 46.7% was extracted from a mixture of silica and 31 wt% aluminium(III) oxide at the same reaction time. This was also observed at 2 mL/min and 9 mL/min acetylacetone not presented here.

The difference in the aluminium extraction may be due to the difference in the mineralogy of fly ash and mixture of silica and 31 wt% aluminium(III) oxide.

Although aluminium(III) oxide's weight percentage in both feed materials were similar; it exists in pure form in a mixture of silica and 31 wt% aluminium(III) oxide, while it exists in both amorphous and mullite phases in fly ash. The difference in aluminium extraction is due to the accessibility of aluminium. Matjie and co-workers (2005) proposed that only aluminium(III) oxide in the amorphous phase is available to react with acids. Loabser & Verryn (2008) showed that aluminium (III) oxide in the mullite phase forms a crystal structure with silicon dioxide, which makes it not easily accessible to react with acids.

Van Dyk and co-workers (2010) showed that iron(III) oxide reacts rapidly with acetylacetone to give iron(III) acetylacetonate, but fly ash from ESKOM, Kendal Power has significantly lower iron(III) oxide weight percentage (0.4 wt%) and it is expected that it will not have a significant influence on the extraction of aluminium from fly ash.

Thus, acetylacetone flow rate has a significant influence on the extraction of aluminium from both a mixture of 31 wt% aluminium(III) oxide and silica and fly ash to a certain extent.

4.3 Introduction of a carrier gas to the system (fluidized bed)

Previous work on gas phase extraction of metals from their solid oxide compounds used nitrogen as a carrier gas to remove the volatile metal complex from the solid gauge (Allimann-Lecourt et al., 1999 & 2002; Potgieter et al., 2006 & Van Dyk et al., 2010). The introduction of nitrogen to the system was carried out at different nitrogen flow rates, 2 mL/min acetylacetone flow rate, 250 °C and 50 g fly ash.

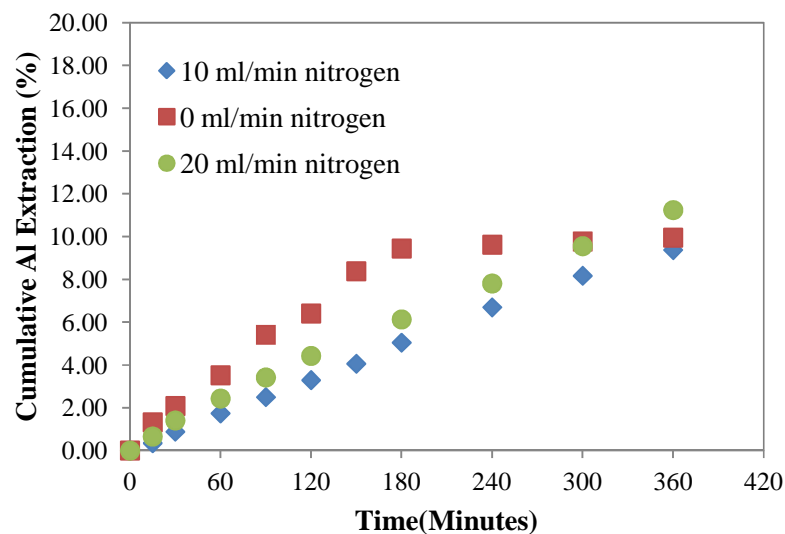


Figure 11: The effect of nitrogen flow rate on the extraction of aluminium at 250 °C, 2 mL/min and 50 g fly ash

The extraction of aluminium from fly ash at 10mL/min, 20mL/min nitrogen and no nitrogen in the system at 250 °C, 2 mL/min acetylacetone flow rate and 50 g fly ash are shown in Figure 11. It can be seen that there is no significant difference on the extraction of aluminium from fly ash in the presence and absence of nitrogen at same reaction conditions. The maximum of 11.2% of the available aluminium was extracted after 360 minutes at 20 mL/min nitrogen flow rate, while only 10.0% was extracted at the same reaction time without nitrogen in the system. This may be due to the fact that in the present of nitrogen, acetylacetone is diluted and the overall flow rate through the bed is increased.

The result agrees with the work done by Van Dyk and co-workers (2010). They observed that varying nitrogen flow rate has no significant influence on the extraction of iron above the volatilization temperature of the metal complex.

4.4 The effect of the bed weight on the extraction of aluminium from fly ash

The concentration (flow rate) of the gas reagent, acetylacetone has an effect on the extraction as was shown in the previous section. Consequently, the effect of the amount of aluminium(III) oxide available for the reaction was investigated. Gas phase extraction of aluminium at different bed sizes was carried out with 2 mL/min acetylacetone and at 220 °C. The results are given in Figure 12.

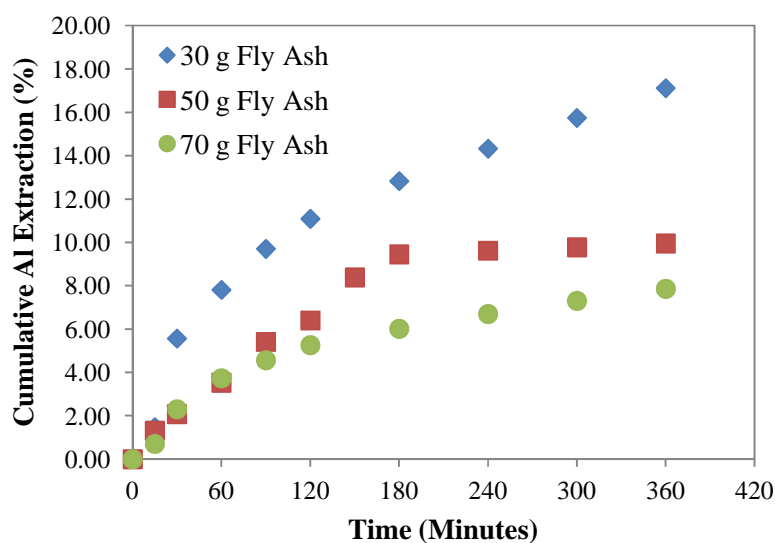


Figure 12: Effect of the fluidized bed size on the extraction of aluminium from fly ash at 2 mL/min and at 220 °C

The extraction of aluminium from fly ash is dependent on the bed size or bed weight. Increasing the bed weight resulted in a decrease in the extraction of aluminium. The highest extraction of 17.1% was obtained with a bed size of 30 g and only 7.9% was extracted at a bed size of 70 g at 220 °C using 2 mL/min acetylacetone flow rate after 360 minutes. It can be seen that increasing the bed weight from 50 g to 70 g has little influence on the extraction of aluminium; 7.9% of the available aluminium was extracted from a bed weight of 70 g and 9.3% was extracted at a bed weight of 50 g under the same reaction conditions. This may be due to the fact that acetylacetone flow rate was lower for the bed weight of 50 g and 70 g.

4.5 The effect of the bed weight and acetylacetone flow

The results also showed that the extraction is dependent on both acetylacetone flow rate and bed weight. The two variables were investigated simultaneous and the experiments were carried out at different acetylacetone flow rate and bed size at constant temperature of 220 °C.

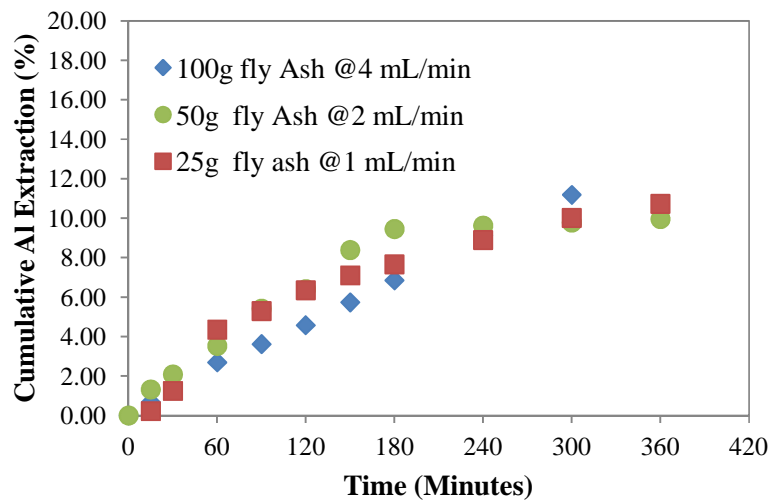


Figure 13: Effect of fluidized bed size and acetylacetone flow rate at 220 °C

Increasing the bed size and acetylacetone flow rate by the same factor has no influence on the extraction of aluminium from fly ash (Figure 13). 10.7% of the available aluminium was extracted from 25 g fly ash and 1 mL/min acetylacetone flow rate after 360 minutes, while 12.6% was extracted from 100 g fly ash and 4 mL/min acetylacetone flow rate after 360 minutes. This suggests that both bed size and acetylacetone flow rate have significant influence on the extraction of aluminium.

It was also observed that at the temperature range 220 °C to 250 °C temperature has no significant influence on the extraction of aluminium from fly ash at 2 mL/min acetylacetone flow rate after 360 minutes; 9.3% of the available aluminium was extracted at 220 °C and 10.0% was extracted at 250 °C. Similar behavior was observed in the previous section with the effect of temperature from a mixture of 31 wt% aluminium(III) oxide and silica.

4.6 The effect of particle size distribution on the extraction of aluminium from fly ash

Coal fly ash heaps consists of a mixture of coarse ash, (coarse ash drop down from the furnace and is collected at the bottom in the ash hopper of the boiler) and fly ash (fly ash is removed from the flue gas stream by means of electrostatic precipitators) (Eskom annual report, 2010). For this reason, the extraction of aluminium was carried out at different particle size fractions. The particle size distribution was determined using 150 μm and 75 μm screens. The PSD of fly ash is shown in Table 11.

Table 11: Fly ash particle size distribution

Screens (μm)	Mass retained (g)	Retained (%)	Cum Retained (%)	Passing (%)
150	17.57	5.91	5.91	94.10
75	58.25	19.58	25.48	74.52
-75	221.73	74.52	100	0
	297.55			

The particle size distribution of fly ash showed that 94.10% of the fly ash particles have a diameter below 150 μm and 74.52% have a diameter below 75 μm . The fly ash particles are mostly spherical in shape (Landman, 2003).

The gas phase extraction of aluminium from fly ash was carried out at -75 μm and -150 μm +75 μm fly ash particle size distributions, 220 $^{\circ}\text{C}$ and at a constant acetylacetone flow rate, 2 mL/min.

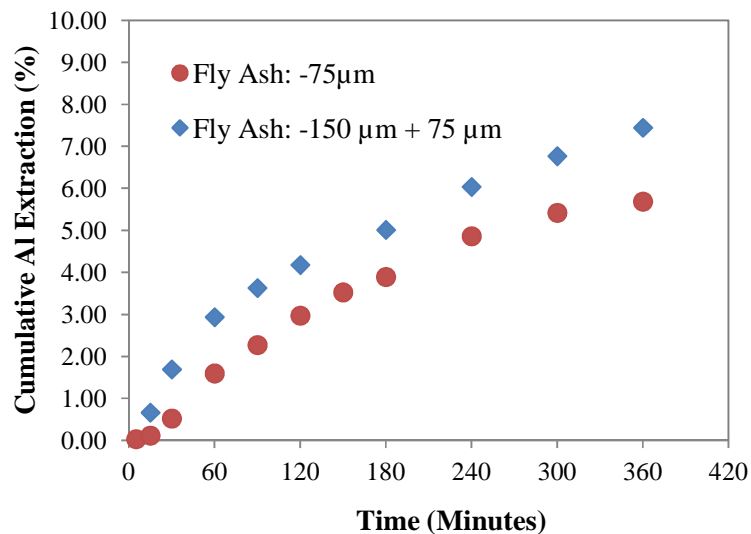


Figure 14: Effect of PSD on the extraction of aluminium at 220 °C, 2 mL/min and 50 g fly ash

The fly ash particle size distribution has no significant influence on the extraction of aluminium from fly ash (Figure 14). Only 5.7% of aluminium was extracted at -75 μm and 7.4% was extracted at -150 +75 μm after 360 minutes at 220 °C and 2 mL/min acetylacetone flow rate. The higher aluminium extraction obtained at -150 +75 μm may suggest that most of aluminium(III) oxide in the amorphous phase is found in this region. Only 19.98% of fly ash particles had a size less than 150 μm and above 75 μm. However, this has to be verified by experiments.

A higher aluminium extraction of 9.3% was obtained on the overall particle size distribution of fly ash under the same reaction conditions. Hence experiments were carried out on the overall fly ash sample.

4.7 Kinetic model

The kinetic model for extraction of aluminium from fly ash was developed in section 2.5. The amorphous factor for the extraction of aluminium from a mixture of 31 wt% aluminium(III) oxide and silica is assumed unity ($\mu = 1$), since the aluminium(III) oxide is in pure form and is accessible for reaction. The particles of aluminium(III) oxide with average size of 112 μm are assumed to be spherically. The surface area of

aluminium(III) oxide is calculated to be $0.4 \text{ m}^2/\text{g}$. The comparison of the kinetic model developed and the experimental data obtained at 6 mL/min acetylacetone flow rate and at $250 \text{ }^\circ\text{C}$ and 50 g of a mixture of 31 wt% aluminium(III) oxide and silica is shown in Figure 15 below.

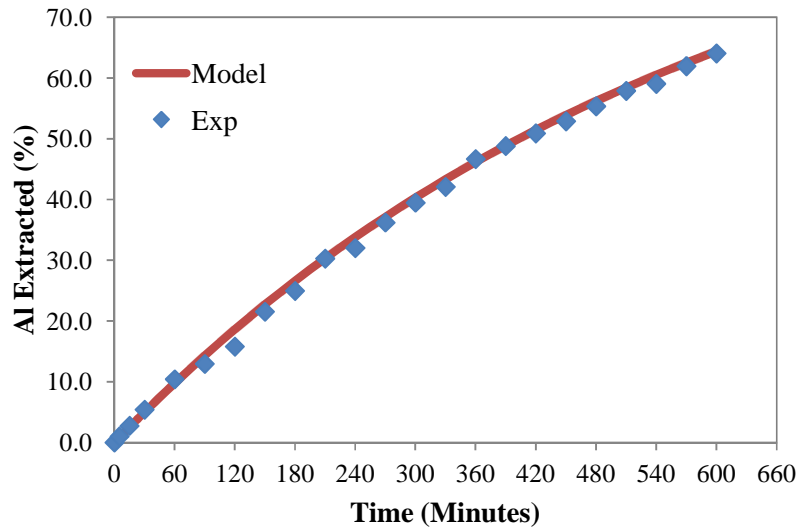


Figure 15: Comparison of the kinetic model and the experimental data obtained at $250 \text{ }^\circ\text{C}$, 6 mL/min and 50 g of 31 wt% aluminium(III) oxide

The kinetic model fit the experimental data obtained from the a mixture of silica and 31 wt% aluminium(III) oxide at $250 \text{ }^\circ\text{C}$ using 6 mL/min acetylacetone flow rate (Figure 15). The kinetic model predicts an aluminium extraction of 64.4% after 600 minutes and 64.0% extraction was extracted experimentally after 600 minutes. The value of the regression coefficient, R^2 is 0.982 and the value of the reaction constant, k_1 is $0.0043 \text{ g}/(\text{min} \cdot \text{m}^2)$. The regression coefficient is a statistical factor that gives a measure of how well future outcomes are likely to be predicted by the model.

The kinetic model was also fitted to the data obtained from the extraction of aluminium from the a mixture of 31 wt% aluminium(III) oxide and silica at $190 \text{ }^\circ\text{C}$ and $220 \text{ }^\circ\text{C}$ as shown in Figure 16 and Figure 17 respectively. The values of the reaction constant and regression coefficients are given in Table 12

Table 12: Values of reaction constant and regression coefficient at different temperatures

Temperature ($^{\circ}\text{C}$)	Reaction constant, k_1	Regression coefficient
190	0.00305	0.994
220	0.00353	0.992
250	0.00430	0.982

It can be seen that the value of the reaction constant, k_1 increases with increasing temperature. This agrees with the Arrhenius theory.

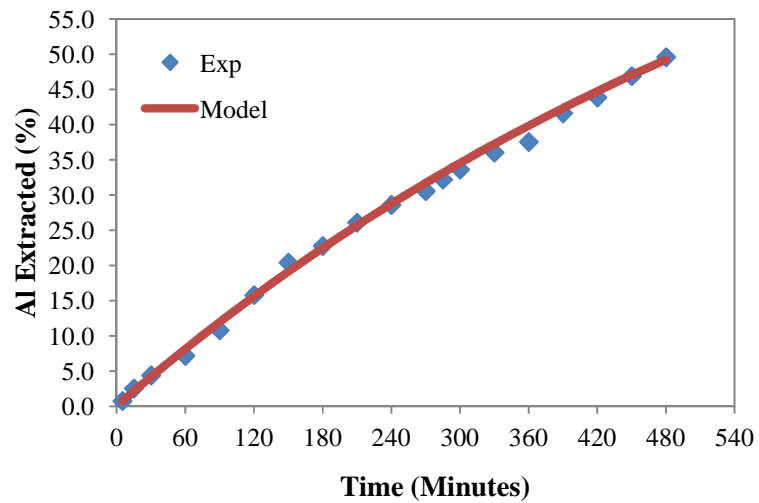


Figure 16: Comparison of the kinetic model and experimental data obtained at 220 $^{\circ}\text{C}$, 6 mL/min and 50 g mixture of silica and 31 wt% aluminium(III) oxide

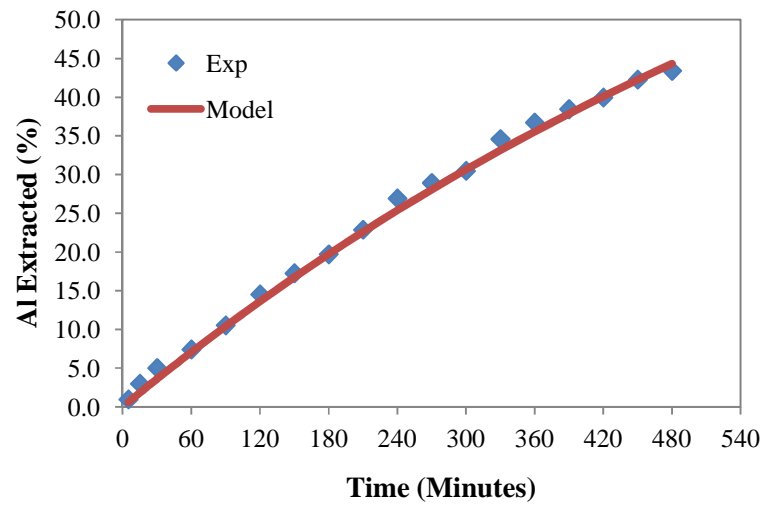


Figure 17: Comparison of the kinetic model and experimental data obtained at 190 °C, 6 mL/min and 50 g mixture of silica and 31 wt% aluminium(III) oxide

It can be seen that the kinetic model fit the experimental data obtained from the extraction of aluminium from a mixture of 31 wt% aluminium(III) oxide and silica at different temperatures (190 °C, 220 °C and 250 °C). The values of the reaction constant, k_1 given in Table 12 are used to determine the value of the activation energy of the reaction using the Arrhenius plot.

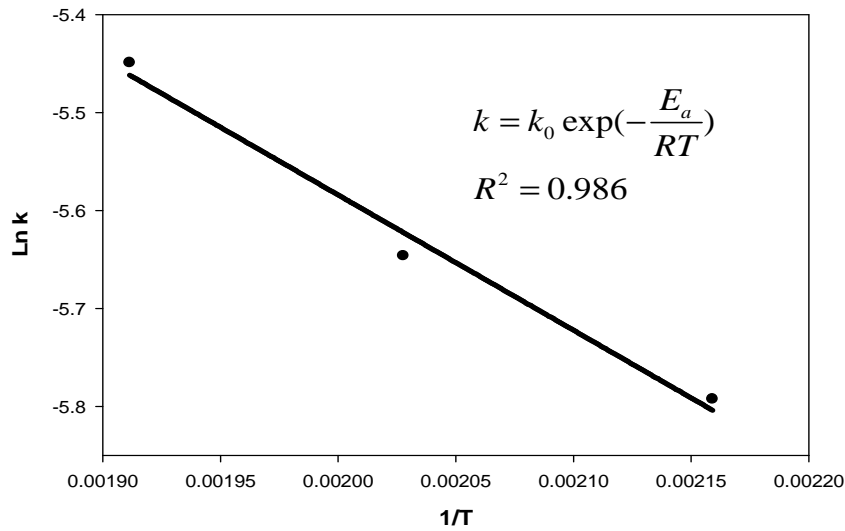


Figure 18: Arrhenius plot at 6 mL/min acetylacetone flow rate and 50 g mixture of 31 wt% aluminium(III) oxide and silica

The magnitude of the activation energy, E_a of the extraction of aluminium from a mixture of 31 wt% aluminium(III) oxide and silica is 11.5 kJ/mol. This value can be used for the extraction of aluminium from aluminium(III) oxide in the amorphous phase contained in fly ash.

The difference in the activation energy obtained by Potgieter and co-workers (2006), (they showed that the activation energy of the extraction of aluminium from a mixture of 1wt% aluminium(III) oxide and silica is 27.7 kJ) and the value obtained in this work may be due to the different weight percentage of aluminium(III) oxide in the feed.

The value of k_0 from the Arrhenius equation ($k = k_0 e^{-\frac{E_a}{RT}}$), is calculated using the regression equation (equation 4.1).

$$\ln k = -1381(1/T) - 2.821 \quad 4.1$$

The reaction constant, k is equal to k_0 at $T = 0k$. It follows from equation 4.1 that at $T = 0k$ the reaction constant, k_0 is given by equation 4.2.

$$\begin{aligned}
 k_0 &= e^{-2.821} \\
 &= 0.0595
 \end{aligned}
 \tag{4.2}$$

Thus, the Arrhenius equation in Figure 19 can be written as equation 4.3 below.

$$k = 0.0595e^{-\frac{E_a}{RT}}
 \tag{4.3}$$

Equation 4.3 is used to calculate the value of the reaction constant, k at different temperatures. The reaction constant, k was calculated at 250 °C using equation 4.3 as shown below:

$$\begin{aligned}
 k &= 0.0595e^{\frac{-11500\text{J/mol}}{8.314\frac{\text{J}}{\text{K}\cdot\text{mol}}(250+273.15)\text{K}}} \\
 &= 0.00423
 \end{aligned}
 \tag{4.4}$$

The reaction constant, $k = 0.00423$ was used to fit the kinetic model to the data obtained from the extraction of aluminium from a mixture of 31 wt% aluminium(III) oxide and silica and fly ash at 250 °C using 6 mL/min acetylacetone flow rate.

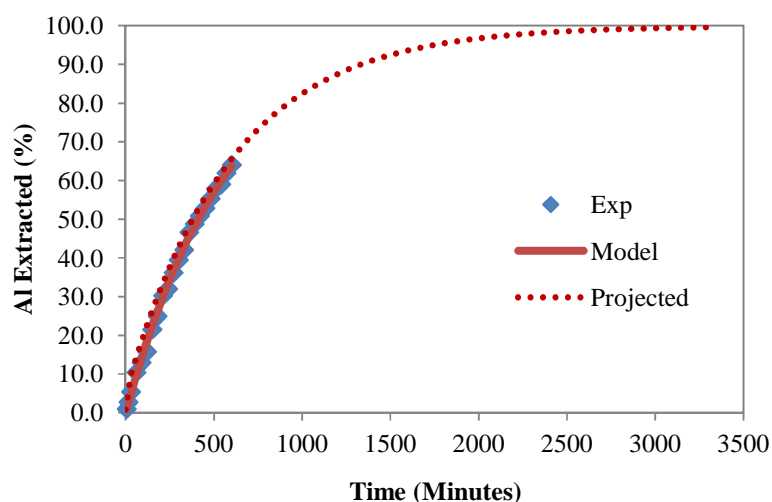


Figure 19: Comparison of the kinetic model, projected kinetic model and experimental data obtained at 250 °C and 50 g 31 wt% aluminium(III) oxide using 6 mL/min acetylacetone flow rate

The kinetic model fit the experimental data obtained at 250 °C and 50 g 31 wt% aluminium(III) oxide using 6 mL/min acetylacetone flow rate better. The kinetic model predicts 63.8% extraction and 64.0% was obtained experimentally after 600 minutes. The dotted curve is the projected aluminium extraction predicted by the kinetic model. The projection curve suggests that the reaction would start to reach equilibrium after 50 hours with extraction efficiency of about 99.4%.

The kinetic model was also fitted to the experimental data obtained from the extraction of aluminium from fly ash at 250 °C using 6 mL/min acetylacetone flow rate. The kinetic model assumed that only aluminium from the amorphous phase is extracted, thus the amorphous factor, μ for the fly ash from Eskom, Kendal Power Station is 0.28. A detailed determination of aluminium(III) oxide in amorphous phase using XRD and XRF analysis is given in Appendix D.

The BET surface area of fly ash was measured to be $0.9696 \pm 0.0053 \text{ m}^2/\text{g}$.

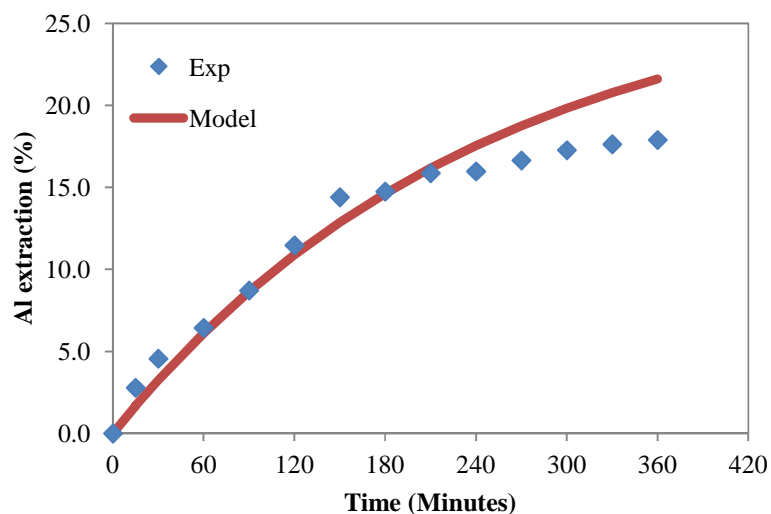


Figure 20: Comparison of the kinetic model and experimental data obtained at 250 °C, 6 mL/min and 50 g fly ash

It can be seen that the kinetic model predicts the experimental data obtained better at the reaction time below 210 minutes (Figure 20). The model predicts an extraction of 16.2% and 15.9% was extracted experimentally after 210 minutes. The kinetic model diverges from the experimental data at the reaction time above 210 minutes. About 18% was extracted experimentally and the model predicts 22% after 360 minutes.

The kinetic model fit the data obtained from a 31 wt% aluminium(III) oxide better compared to the data obtained from the fly ash. This may be due that the reaction of acetylacetone and 31 wt% aluminium(III) oxide has not reached equilibrium, while the reaction of acetylacetone and fly ash has approach equilibrium. However, this will have to verified by carrying out an experiment on the 31 wt% aluminium(III) oxide until it approaches maximum aluminium convention.

Experimental results showed that the extraction of aluminium is also influenced by the flow rate of acetylacetone. The kinetic model is fitted to the experimental data obtained at 2 mL/min and 9 mL/min acetylacetone flow rate. The comparison of the kinetic model and data obtained at 250 °C (thus, the reaction constant is 0.00423) using 2 mL/min and 9 mL/min acetylacetone flow rates is given in Figure 21.

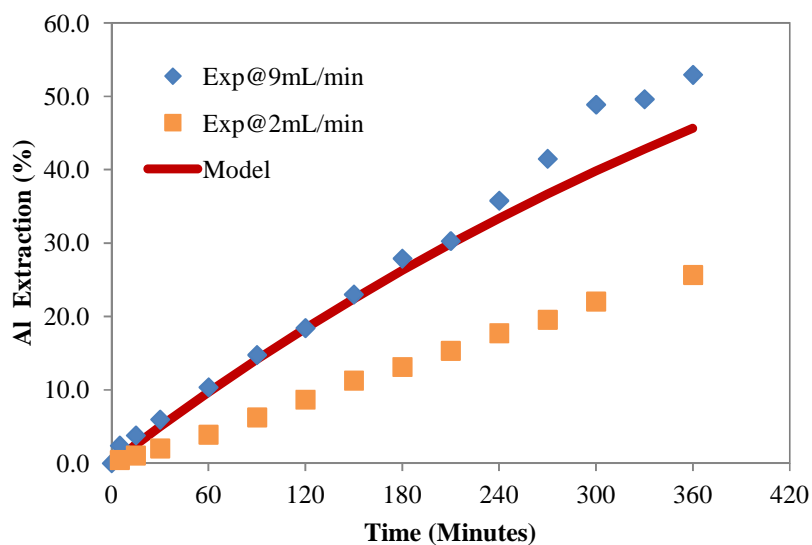


Figure 21: Comparison of the kinetic model and experimental data obtained at 250 °C using 2 mL/min and 9 mL/min respectively

The kinetic model fit the experimental data obtained from a mixture of 31 wt% aluminium(III) oxide at 250 °C using 9 mL/min acetylacetone flow rate at a time reaction below 240 minutes well, but the model does not fit at higher reaction times. It can be seen that the kinetic model does not fit the experimental data obtained at 250 °C using 2 mL/min acetylacetone flow rate at all. The kinetic model which takes into account the flow rate of acetylacetone and the reaction temperature should be developed

5. CONCLUSIONS

The aim of this project was to investigate the extraction of aluminium from fly ash using acetylacetone. The fly ash that was used contained 30.52 wt% aluminium(III) oxide. A mixture of 31 wt% aluminium(III) oxide and silica was first prepared based on the aluminium(III) oxide composition in the fly ash to do initial studies on the extraction of aluminium. A higher aluminium extraction from a mixture of 31 wt% aluminium(III) oxide and silica was obtained while using acetylacetone in the gas phase as compared to acetylacetone in the liquid phase. A maximum of 46.7% of the available aluminium was extracted using acetylacetone in gas phase at 250 °C using 6 mL/min acetylacetone flow rate after 360 minutes, while only 8.9% was extracted after 360 minutes using acetylacetone in the liquid phase.

The gas phase extraction result agrees with work done by Potgieter and co-workers, (2006). The extraction of aluminium from a mixture of 31 wt% aluminium(III) oxide and silica was shown to depend on the following variables:

- Temperature: The extraction of aluminium increased with increasing temperature from 90 °C to 250 °C. 250 °C was chosen as the highest temperature in this study to avoid the decomposition of aluminium(III) acetylacetonate into aluminium(III) oxide.
- Acetylacetone flow rate: The extraction of aluminium increased with increasing acetylacetone flow rate to a certain threshold level.

The extraction of aluminium from fly ash stabilized at about 18% at 250 °C using 6 mL/min acetylacetone flow rate after 360 minutes. The extraction of aluminium from fly ash was shown to depend on the following variables:

- Time: Increasing time resulted in an increase in aluminium extraction.
- Acetylacetone flow rate: The extraction of aluminium increased with increasing acetylacetone flow rate from 2 mL/min to 6 mL/min and there is no difference in the extraction of aluminium as the acetylacetone flow rate is increased from 6 mL/min to 9 mL/min.

- Bed size: The extraction of aluminium increased with decreased bed size.
- Particle size distribution: No difference on the extraction of aluminium at different particle size distributions was observed for the two size distributions investigated
- Carrier gas: No significant difference on the extraction of aluminium when nitrogen was introduced into the system.

The extraction of aluminium is dependent on the feed material used. Despite the same aluminium(III) oxide content of the fly ash and a mixture of 31wt% aluminium(III) oxide and silica a difference in aluminium extraction was observed from each due to differences in the mineralogy. Thus, the extraction of aluminium depends on the mineralogy of feed material. The kinetic model developed fit the experimental data obtained from the extraction of aluminium from a mixture of 31 wt% aluminium(III) oxide and silica at 190 °C, 220 °C and 250 °C. The activation energy for the gas phase extraction of aluminium from a 31 wt% aluminium(III) oxide was found to be 11.5 kJ/mol. The reaction constant, ($k=0.00423$) was calculated using the Arrhenius equation and it was used to fit the kinetic model to the data obtained from fly ash and a mixture of 31 wt% aluminium(III) oxide at 250 °C using 6 mL/min acetylacetone flow rate. The kinetic model fitted the data from a mixture of 31 wt% aluminium(III) oxide and silica better compared to data obtained from fly ash. It fit the data from the fly ash better at the reaction time below 240 minutes. The kinetic model can be used to predict the extraction of aluminium from aluminium(III) oxide in the amorphous phase using 6 mL/min acetylacetone flow rate. However there is a need to develop a model which takes into account the influence of temperature as well as acetylacetone flow rate.

6. RECOMMENDATIONS

Based on the findings of this study, the following recommendations for further studies are made:

- The extraction of aluminium from sintered fly ash using acetylacetone in gas phase should be investigated, because by sintering the fly ash more aluminium (III) oxide becomes accessible for extraction.
- Recovery of aluminium(III) oxide from aluminium(III) acetylacetonate should be investigated,
- The kinetics of gas phase extraction should be studied in more detail.

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8. APPENDICES

8.1 Appendix A: Determination of Mass Extracted

8.1.1 Extraction Percentage of Aluminium

The concentration of aluminium(III) acetylacetonate, $\text{Al}(\text{acac})_3$ was measured using Ultra Violet Spectrometry at 255 nm. The concentration at time (t) was measured in parts per million (ppm), which can be represented as milligrams per litre (mg/l). Thus,

$$C_{\text{Al}(\text{acac})_3}(t) = \frac{m_{\text{Al}(\text{acac})_3}}{V_{\text{collected}}(t)} \quad \text{A.1}$$

Where:

$m_{\text{Al}(\text{acac})_3}$: Mass of aluminium(III) acetylacetonate,

$V_{\text{collected}}(t)$: Volume of the extraction liquor collected at time t,

$C_{\text{Al}(\text{acac})_3}(t)$: Concentration of aluminium(III) acetylacetonate at time t.

Rearranging A.1,

$$C_{\text{Al}(\text{acac})_3}(t)V_{\text{collected}}(t) = m_{\text{Al}(\text{acac})_3} \quad \text{A.2}$$

Cumulative mass of $\text{Al}(\text{acac})_3$ was determined using the equation A.3 below:

$$\text{Cum } m_{\text{Al}(\text{acac})_3}(t_i) = m_{\text{Al}(\text{acac})_3}(t_i) + m_{\text{Al}(\text{acac})_3}(t_{i-1}) \quad \text{A.3}$$

Cumulative mass of aluminium was calculated using the molecular formula of aluminium(III) acetylacetonate ($\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$).

1 mole of Al in $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$, thus 26.98 g of Al in 324.31 g (molar mass of $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$).

$$\text{Cum } m_{\text{Al}}(t_i) = \text{Cum } m_{\text{Al}(\text{acac})_3}(t_i) \left(\frac{\text{Molar mass}_{\text{Al}}}{\text{Molar mass}_{\text{Al}(\text{acac})_3}} \right) \quad \text{A.4}$$

$$Cum\ m_{Al}(t_i) = Cum\ m_{Al(acac)_3}(t_i) \frac{26.98g}{324.31g}$$

Cumulative Al extraction percentage was calculated using equation A.5 below:

$$Cum\ Al\ Ext\ (\%) = \frac{Cum\ m_{Al}(t_i)}{m_{Al\ in\ the\ feed}} \cdot 100\% \quad A.5$$

8.1.2 Density of the fly ash from Kendal Power Station

The density of fly ash was calculated using the composition of fly ash. Aluminium(III) oxide and silicon dioxide percentages in fly ash were used.

Table A. 1: Determination of fly ash density

	Density (g/cm ³)	Composition (%)	Density in fly ash (g/cm ³)
Al ₂ O ₃	3.95	30.52	1.21
Silicon dioxide	2.65	56.14	1.49

The density of the fly ash is **2.70 g/cm³**.

8.1.3 Amount of acetylacetone required for complete reaction

The stoichiometric volume of the acetylacetone was calculated using the stoichiometric equation (equation 1.1).

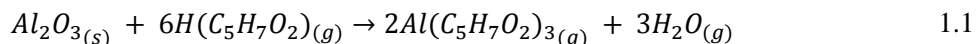


Table A. 2: Mass balance of 1 mole Al₂O₃ reacting with 6 moles acetylacetone

Al ₂ O ₃	C ₅ H ₈ O ₂	Al(C ₅ H ₇ O ₂) ₃	H ₂ O
1 mol	6 moles	2 moles	3 moles
101.96 (g)	600.72 (g)	648.68 (g)	54 (g)

Consider 50 g of a mixture of 31 wt% Al_2O_3 and silica. There are 0.152 moles of Al_2O_3 in 15.5 g. 1 mole Al_2O_3 react with 6 moles acetylacetone (equation 1.1). Thus, 0.152 mol of Al_2O_3 react with 0.912 mol of acetylacetone which is equivalent to 91.331 g.

Therefore, the stoichiometric amount required for the reaction to proceed to completion is 0.912 mol.

Stoichiometric volume required for complete reaction

The stoichiometric volume of acetylacetone required is mass divide density liquid acetylacetone (0.98 g/cm^3).

$$\begin{aligned} V &= m/\rho \\ &= 93.195 \text{ mL} \end{aligned}$$

Thus, 93.195 mL is the stoichiometric volume of acetylacetone required to react with 50 g of 31 wt% Al_2O_3 .

The amount of acetylacetone supplied after 10 hours

The mass of acetylacetone supplied after 10 hours at 6 mL/min acetylacetone flow rate is

$$\begin{aligned} m &= \rho \times \text{flow rate} \times \text{time} \\ &= 0.975 \times 6 \times 600 \\ &= 3510 \text{ g} \end{aligned}$$

The amount of acetylacetone supplied after 10 hours is therefore

$$n = \frac{m}{Mr} = \frac{3510 \text{ g}}{100.13 \text{ g/mol}} = 35.05 \text{ mol}$$

The amount of acetylacetone supplied (35.05 mol) after 10 hours using 6 mL/min is therefore much higher than the stoichiometric amount required for the reaction to proceed to completion (0.912 mol).

The amount of acetylacetone supplied after 6 hours

The mass of acetylacetone supplied after 6 hours at 2 mL/min acetylacetone flow rate is

$$\begin{aligned}m &= \rho \times \text{flow rate} \times \text{time} \\ &= 0.975 \times 2 \times 360 \\ &= 702g\end{aligned}$$

The amount of acetylacetone supplied after 6 hours is therefore

$$n = \frac{m}{Mr} = \frac{702g}{100.13g/mol} = 7.01mol$$

The amount of acetylacetone supplied (7.01 mol) after 6 hours using 2 mL/min is therefore much higher than the stoichiometric amount required for the reaction to proceed to completion (0.912 mol).

8.2 Appendix B: Summary of Experimental Results

The samples were collected after 15 minutes until 30 minutes, thereafter 30 minutes interval. 10 mL is collected from each of the collected samples and the 10 mL is diluted to 100 mL unless stated otherwise. The diluted solution is analysed using UV/Vis for the concentration of aluminium(III) acetylacetonate.

In each table the following are defined as follows:

- Conc of $\text{Al}(\text{acac})_3$ in the diluted solution is the concentration of the $\text{Al}(\text{acac})_3$ in the diluted solution measured by UV/Vis spectroscopy,
- Conc of $\text{Al}(\text{acac})_3$ in the sample is the total concentration of $\text{Al}(\text{acac})_3$ in the sample collected,
- Volume collected is the total volume of the sample collected,
- Mass of $\text{Al}(\text{acac})_3$ is concentration of $\text{Al}(\text{acac})_3$ in the sample multiply by volume collected,
- Cumulative mass of $\text{Al}(\text{acac})_3$ is calculated using equation A. 3,

- Cumulative mass of aluminium is calculated using equation A. 4
- Cumulative extraction of Al is calculated using equation A. 5

Table B. 1: The extraction of Al from 50 g 31 wt% Al₂O₃ and silica at 190 °C and 6 mL/min acacH flow rate/

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
5	1100	11000	78	0.9	0.9	0.1	1.0
15	1650	16500	109	1.8	2.7	0.2	3.0
30	1300	13000	138	1.8	4.5	0.4	5.0
60	983	9833	216	2.1	6.6	0.5	7.4
90	1300	13000	214	2.8	9.4	0.8	10.5
120	1633	16333	216	3.5	12.9	1.1	14.5
150	1133	11333	214	2.4	15.3	1.3	17.3
180	1003	10030	218	2.2	17.5	1.5	19.7
210	1300	13000	216	2.8	20.3	1.7	22.9
240	1633	16333	220	3.6	23.9	2.0	26.9
270	817	8167	217	1.8	25.7	2.1	28.9
300	617	6167	224	1.4	27.1	2.3	30.5
330	1633	16333	223	3.6	30.7	2.6	34.6
360	850	8500	224	1.9	32.6	2.7	36.7
390	683	6833	224	1.5	34.1	2.8	38.5
420	600	6000	221	1.3	35.5	2.9	40.0
450	933	9333	220	2.1	37.5	3.1	42.3
480	450	4500	226	1.0	38.5	3.2	43.4

Table B. 2: The extraction of Al from 50 g 31 wt% Al₂O₃ and silica at 200 °C and 6 mL/min acacH flow rate

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
5	1250	12500	77	1.0	1.0	0.1	1.1
15	2050	20500	110	2.3	3.2	0.3	3.6
30	2067	20667	140	2.9	6.1	0.5	6.9
60	1600	16000	214	3.4	9.5	0.8	10.7
90	1767	17667	206	3.6	13.2	1.1	14.8
120	1883	18833	158	3.0	16.1	1.3	18.2
150	1417	14167	184	2.6	18.8	1.6	21.1
180	850	8500	168	1.4	20.2	1.7	22.7
210	2217	22167	172	3.8	24.0	2.0	27.0
240	1883	18833	201	3.8	27.8	2.3	31.3
270	500	5000	198	1.0	28.8	2.4	32.4
285	767	7667	180	1.4	30.2	2.5	34.0
300	1567	15667	172	2.7	32.8	2.7	37.0
330	1100	11000	168	1.8	34.7	2.9	39.1
360	867	8667	210	1.8	36.5	3.0	41.1
390	367	3667	220	0.8	37.3	3.1	42.1
420	850	8500	220	1.9	39.2	3.3	44.2
450	1183	11833	222	2.6	41.8	3.5	47.1
480	600	11833	226	2.7	44.5	3.7	50.1

Table B. 3: The extraction of Al from 50 g 31 wt% Al₂O₃ and silica at 220 °C and 6 mL/min acacH flow rate

Time (Min)	Aluminium Acetylacetonate					Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
5	833	8333	80	0.667	0.7	0.1	0.8
15	1517	15167	106	1.608	2.3	0.2	2.6
30	1150	11500	142	1.633	3.9	0.3	4.4
60	1100	11000	226	2.486	6.4	0.5	7.2
90	1433	14333	223	3.196	9.6	0.8	10.8
120	1983	19833	224	4.443	14.0	1.2	15.8
150	1933	19333	212	4.099	18.1	1.5	20.4
180	983	9833	214	2.104	20.2	1.7	22.8
210	1400	14000	210	2.940	23.2	1.9	26.1
240	1150	11500	194	2.231	25.4	2.1	28.6
270	917	9167	190	1.742	27.1	2.3	30.6
285	1150	11500	126	1.449	28.6	2.4	32.2
300	950	9500	134	1.273	29.9	2.5	33.7
330	1017	10167	212	2.155	32.0	2.7	36.1
360	617	6167	214	1.320	33.3	2.8	37.6
390	1700	17000	214	3.638	37.0	3.1	41.7
420	950	9500	208	1.976	39.0	3.2	43.9
450	1333	13333	202	2.693	41.7	3.5	46.9
480	1150	11500	208	2.392	44.0	3.7	49.6

Table B. 4: The extraction of Al from 50 g 31 wt% Al₂O₃ at 250 °C and 6 mL/min acacH flow rate

Time (Min)	Aluminium		Acetylacetonate			Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
5	1233	12333	80	1.0	1.0	0.1	1.0
15	1650	16500	104	1.7	2.7	0.2	2.7
30	1850	18500	142	2.6	5.3	0.4	5.4
60	2167	21667	228	4.9	10.3	0.9	10.4
90	1133	11333	220	2.5	12.8	1.1	12.9
120	1250	12500	225	2.8	15.6	1.3	15.8
150	2667	26667	212	5.7	21.2	1.8	21.5
180	1517	15167	223	3.4	24.6	2.0	25.0
210	2383	23833	220	5.2	29.9	2.5	30.3
240	783	7833	218	1.7	31.6	2.6	32.0
270	1950	19500	212	4.1	35.7	3.0	36.2
300	1533	15333	210	3.2	38.9	3.2	39.5
330	1233	12333	209	2.6	41.5	3.5	42.1
360	2117	21167	213	4.5	46.0	3.8	46.7
390	1017	10167	207	2.1	48.1	4.0	48.8
420	1033	10333	200	2.1	50.2	4.2	50.9
450	950	9500	206	2.0	52.1	4.3	52.9
480	1150	11500	212	2.4	54.6	4.5	55.3
510	1183	11833	212	2.5	57.1	4.7	57.9
540	483	4833	234	1.1	58.2	4.8	59.0
570	1300	13000	221	2.9	61.1	5.1	62.0
600	917	9167	225	2.1	63.1	5.3	64.0

Table B. 5: The extraction of Al from 50 g of a mixture of 31 wt% Al₂O₃ and silica at 250 °C and 9 mL/min acacH flow rate

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
5	2333	23333	91	2.1	2.1	0.2	2.4
15	850	8500	146	1.2	3.4	0.3	3.8
30	1067	10667	180	1.9	5.3	0.4	6.0
60	1300	13000	300	3.9	9.2	0.8	10.3
90	1267	12667	308	3.9	13.1	1.1	14.7
120	1083	10833	300	3.2	16.3	1.4	18.4
150	1367	13667	298	4.1	20.4	1.7	23.0
180	1400	14000	310	4.3	24.7	2.1	27.9
210	683	6833	309	2.1	26.9	2.2	30.3
240	1550	15500	315	4.9	31.7	2.6	35.8
270	1633	16333	310	5.1	36.8	3.1	41.5
300	1900	19000	345	6.6	43.4	3.6	48.9
330	233	2333	284	0.7	44.0	3.7	49.6
360	983	9833	300	2.9	47.0	3.9	52.9

Table B. 6: The extraction of Al from 50 g of a mixture of 31 wt% Al₂O₃ and silica at 250 °C using 2 mL/min acacH flow rate

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
5	660	6603	59	0.4	0.4	0.0	0.4
15	777	7770	69	0.5	0.9	0.1	1.0
30	1083	10833	80	0.9	1.8	0.1	2.0
60	1567	15667	106	1.7	3.5	0.3	3.9
90	1950	19500	107	2.1	5.5	0.5	6.2
120	2050	20500	105	2.2	7.7	0.6	8.7
150	2233	22333	103	2.3	10.0	0.8	11.3
180	1567	15667	105	1.6	11.6	1.0	13.1
210	1833	18333	106	1.9	13.6	1.1	15.3
240	2067	20667	104	2.1	15.7	1.3	17.7
270	1533	15333	106	1.6	17.4	1.4	19.6
300	2083	20833	105	2.2	19.5	1.6	22.0
360	1917	19167	168	3.2	22.8	1.9	25.7

Table B. 7: The extraction of Al from 50 g fly ash at 250 °C, 9 mL/min acacH flow rate

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
5	1167	11667	091	1.1	1.1	0.1	1.1
15	1067	10667	146	1.6	2.6	0.2	2.7
30	817	8167	180	1.5	4.1	0.3	4.2
60	1167	11667	300	3.5	7.6	0.6	7.8
90	800	8000	308	2.5	10.1	0.8	10.4
120	1300	13000	300	3.9	14.0	1.2	14.4
150	1133	1133	298	0.3	14.3	1.2	14.7
180	1633	1633	310	0.5	14.8	1.2	15.2
210	50	50	309	0.0	14.8	1.2	15.3
240	683	683	315	0.2	15.0	1.3	15.5
270	1633	1633	31	0.5	15.5	1.3	16.0
300	1900	1900	345	0.7	16.2	1.3	16.7
330	733	733	284	0.2	16.4	1.4	16.9
360	983	983	300	0.3	16.7	1.4	17.2

Table B. 8: The extraction of Al from 50 g fly ash at 250 °C & 6 mL/min acacH flow rate

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
15	1918	19183	141	2.7	2.7	0.2	2.8
30	1152	11517	149	1.7	4.4	0.4	4.6
60	802	8017	228	1.8	6.2	0.5	6.4
90	952	9517	232	2.2	8.5	0.7	8.7
120	1168	11683	229	2.7	11.1	0.9	11.5
150	1285	12850	222	2.9	14.0	1.2	14.4
180	752	1503	223	0.3	14.3	1.2	14.7
210	478	4782	226	1.1	15.4	1.3	15.9
240	50	500	221	0.1	15.5	1.3	16.0
270	1485	2970	219	0.7	16.2	1.3	16.6
300	1385	2770	219	0.6	16.8	1.4	17.3
330	781	1562	224	0.3	17.1	1.4	17.6
360	561	1122	228	0.3	17.4	1.4	17.9

50 ml of the sample was diluted to 100 ml.

Table B. 9: The extraction of Al from 50 g fly ash at 250 °C & 2 mL/min acacH flow rate

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
15	1683	16833	76	1.3	1.3	0.1	1.3
30	950	9500	78	0.7	2.0	0.2	2.1
60	1300	13000	108	1.4	3.4	0.3	3.5
90	1683	16833	109	1.8	5.3	0.4	5.4
120	900	9000	107	1.0	6.2	0.5	6.4
150	1750	17500	110	1.9	8.1	0.7	8.4
180	950	9500	109	1.0	9.2	0.8	9.4
240	983	9833	315	0.2	9.4	0.8	9.6
300	1033	10333	345	0.1	9.5	0.8	9.8
360	367	3667	300	0.2	9.7	0.8	10.0

**Table B. 10: The extraction of Al from 50 g fly ash at 220 °C & 2 mL/min acacH
flow rate**

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
15	1063	10633	71	0.8	0.8	0.1	0.8
30	950	9500	76	0.7	1.5	0.1	1.5
60	920	9200	105	1.0	2.4	0.2	2.5
90	983	9833	107	1.1	3.5	0.3	3.6
120	870	8700	107	0.9	4.4	0.4	4.6
150	950	9500	105	1.0	5.4	0.5	5.6
180	950	9500	103	1.0	6.4	0.5	6.6
240	923	9233	168	1.6	8.0	0.7	8.2
300	433	4333	149	0.6	8.6	0.7	8.9
360	267	2667	170	0.5	9.1	0.8	9.3

**Table B. 11: The extraction of Al from 30 g fly ash at 220 °C & 2 mL/min acacH
flow rate**

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
15	1117	11167	77	0.9	0.9	0.1	1.5
30	3017	30167	79	2.4	3.2	0.3	5.6
60	1233	12333	106	1.3	4.6	0.4	7.8
90	2650	10600	104	1.1	5.7	0.5	9.7
120	1883	7533	107	0.8	6.5	0.5	11.1
180	1583	6333	160	1.0	7.5	0.6	12.8
240	1350	5400	162	0.9	8.3	0.7	14.3
300	1267	5067	163	0.8	9.2	0.8	15.7
360	1233	4933	162	0.8	10.0	0.8	17.1

**Table B. 12: The extraction of Al from 70 g fly ash at 220 °C & 2 mL/min acacH
flow rate**

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
15	1217	12167	79	1.0	1.0	0.1	0.7
30	2717	27167	80	2.2	3.1	0.3	2.3
60	1833	18333	106	1.9	5.1	0.4	3.7
90	2650	10600	107	1.1	6.2	0.5	4.6
120	2283	9133	103	0.9	7.2	0.6	5.3
180	1583	6333	162	1.0	8.2	0.7	6.0
240	1450	5800	160	0.9	9.1	0.8	6.7
300	1267	5067	163	0.8	9.9	0.8	7.3
360	1133	4533	166	0.8	10.7	0.9	7.9

**Table B. 13: The extraction of Al from 100 g fly ash at 220 °C & 4 mL/min acacH
flow rate**

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
15	1233	12333	105	1.3	1.3	0.1	0.7
30	1433	14333	107	1.5	2.8	0.2	1.5
60	1450	14500	165	2.4	5.2	0.4	2.7
90	1100	11000	163	1.8	7.0	0.6	3.6
120	1117	11167	167	1.9	8.9	0.7	4.6
150	1350	13500	167	2.3	11.1	0.9	5.7
180	1300	13000	166	2.2	13.3	1.1	6.8
240	1633	16333	272	4.4	17.7	1.5	9.1
300	1517	15167	262	4.0	21.7	1.8	11.2
360	1022	10225	260	2.7	24.4	2.0	12.5

**Table B. 14: The extraction of Al from 100 g fly ash at 220 °C & 6 mL/min acacH
flow rate**

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
15	1717	17167	136	2.3	2.3	0.2	1.2
30	1700	17000	146	2.5	4.8	0.4	2.5
60	1750	17500	226	4.0	8.8	0.7	4.5
90	1783	17833	228	4.1	12.8	1.1	6.6
120	2000	20000	225	4.5	17.3	1.4	8.9
150	1233	12333	230	2.8	20.2	1.7	10.4
180	733	7333	224	1.6	21.8	1.8	11.2
210	1067	10667	226	2.4	24.2	2.0	12.5
240	876	8755	230	2.0	26.2	2.2	13.5
270	231	2307	222	0.5	26.8	2.2	13.8
300	257	2568	225	0.6	27.3	2.3	14.1
330	570	5700	223	1.3	28.6	2.4	14.7
360	358	3578	230	0.8	29.4	2.4	15.2

**Table B. 15: The extraction of Al from 50 g fly ash at 220 °C & 2 mL/min acacH
flow rate and -75 µm PSD**

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
5	50	500	58	0.0	0.0	0.0	0.0
15	117	1167	70	0.1	0.1	0.0	0.1
30	500	5000	79	0.4	0.5	0.0	0.5
60	983	9833	106	1.0	1.5	0.1	1.6
90	1533	6133	107	0.7	2.2	0.2	2.3
120	1633	6533	104	0.7	2.9	0.2	3.0
150	1233	4933	109	0.5	3.4	0.3	3.5
180	867	3467	103	0.4	3.8	0.3	3.9
240	1417	5667	166	0.9	4.7	0.4	4.9
300	856	3425	158	0.5	5.3	0.4	5.4
360	383	1533	169	0.3	5.5	0.5	5.7

**Table B. 16: The extraction of Al from 50 g fly ash at 220 °C & 2 mL/min acacH
flow rate and -150 µm +75 µm PSD**

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
15	833	8333	77	0.6	0.6	0.1	0.7
30	1250	12500	80	1.0	1.6	0.1	1.7
60	1150	11500	105	1.2	2.8	0.2	2.9
90	1617	6467	104	0.7	3.5	0.3	3.6
120	1267	5067	105	0.5	4.1	0.3	4.2
180	1250	5000	162	0.8	4.9	0.4	5.0
240	1483	5933	168	1.0	5.9	0.5	6.0
300	1067	4267	166	0.7	6.6	0.5	6.8
360	983	3933	167	0.7	7.2	0.6	7.4

25 mL of the sample was diluted to 100 mL.

**Table B. 17: The extraction of Al from 50 g fly ash at 250 °C & 2 mL/min acacH
flow rate and 10 mL/min nitrogen**

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
15	450	4500	75	0.3	0.3	0.0	0.3
30	675	6749	77	0.5	0.9	0.1	0.9
60	784	7840	106	0.8	1.7	0.1	1.7
90	675	6750	109	0.7	2.4	0.2	2.5
120	700	7000	110	0.8	3.2	0.3	3.3
150	676	6760	110	0.7	3.9	0.3	4.1
180	979	9794	98	1.0	4.9	0.4	5.0
240	976	9762	164	1.6	6.5	0.5	6.7
300	889	8886	161	1.4	7.9	0.7	8.2
360	688	6875	170	1.2	9.1	0.8	9.4

**Table B. 18: The extraction of Al from 50 g fly ash at 250 °C & 2 mL/min acacH
flow rate and 20 mL/min nitrogen**

Aluminium Acetylacetonate						Cumulative mass of Aluminium (g)	Cumulative extraction of Al (%)
Time (Min)	Conc of Al(acac) ₃ in the diluted solution(ppm)	Conc of Al(acac) ₃ in the sample(ppm)	Volume collected (ml)	Mass of Al(acac) ₃ (g)	Cumulative mass of Al(acac) ₃ (g)		
15	899	8992	71	0.6	0.6	0.1	0.7
30	908	9083	80	0.7	1.4	0.1	1.4
60	904	9044	110	1.0	2.4	0.2	2.4
90	878	8782	109	1.0	3.3	0.3	3.4
120	882	8822	111	1.0	4.3	0.4	4.4
180	924	9244	179	1.7	6.0	0.5	6.1
240	906	9060	180	1.6	7.6	0.6	7.8
300	941	9405	180	1.7	9.3	0.8	9.6
360	920	9202	178	1.6	10.9	0.9	11.2

8.3 Appendix C: Experimental set up and standards preparation

8.3.1 Gas Phase Extraction Experimental Set up

8.3.1.1 Set up procedure

The set up procedure of the fluidized bed reactor can be described in the following steps:

- Place 5 meters coiled stainless steel tubing in the oil bath filled with oil
- Connect the stainless steel to the nitrogen flow meter connected to the nitrogen
- Place 500 ml round bottom flask in the heating mantle with variable temperature settings.
- Connect a column with a diameter of 2 cm and height of 50 cm to 500 ml round bottom flask
- Wrap the heating wire around the column
- Pour required mass of the feed into the column
- Connect a condenser on the top of the column and connect cooler pipes to the condenser
- Cover the glass column and round bottom flask with ceramic blanket
- Connect a collecting flask with a solvent to the condenser and place in ice water
- Place the reactor in the fume hood and switch on the fume hood
- Connect the peristaltic pump, nitrogen tube and the thermocouple to 500 ml round bottom flask
- Connect the thermocouple to the column and the temperature controller connected to the heating wire (heating tape wrapped around the column)

8.3.1.2 Start up and Operating procedure

The experimental procedure below describes the measuring process of the samples collected per time interval.

- Open the tap for water/cooler to cool the condenser
- Switch on the heating mantle
- Switch on the temperature controller and set to require temperature

When the operating conditions are reached;

- Switch on the peristaltic pump (at required acetylacetone flow rate) and simultaneous switch on the timer (timer set on time interval 5 or 15 or 30 minutes).
- Switch off the peristaltic pump after each time interval
- Replace the collecting flask (50 ml ethanol poured in the flask)
- Measure the volume collected in the collecting flask
- Dilute 10 ml of the sample to 100 ml for the UV/Vis analysis.

Effect of carrier gas

In cases where a carrier gas is introduced to the system, preheat nitrogen before introducing it to the system by heating the heating oil to 110 °C before opening the nitrogen regulator at required pressure and flow meter at the required nitrogen flow rate. Then follow the start up and operating procedure described above.

8.3.1.3 Shut down procedure

The operational shut down procedure is described below:

- Switch off the peristaltic pump
- Close the nitrogen flow
- Switch off the heating mantle
- Switch off the oil bath
- Switch off the temperature controller
- Close the water/cooler tap

- Disconnect the apparatus and switch off the fume hood

8.3.2 Preparation of Al(acac)₃ standards

Calibration standards for the Ultra Violet-Visible spectrophotometry analysis were prepared from synthesized aluminium acetylacetonate complexes (Potgieter et al., 2006; Hon et al., 1965 and Stary and Hladky, 1963). Stock solution containing 5000 ppm (mg L⁻¹) of aluminium(III) acetylacetonate was prepared in absolute ethanol. Dilutions were made from the stock solution to prepare a series of standards (250, 500, 750, 1000, 1500, 2000, 2500 and 3000 ppm). The wavelength of maximum absorbance for aluminium(III) acetylacetonate was selected by scanning a solution of aluminium(III) acetylacetonate over a range of wavelengths from 190 to 900 nm. The wavelength of maximum absorbance is 255.0 nm.

8.4 Appendix D: Determination of aluminium(III) oxide in the mullite phase and the amorphous phase

Molecular weight of fly ash species (some):

Aluminium	-	27 g
Silicon	-	28 g
Oxygen	-	16 g
Aluminium(iii) oxide	-	102 g
Mullite (3Al ₂ O ₃ ·2SiO ₂)	-	426 g

XRF Analysis:

% of aluminium(iii) oxide = 30.52 wt%

Consider 100 g fly ash,

%Total aluminium(iii) oxide in 100 g fly ash=30.52g

Total aluminium in 100 g fly ash = 16.16 g

D.1

XRD Analysis:

$$\% \text{ of mullite in fly ash} = 30.68 \text{ wt\%}$$

D.2

$$\text{Total mullite in 100 g fly ash} = 30.68 \text{ g}$$

$$\text{Aluminium(iii)oxide in mullite} = \frac{30.68 \cdot 3 \cdot 102}{426} = 22.04 \text{ g}$$

D.3

$$\text{Aluminium in mullite} = \frac{22.04 \cdot 2 \cdot 27}{102} = 11.67 \text{ g}$$

From equation D.2 and D.3:

$$\% \text{ of aluminium(iii)oxide in the mullite} = \frac{22.04}{30.52} \cdot 100\% = 72.22\%$$

D.4

Thus,

$$\begin{aligned} \% \text{ of aluminium(iii) oxide in amorphous} &= 100\% - 72.22\% \\ &= 27.78\% \end{aligned}$$

D.5

In a similar way, there is 72.22% and 27.78% of aluminium in the mullite and amorphous phase respectively.