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Vapour Phase Extraction:
A Re-Evaluation

Douglas Gwyllm Bailey

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

School of Chemical and Metallurgical Engineering
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Declaration

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



21st day of August 2024

Abstract

Research undertaken at the University of the Witwatersrand has pursued the recovery of valuable metals using vapour-phase extraction. VPE is a process in which an organic ligand reacts with an element of interest; the product, an organo-metallic complex, reports to the vapour/gas phase and so is separated from the bulk material. Contacting with the solid particulate material occurs in a fluidized bed. The stable organo-metallic complexes, being removed, are condensed and recovered. VPE seems a promising technology and so the use of acetylacetone (acac) to extract several metals from various sources was investigated at Wits. The extractions of (1) iron from iron ore fines and synthetic sources and (2) chromium and tantalum from synthetic samples were investigated; so, too, was (3) aluminium from fly ash and synthetic sources; (4) vanadium from depleted catalysts; and (5) gold from tailings. Gold and tantalum cannot be extracted by acac at all, yet it was thought that they could be. Ligands may also not react with—or react in the same way with—different structural states of the same compound; this was not considered in previous studies, which only mentioned that higher extractions were obtained from synthetic samples. The underlying causes were not adequately considered. Essential properties—such as phase and composition—were not identified, much less characterized. Other limitations include fractionation and fluidization. If the grade of the material is very low, there may not be sufficient metal recovered to isolate it by means of fractionation. This would require high selectivity, which precludes the use of acac. A lack of fluidization prevented reagents from reaching the target species, starving the reactions. Thus, the conditions needed to undertake kinetic studies were not met, invalidating previous tests and their findings. Previous work which reported success has been shown to be unreliable or misguided by experimental anomalies. However, the possibility of using such a process cannot be ruled out altogether. That is to say, alternative ligands can be considered, but only if they can be shown to react with a target species in the phase in which it occurs. The mechanisms involved in the process need to be properly understood and employed before a process can be conceived and developed.

Dedication

Δόξα τω Θεώ

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Nomenclature

Acetylacetone	Acac
Atomic Absorption Spectrometry	AAS
Backscattered-Electron	BSE
Brunauer-Emmett-Teller	BET
Chemical Vapour Deposition	CVD
Chemical Vapour Transport	CVT
Density Function Theory	DFT
Fluidized Bed Reactor	FBR
Hexafluoroacetylacetone	HFA
Particle Size Distribution	PSD
Selective Extraction and Recovery of Metals using Volatile Organic Compound	SERVO
Treatment of Refractory Copper Ore	TORCO
Trifluoroacetylacetone	TFA
Vapour Phase Extraction	VPE

Chapter 1

The Origins of Vapour Phase Extraction

Research undertaken at the University of the Witwatersrand pursued the recovery of metals using vapour-phase extraction (VPE). VPE describes the extraction into a gas phase of elements from solids (elemental or compounds—as minerals or phases) by means of reaction with a volatile compound, especially one that is organic. The product is a volatile organo-metallic complex. As it, too, is a vapour at elevated temperatures, it readily separates the element of interest from the solid. If the reaction is selective, it has the potential to recover elements from materials (ores or discarded tailings) of low-grade. A critical part of the history of this technology is chemical vapour transport. In CVT a condensed phase, usually a solid, is volatilized by a gaseous reactant, and then deposited as a crystal elsewhere (Binnewies *et al.* 2012:1).

This phenomenon was first noted by Bunsen (1852) when he observed the formation of minerals in the presence of volcanic gases containing chlorine compounds. Binnewies and his colleagues (2013:219–20) describe further work done by Bunsen. He later determined that haematite was being transported in the vapour phase via a reaction with hydrogen chloride. This takes place according to Equation 1 when the reactions occurs at around 1000°C, and according to Equation 2 from 300-400°C (Binnewies *et al.* 2012:213). Bunsen was able to reproduce the reaction synthetically, and he coined the term "pneumatolysis" to describe the phenomenon.

$$Fe_2O_3(s) + 6HCl(g) = 2FeCl_3(g) + 3H_2O(g) \qquad \textit{Equation 1}$$

$$Fe_2O_3(s) + 6HCl(g) = Fe_2Cl_6(g) + 3H_2O(g) \qquad \textit{Equation 2}$$

The Mond process

The next significant advancement was the development of the Mond Process. Coming from a middle-class family with limited opportunities in more traditional

sectors, industrialist Ludwig Mond—born in Germany in 1839—became interested in the sciences with a view to improving his social standing and society at large (Morris 1989:34). He was educated in chemistry and entered the chemical industry when it was in its relative infancy. The mid-nineteenth century saw a transition from previous practice which was often wasteful and had little regard for pollution and its effect on the population. Mond saw an opportunity to increase profits by recycling waste products and make existing processes more efficient. This defined the rest of his career, in which he sought to understand the chemistry behind industrial processes to improve various processes.

In the operation of a magnesia plant, there was extensive and rapid corrosion of nickel valves owing to trace carbon monoxide in the nitrogen flushing stage (Morris 1989:38). This motivated Mond to study the interaction between carbon monoxide and nickel. One test consisted of passing a stream of carbon monoxide over nickel metal at high temperature. The effluent stream was burned to oxidise the carbon-monoxide to carbon dioxide. The apparatus was cooled at the end of the test, with carbon-monoxide still flowing over the nickel. At a particular range of temperatures the gas reacted with the nickel and the flame became a bright, luminous green colour (Abel 1990:14,18). A porcelain dish placed in the stream soon became coated with nickel, and heating the stream caused the effluent tube itself to become coated. Raising the temperature caused the nickel compound to decompose to nickel and carbon monoxide, with the nickel depositing on exposed surfaces.

Thus, in 1889, Mond concluded that the interaction between nickel and carbon monoxide results in the formation of a volatile compound that he proposed calling nickel-carbon-oxide (Mond *et al.* 1890:750). Incidentally, Mond and one of his co-authors, Quincke, were both students of Bunsen. He had unwittingly discovered a new class of compound now known as carbonyls (Morris 1989:38). He successfully synthesized carbonyls with several metals, among them cobalt, iron, molybdenum, and ruthenium (Mond *et al.* 1910:800). Only nickel formed a carbonyl at ambient pressures (~1 atm), which meant that it could be extracted selectively from materials containing other base metals that often occur with nickel.

The reactivity and selectivity of nickel allowed for the development of the first process known to use CVT. Nickel is reacted with carbon monoxide at 100°C to form nickel tetracarbonyl (see Equation 3; Allimann-Lecourt 2004:42). Heating the compound liberates carbon monoxide for recycling, forming pure nickel deposits. Mond procured land in Canada to mine nickel, which was reduced before being shipped to Wales for refining using his new process (Morris 1989:38). It came into operation in 1902 with Inco running it commercially in Ontario (Allimann-Lecourt 2004:42). This is still operational today under Vale Canada Limited, as Inco is known since it was purchased by Vale in October 2006 (Block 2015).

$$Ni + 4CO \xrightarrow{100°C} Ni(CO)_4 \xrightarrow{200-300°C} Ni + 4CO \qquad \textit{Equation 3}$$

Processes involving the direct extraction of metals as a volatile species can be a cost-effective means to treat lower grade ores. These processes would require reagents to remove only the desired elements, a selectivity and separation that stands in contrast to the separation of phases in a traditional pyrometallurgical process that would upgrade the ore. Such processes entail heating large quantities of gangue material that do not contribute directly to the process, making it costly to process low-grade ore. Inefficiencies in the removal of gangue, moreover, add to the losses of valuable material. Thus, a process capable of extracting the metal directly is advantageous, and the Mond process demonstrated that is possible to extract metals in the vapour phase.

Langmuir on tungsten CVT and the van Arkel process

Langmuir (1913:108) studied a common phenomenon observed in tungsten-filament light bulbs, where bulbs gradually darken over time. It was well known that tungsten oxidizes in air to form WO_3. He thought that the oxide volatilized easily, and then migrated to the bulb and deposited on the cooler glass. He also found that this occurred more readily if water vapour was present in the system and concluded that the process was actually a CVT reaction (see Equation 4). As the reaction is endothermic, its equilibrium favours the reverse reaction when the tungsten acid vapour comes into contact with the cooler glass (Binnewies *et al.* 2012:205–6), depositing WO_3 on the bulb. Tungsten can also be transferred in this manner directly

according to Equation 5, which is also an endothermic reaction (Binnewies *et al.* 2012:124).

$$WO_3(s) + H_2O(g) = H_2WO_4(g) \qquad \textit{Equation 4}$$

$$W(s) + 4H_2O(g) = H_2WO_4(g) + 3H_2(g) \qquad \textit{Equation 5}$$

Langmuir (1915:1154, 1162) later found that introducing chlorine into the bulb would remove the tungsten deposits. He further found that if there are two tungsten filaments, the colder of the two will gradually disappear as tungsten migrates to the hotter filament. He suggested that chlorine was reacting to form WCl_6. This was verified by van Arkel in 1923 (Binnewies *et al.* 2013:220), who found that tungsten is transported to the hotter filament from the glass via the exothermic reaction in Equation 6.

$$W(s) + 3Cl_2(g) = WCl_6(g) \qquad \textit{Equation 6}$$

Van Arkel and de Boer (1925), applying this same principle, then developed a process for extracting titanium, zirconium, hafnium, and thorium. It was the first process producing several of these metals in their pure form. Titanium was later replaced by the Kroll process (Schaschke 2014:397). It is, however, still a popular method for extracting hafnium (Risovany *et al.* 2001:1), as well as highly pure titanium. It consisted of using iodine to transport the metal via an exothermic reaction to a hot wire, where the metal would be deposited. This was the first time specific transport reactions were studied (Binnewies *et al.* 2012:2). Up until this point, the focus had been on practical applications and on addressing specific industrial challenges. However, the studies were becoming more academic in nature.

CVT is established as a field of research

This shift brought about studies such as those by Biltz and colleagues (Biltz *et al.* 1928; Fischer & Biltz 1928), in which they discussed CVT reactions that occur with gold. Their focus was on chloride species. Gold, they found, can be transported both as $AuCl_3$ and AuCl. Fischer and Gewehr (1932:17–18) went on to describe in detail the mechanism whereby CVT reactions take place, with particular regard to the equilibrium shifts which make the reactions possible. They appear to have been the first to have clarified the mechanism in this way, reserving the term pneumatolysis

(from the Greek, 'to separate by a gas in motion') to describe this type of reaction (Binnewies *et al.* 2013:220).

The next major advancement came with numerous studies undertaken by Schäfer and colleagues. Most notable among these was the paper 'On the transport of a condensed phase in a temperature gradient by means of heterogeneous equilibria' (Schäfer *et al.* 1956). The paper details experimental procedures that are still in use, as well as coining the term 'chemical vapour transport' itself. Today it describes the class of phenomena; pneumatolysis is reserved for the phenomenon when it occurs naturally. It is here that CVT came into its own and established itself as a field of study and an industrial technique and process. It is also here that our interests diverge from CVT and focus more on its application in extractive metallurgy.

CVT is explored for use in extractive metallurgy

The potential of CVT reactions in extractive metallurgy was soon realized. Nieuwenhuis (1968:456–58) refers to several studies into volatilization for metal extraction. He focused on tin species. Past attempts at developing processes involving volatilized tin had failed largely because externally heated retorts were used: gaseous species attacked the retort lining and the charge—what goes into the reactor—sintered. Conditions need to be reducing for the reaction to proceed. The temperature and gas composition control required narrowed the reactor choice to either a rotary kiln or a fluidized bed. Both reactor types provide the contact needed between reducing and chlorinating agents, and each keeps corrosive gases away from moving parts (*i.e.*, rotary kiln) or dispenses with moving parts (fluidized bed). Ease of operation, particularly in respect of a continuous process, was another design criterion. Nieuwenhuis concluded that both reactor types mentioned are suitable but that the fluidized bed performed better.

Around the same time, the then Anglo American Corporation of South Africa started a project it called the Treatment of Refractory Copper Ore, or TORCO for short (Pinkney & Plint 1967:559). A fluidized bed reactor was selected because of the associated high thermal transfer efficiency, tight control of temperature, and ease of operation (Pinkney & Plint 1967:571), which mirrors the design decisions made by

Nieuwenhuis. The TORCO team studied the segregation process that van Arkel had discovered in 1923, which also volatilized the target metal by chlorination. [1]

TORCO extracts copper by mixing an oxidized ore with a reducing agent, typically coal or coke, and a halide salt such as sodium chloride. This mixture is often preheated to 700°C in a rotary kiln, with the reaction taking place in a second rotary kiln at a similar temperature. Heating the ore releases moisture from hydrated clay minerals. The water reacts with the salt to produce hydrochloric acid vapour (Rampacek *et al.* 1959:4–6). The acid reacts with the copper oxides, which form cupric and cuprous chlorides (see Equation 7 and Equation 8). At 700°C, any cupric chloride that forms decomposes to cuprous chloride.

$$CuO + 2HCl = CuCl_2 + H_2O \qquad \textit{Equation 7}$$

$$2CuO + 4HCl = Cu_2Cl_2 + 2H_2O + Cl_2 \qquad \textit{Equation 8}$$

The volatile chlorides diffuse out of the mineral grains. Rampacek and colleagues (1959:5–6) explain that a weakly reducing environment is ideal for the segregation process. This allows the copper chlorides to be reduced to metallic copper, forming discrete flakes on carbon particles in the system. They list several reduction mechanisms, with the principal reaction being provided as Equation 9. Techniques such as froth flotation and leaching can extract the copper (Pinkney & Plint 1967:559).

$$Cu_2Cl_2 + C + H_2O = 4Cu + 4HCl + CO_2 \qquad \textit{Equation 9}$$

The TORCO group initially used a reactor comprising a vertical packed bed moving downward within a fluidized outer chamber which served as a heating unit by means of coal combustion (Pinkney & Plint 1967:562–64; Brittan 1970:278). The packed bed contained the ore which had been premixed with sodium chloride and coal or coke before heating, and was thus referred to as being 'one-stage testwork' (Pinkney & Plint 1967:562–64). However, the resultant recoveries and concentrate

[1] Economic conditions in the 1930s and a subsequent slump in copper prices resulted in plants using the process being shut down (Pinkney & Plint 1967:560). World War II extended the shut down as metal prices were fixed even as demand increased. As the price of copper recovered after the war, the treatment of refractory ores became profitable once more, which renewed interest in the process. This is what brought about projects such as TORCO.

grades were poor. This was later attributed to fluidized beds being unsuitable as segregation units owing to the "reaction [being] a gaseous one" (*ibid.*:562); excess coal reduced the copper without it being volatilized, leaving it inaccessible to flotation; and the difficulty of controlling the addition of the reducing reagent.

Although the limitations were not fully understood, the results were promising enough that the TORCO Group did not abandon the idea to use fluidized beds as other groups did (Pinkney & Plint 1967:570–71). However, it became necessary to adapt the design to overcome the shortcomings. A two-stage operation was designed in which the ore was first heated in a fluidized bed, and then mixed with the chloride salt and reducing agent in a second vessel. This takes advantage of the favourable characteristics of the bed, and allows for an oxidizing environment in the preheating stage. This converts trace sulfides to oxides, which eliminates the need for comminution prior to the flotation phase to recover the sulfides. Thus, the resulting design paired a fluidized bed with a vertical segregation tube to take advantage of the strengths of both technologies (Pinkney & Plint 1967:571–73).

The development of the SERVO process and later work

Following the successful implementation of the TORCO process and promising results from similar projects, the concept was picked up by a research group based at the Hatfield Polytechnic—now the University of Hertfordshire (Cox *et al.* 1985a:34–36). Incidentally, these successes followed the work of Schäfer in the 1950s. The improved understanding of the mechanisms behind CVT may well have been a contributing factor. The operating principle adopted by the Hertfordshire group is similar to that in the TORCO process, but utilizes a volatile organic compound as the extractive reagent at much lower temperatures. Relatively stable volatile complexes form and can be removed from the vicinity of the ore, which is closer to the operating principle of traditional CVT processes (Cox *et al.* 1985b:5). This allows the products of the reaction to be treated directly, unlike TORCO which requires a separation stage. However, this requires the use of a secondary reagent to recover the metal from the complex, unlike the temperature equilibria established in typical CVT processes. This

distinction allowed for the new process to be patented and is the criterion which we shall use when referring to vapour phase extraction processes.

The process that the team at Hertfordshire developed was named SERVO, which stood for Selective Extraction and Recovery of metals using Volatile Organic Compounds (Allimann-Lecourt 2004:40). Cox and his colleagues (1985a:34–35) proposed using volatile organic reagents to extract valuable metals from waste materials in a fluidized bed. The studies at the University of Hertfordshire were continued, which later became the basis for further research at Wits University. The Wits research group undertook several studies, later with a particular focus on gold extraction using acetylacetone (acac). One of the later studies in the group was unable to replicate the gold extraction that had been recorded previously. Wood (2022:89–91) speculated that the reported extraction curves could be ascribed to an experimental anomaly due to testing being performed close to the limits of the analytical techniques employed, and the cumulative effect of this uncertainty (see chapter 5).

There is potential in developing viable processes that utilize VPE. Pichugin and Cox (1997:125) successfully used the SERVO process to extract nickel from laterite ores, and yet indications point to its no longer being pursued. Wood (2022) challenged previous work done at Wits, and questioned the viability of the technology, particularly with regards to gold extraction. Given the apparent disparities in viability and potential, it is necessary to assess where the technology stands today. Resolving the disagreements within the literature may provide insights into a way forward and reveal any unrecognized potential in this area.

Chapter 2

The Development of the SERVO Process

The advent of modern vapour phase extraction occurred in the 1970s with the introduction of the SERVO process (Allimann-Lecourt 2004:40), which lay the foundation, albeit a precarious one, for future research, primarily at the University of the Witwatersrand. Cox *et al.* (1985a:35–37) focused on selectively extracting copper whilst rejecting iron using various β-diketones, particularly acetylacetone with various combinations of halide substitutions. It is worth discussing the motivations behind its invention and the thinking that shaped the design approach before looking at the process itself.

Foundational principles

Woollacott and Eric (1994) define extractive metallurgy as a chemical means to extract valuable elements that are chemically bound to other components of a mineral. The discipline is then divided into pyrometallurgy and hydrometallurgy. A third category, electrometallurgy, is sometimes used to describe systems that are engineered and controlled electrically (*ibid.*:203). Electrometallurgical processes can also be classified as being either hydrometallurgical or pyrometallurgical, but this distinction can sometimes be useful to group processes with similar characteristics, regardless of which category the process falls under.

Extraction is said to consist of two *aspects*, namely reaction and separation (*ibid.*:203–4). The reaction aspect, which may consist of multiple reactions in multiple reactors to achieve the desired outcome, must manipulate the material such that the chemical associations of the target species change. The species must report to a different phase, which would preferentially be a single phase. The species can then separate, which further affects the recovery of the species, as any material not reporting to this phase may be lost. The separation aspect consists of a physical process to separate the

phases established during the chemical treatment. It may occur in the reactor vessel itself, or in a separate unit operation.

In hydrometallurgy, the reaction and separation occur in an aqueous environment. In pyrometallurgy, they are facilitated by adding energy, typically resulting in these processes having high operating temperatures. An alternative term to describe pyrometallurgy which is perhaps more descriptive of this aspect, would be to refer to it as thermal processing (Eric, pers. comm.). With this understanding, we can classify VPE processes as being pyrometallurgical in nature.

Woollacott and Eric (1994:204–6) refer to the stages of metal extraction. This starts with the preparation or pre-treatment stages. This involves chemical treatments to prepare the material for the coming reactions. As such, there is no phase separation here. The extraction stages involve discarding as much unwanted material as possible whilst limiting losses of the targeted species. The focus of these stages is to recover as much of the target species as possible. The refining stages similarly seek to remove impurities, but here the metal composition becomes the focus. Minor metal losses are acceptable—discard streams can be retreated if necessary—in order to obtain the required purity. In the metal recovery stages, the metal is prepared such that it is in the final form that the market requires.

These stages are sometimes carried out in a single processing unit. This is more typical of pyrometallurgical processes where reactions and phase separation can occur together. However, this does not necessarily mean the process itself is less complicated. One also needs to look at the process in its entirety with all of these stages, and not look at individual unit processes. From this perspective, it cannot be said that pyrometallurgy is any less selective than hydrometallurgy given that both fields consist of many different processes, each with different characteristics, and each performing its required function and giving the desired product.

In the earliest published paper on the SERVO process, Cox refers to extraction processes available at the time being classified as either hydrometallurgical or pyrometallurgical in nature (Cox *et al.* 1985a:33–35). He explained that hydrometallurgical processes consist of leaching metallic species from their source

material, followed by separation and recovery. A shortcoming of this route is said to be the complexity of the processes as they tend to take place in multiple stages. The pyrometallurgical route is defined as sometimes involving smelting to separate a concentrate from the gangue material, with selectivity being the shortcoming of this route. It is suggested that VPE as it is used in the SERVO process does not fall into either of these categories, as it takes advantage of the selectivity of hydrometallurgy together with the simplicity of pyrometallurgy. With the understanding gained from Woollacott and Eric (1994), we can see that this is a distorted understanding of extractive metallurgy.

It is useful to view VPE within the scope of pyrometallurgy. It is more accurate to do so as it allows VPE to be studied in the appropriate context by associating it with other technologies that have similar characteristics. This will give the researcher, and the target audience of the research, a better understanding of the process being studied. This is apparent when looking at the work of Allimann-Lecourt (2004:40–42) where the author uses three classes in extractive metallurgy, *viz*. hydrometallurgy, pyrometallurgy, and the Mond vapour-phase process. It states that the Mond process is both simple and selective. However, this is removing the process from its correct context.

One needs to be mindful that the Mond process was treating nickel in Wales that had been mined, concentrated, and reduced in Canada (Morris 1989:38). If we use the understanding of the stages as defined by Woollacott and Eric (1994:204–6), then the pretreatment and extraction stages had been completed in Canada, with the refining and metal recovery taking place in Wales. The Mond process can be considered as the separation aspect of an extractive metallurgical process, rather than a full process. Thus, it would not be a fair comparison to say that it has only one or two simple stage operations as stated by Allimann-Lecourt (2004:42), as compared to a full extractive process.

Projects involving the SERVO process

The research group based at the University of Hertfordshire sought to design a process which was both simple and selective.[2] They drew inspiration from the Mond process. Cox *et al.* (1985a:34–35) suggested using a volatile reagent with a carrier gas to extract a metal from ore by forming a product which reports to the vapour phase. It was initially specified that a Schiff base would be used (Cox *et al.* 1985b:2–3). Schiff bases are imines which have a double bond between a carbon group and a nitrogen group (Cammack 2006:602)—*i.e.*,

$R_1R_2C{=}NR_3$, R_1 = H or alkyl, R_2 and R_3 = alkyl

They can be formed by the condensation of an aldehyde or ketone with an amine. Cox and his colleagues focused on fluorinated β-diketones. They found that hexafluoroacetylacetone (HFA) could extract copper from chalcopyrite, but that it did not reject iron sufficiently. After the extraction stage, the volatile metal complexes undergo selective fractionation. Gas chromatography could be applied to the mixture of volatile complexes to isolate the desired metal complex. At this stage, it could be hydrogenated to liberate the metal and recover the reagent for recycling.

Phillip Duke developed the idea in his master's in 1985, which is not available in South Africa. He tested 20 reagents and their associated complexes with copper to find which was the most suitable to this application (Duke 1985 as cited in Barr 1989:35–37). Tests were conducted to determine which complexes were sufficiently volatile and stable enough to minimize decomposition. Two were selected for further testing,

bis(pentan-2,4-dione)propan-1,2-di-imine

bis(pentan-2,4-dione)butan-2,3-di-imine

(*ibid.*:37). Pure copper(II)oxide and copper sulfide were tested. The ligand reacted with the oxide, but not with the sulfide owing to copper having an oxidation state of +1 in the particular crystal lattice that was used. Further tests with copper ore (the

[2] The application of the process changed over time.

minerals of which were not specified) resulted in pure copper being extracted, with iron being completely rejected as it had an oxidation state of +3.

Hereafter, the work diversified from extracting copper to other metals. Duke found that it was possible to extract nickel and cobalt from their sulfides. Duke noted too, that whereas palladium and platinum complexes with these ligands do exist, no test work was done on these metals because they cannot not be extracted as they occur as noble metals in their ores (*ibid.*:39). Barr continued the work towards developing an extraction process using bis(pentan-2,4-dione)propan-1,2-di-imine to extract nickel from lateritic ore. Nickel was successfully extracted selectively from the ore. It seems that this was the last advance in the field until a publication by Pichugin and Cox (1997) which seems to have repeated the work done by Barr, using the same ligand to extract nickel, with the only difference being that it studied Greek laterite ore rather than lateritic ores from New Caledonia as was the case with Barr. This was the last example of a study that I could find involving the use of the SERVO process to extract metal from an ore.

Corinne Allimann-Lecourt, a student of Cox's, performed the last study which used the SERVO process. She used it to remediate contaminated sediments and industrial waste (2004:IV)—in particular, to remove heavy metals from soil and fly ash so that they could be used in other industries or discarded safely. Three ligands were used. One of them was acac, which was the cheapest; the other two would have had limited application as they were costly. None the less, Allimann-Lecourt did not recommend acac as it extracted too little of the heavy metals (*ibid.*) The studies at Hertfordshire formed the basis of future work done in the School of Chemical and Metallurgical Engineering at Wits. The studies at Wits used a β-diketone—acac—to extract a variety of metals in the vapour phase from various sources. The proposed simplicity and selectivity of the SERVO process were attractive and inspired the work. The projects at Wits are assessed in the following chapter.

Chapter 3

Applications of the Servo Process

The research group at Wits university sought to develop the SERVO process further. This involved several projects which shall be discussed in this chapter. They deviated from the work done in Hertfordshire in that every project at Wits exclusively used acac as the ligand.

The projects had a similar format, which allows for the topics within them to be discussed together, rather than discussing each project separately. The first study was independent of the others and investigated the feasibility of extracting various metals with acac in a fluidized bed (Potgieter *et al.* 2006). Acac vapour was successfully reacted with synthetic oxides[3] of aluminium, chromium, iron, and vanadium. The interaction generated vapour phase complexes which were collected as a condensate. The separation aspect of extraction was not studied here, but determining that acac can form metal complexes in the vapour phase by reacting with these metal oxides was a necessary preliminary for future work and confirmed that such extraction could be feasible.

The following four studies each focused on a particular metal. The first was undertaken by Mariba in 2010. It studied the extraction of iron and chromium from their synthetic oxides, Cr_2O_3 and Fe_2O_3. This was followed by Mpana in 2012, where the extraction of aluminium from fly ash was attempted. It also studied a synthetic sample of Al_2O_3 and silica (SiO_2, quartz) in a similar proportion to that present in the fly ash. In 2014, Tshofu studied the extraction of iron from iron ore fines — predominantly haematite — using acac in both the vapour and liquid phases. Iron recovery was also achieved by hydrogenation of the iron-acac complex. The last

[3] Al_2O_3, Cr_2O_3, Fe_2O_3, and V_2O_5.

study in this phase was done by Olehile in 2017, which involved the extraction of vanadium from spent catalysts, and tantalum from a synthetic sample of Ta_2O_5 and silica which was prepared so as to imitate a low-grade ore.

Mariba assembled an experimental setup which remained largely unchanged in studies that followed (see Figure 1). A round-bottomed flask served as an evaporation chamber for the ligand, which would then fluidize the bed. A peristaltic pump fed ligand to the flask. There was some uncertainty just how the vapour flow rate was controlled, but this was clarified by Mpana (2012:26). The evaporation flask is heated sufficiently such that the ligand vaporizes very quickly. [4] This ensures that there is no accumulation of ligand in the flask. Thus, the net flow rate of ligand is controlled by the incoming flow rate from the pump, achieving the desired average flow rate. Peristaltic pumps are known to deliver their charges in pulses, which would not smoothly fluidize a bed. However, as the reagent flowed into the flask it may be that a somewhat steady flow was established on the side of the flask before it evaporated. The fluidized-bed reactor was a glass column (Mariba 2010:43–45). The temperature of the reactor was controlled at the desired set point using a thermocouple inserted into the vessel. Heating tape maintained the desired temperature. The exiting vapour stream passed through a condenser; the condensate collected in a conical flask immersed in an ice bath.

[4] Later studies used an oil bath to preheat the ligand before injection into the evaporation chamber.

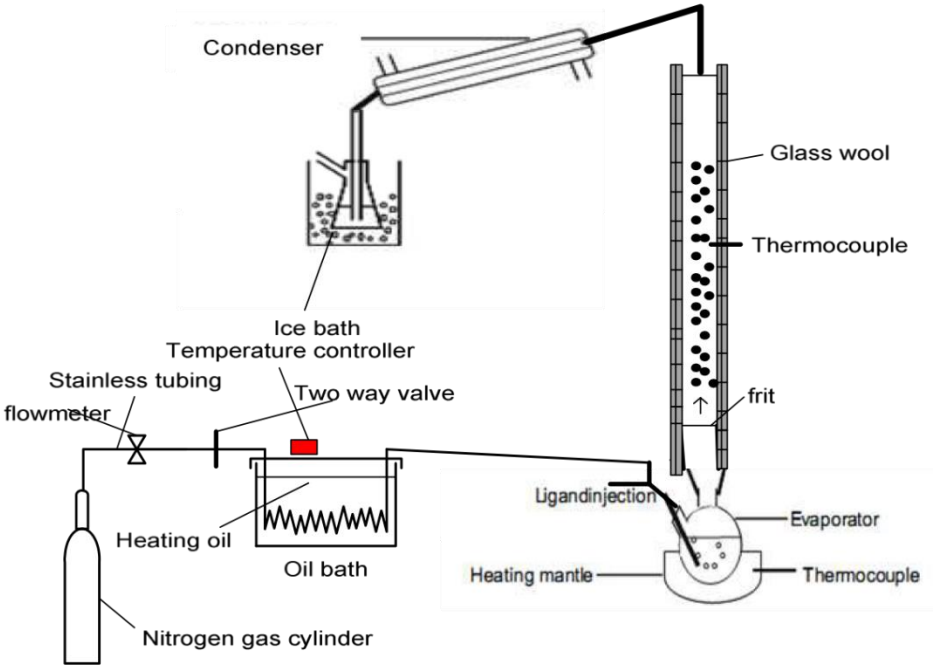


Figure 1: Experimental setup (Mpana 2012:31)

Mariba examined several conditions that affect the reaction and provided a basis from which to develop a process and work towards establishing optimal operational conditions. An iron extraction in excess of 80% was achieved, but there are aspects of the report which cast doubt on these results. Let me illustrate. Mariba maintained that VPE is a distinct field from established branches of extractive metallurgy. However, the distinction was not carried into most later studies as the focus shifted to other work on VPE. Olehile (2017:4) was the only project that maintained this precedent of distinguishing between VPE and other metallurgical fields.

As such, there was no review or link of this technology to CVT. Ironically, Mariba (2010:28) notes that the complexes can be used in chemical vapour deposition (CVD), but does not recognize that this is essentially the mechanism whereby the complexes were generated in the study. Mpana (2012:4, 19–20) and Tshofu (2014:17–18) both mentioned CVD in the same capacity as Mariba—*i.e.*, as an application which utilizes metal acetylacetonates—but they likewise did not review the technology or realise its significance in the scope of this work.

Mariba (2010:45–46) notes in the experimental setup that all equipment was either glass or silica to prevent interactions with the ligand. It was mentioned that stainless steel tubing was used previously in the group, and that the ligand visibly corroded it.

Further, Mariba (2010:68–69) was unable to reproduce the significantly higher extent of chromium extraction reported by Potgieter *et al.* (2006). It was then stated that there was no plausible explanation for this difference. However, as a major component of stainless steel, chromium is likely one of the components which was vulnerable to the corrosion mentioned in the study.[5]

This indicates that chemical mechanisms were overlooked. Mariba (2010:53) provided a chemical equation which could describe the reaction between haematite and acac. However, no equation was given for the reaction with chromium. Mpana (2012) and Tshofu (2014) did not suggest a reaction equation for the species they studied at all. Olehile (2017:29) gave a reaction for vanadium, but none for tantalum. The equation for vanadium cites a source with no corresponding reference. However, the author cited as the primary author was a contributing author to another source in the references in the same year, so perhaps this was the source being referred to.

Tantalum does not form complexes directly with acac. In the foundational work on VPE, Cox and his colleagues (1985a:35) used compounds such as HFA to form complexes that can be separated by gas chromatography. The significance of this is that Moshier and Sievers (1965:100–105), the source they cited, were able to synthesize tantalum complexes directly with HFA but not with acac. They report two complexes comprising acac and tantalum: $Ta(OCH_3)_2Cl_2(acac)$ and $Ta(OCH_2CH_3)_2Cl_2(acac)$. The original sources for these date back to the 1930s (*ibid.*:144, 150, 152). Tantalum and niobium co-ordination complexes have been well understood for almost a century. These complexes were studied in the 1960s and 1970s in a series of papers, the first of which specifically involved acac and reaffirmed that acac does not complex directly with tantalum (Djordjević & Katović 1963:1102). Olehile (2017:20) reviewed similar studies and summarized several complexes of tantalum and acac with other constituents; he included the two given by Moshier and Sievers which are formed by reacting acac with $TaCl_5$ in a solution of methanol. Methanol participates in the reaction and the reaction is not simply a substitution of acac. Contrary to what Olehile stated, there is no indication that acac forms a complex with tantalum by

[5] Mariba (2010:68–69) refers to chromium and oxides of chromium as 'chrome' interchangeably.

reacting tantalum oxide directly with acac. The process that Olehile proposed could not extract tantalum as there was neither methanol nor chlorine present to produce the stable complexes that he had studied. No description was given for a hypothetical complex comprising solely tantalum and acac.

Thus, it is doubtful that the reported extraction of 93.4% occurred, unless it resulted from a reaction with decomposition products (Olehile 2017:57). However, as his tests were conducted at 150°C, it is unlikely that there was decomposition. A ligand will not necessarily react with any phase of a metal simply because complexes involving the ligand exist, particularly when those complexes involve other constituents not present in the system. The correct constituents need to be present under the correct conditions for the reactions to take place in the desired way and generate the desired complex. It is advisable that the reaction first be attempted with a pure sample to gain an understanding of the mechanism before testing ores.

Stabilities of complexes and associated temperatures

The complexes of acac are unstable at high temperatures and typically undergo thermal degradation above 200°C (Moshier & Sievers 1965:17–18). The products of decomposition can also react with the metals, and may be volatile, so it is not sufficient to only test for the metals in a collected product stream, but to determine the specific complex that was carried through. This would be of particular importance when trying to recycle the reagent. Furthermore, most of the studies were conducted above 200°C, so it is possible that none successfully extracted metals as acetylacetonates, but rather as complexes with other decomposition products. This was not explored in any of the studies, although this information was provided by one of the primary sources (*ibid.*) used by the Hertfordshire Group, which served as the basis for the development of a process at Wits.

Mariba (2010:55) found that extraction increased with increasing temperature, but that it more than doubled when increasing from 210 to 230°C. This is dissimilar to the increases from 190 to 210°C and from 230 to 250°C. The difference is marked (see Figure 2). This jump is more likely due to a different reaction taking place, rather

than an unexpected change in reactivity. It may also be possible that more decomposition products are forming as the temperature increases, resulting in the increased extraction observed. A test run by Moshier and Sievers may provide evidence for this decomposition. They tested iron with HFA, which forms a more stable complex with iron than does acac (*ibid.*:21–23). There was iron-HFA complex decomposed to a degree. A residue was found at an outlet, which was set at 135°C. Mariba worked at higher temperatures with a less stable complex, so more decomposition may well have occurred.

The experimental design should have accounted for possible decomposition, which could have affected the results. The condensate was tested for the presence of iron, not iron acetylacetonate, so it is not certain whether this was the expected complex, or a decomposition product. When describing such situations, Moshier and Sievers (*ibid.*) note "how easy it might be to arrive at incorrect conclusions when sufficient evidence regarding the identity of the eluate is not obtained."

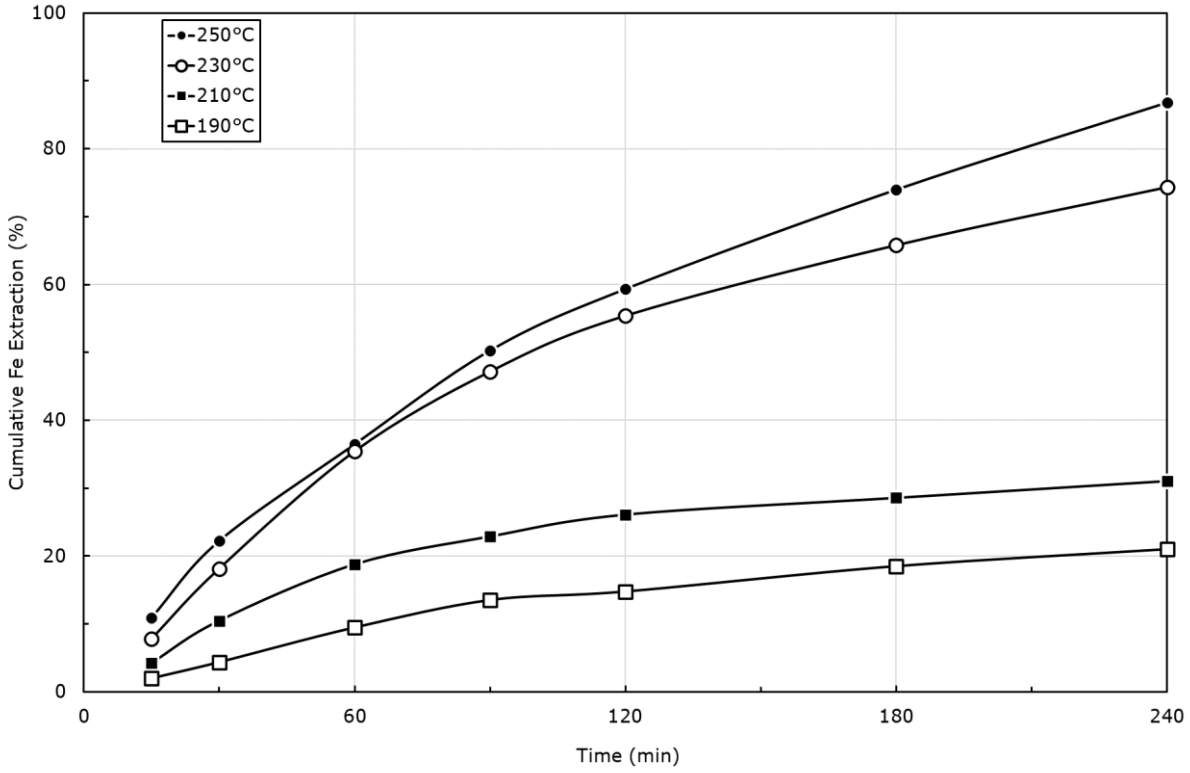


Figure 2: Effect of temperature on extraction of Fe_2O_3 (Mariba 2010:55)

Overall, the extractions fell when increasing the haematite load. Perhaps the reaction was being starved of reagent owing to the decomposition of acac. Increasing the

ligand flow rate did increase the extraction, but higher bed charges still achieved a lower extraction. This suggests that there may have still been insufficient ligand. A diffusion-controlled process could also have increased extraction with increased ligand flow, although diffusion is not expected to be controlling owing to the turbulent nature of fluidized beds. Introducing a carrier gas did not significantly increase the extraction, as one might have expected had diffusion been limiting, which indicates that the reaction was starved.

The extraction of chromium decreased as the temperature rose from 210 to 250°C. Mariba (2010:68) attributes this to decomposition, a conclusion supported by a previous study, which showed that the extraction of chromium ceases when the temperature is raised beyond 210°C (Potgieter *et al.* 2006:143). That iron behaves differently may be because iron is more reactive with the products of decomposition, or that the decomposition products formed with chromium are not volatile. Chromium and iron complexes with trifluoroacetylacetone (TFA) are volatilized with similar ease, with those of chromium being more stable (Moshier and Sievers 1965:16–18). Thus, it is not clear why the extraction of chromium decreased if the complexes with acac behave similarly to those with TFA.

Moshier and Sievers (*ibid.*) found that chromium was one of four elements that form stable complexes in the vapour phase at elevated temperatures, the others being beryllium, aluminium, and vanadium in the form of a vanadyl group (the VO^{2+} cation).[6] The stability of aluminium is demonstrated in Figure 3 which shows that in the absence of decomposition the extent of extraction is not dependent on temperature. The complexes of these four elements have low vapour pressures—the vapours form readily—and the vapours of the complexes are stable enough not to decompose when formed. The vapours were formed at temperatures from 150 to 180°C, but they have been vaporized without apparent decomposition with temperatures as high as 300°C (*ibid.*).

[6] Together with the four elements mentioned above, copper, gallium, indium, rhodium, and scandium also form stable volatile complexes with HFA (*ibid.*:22–26).

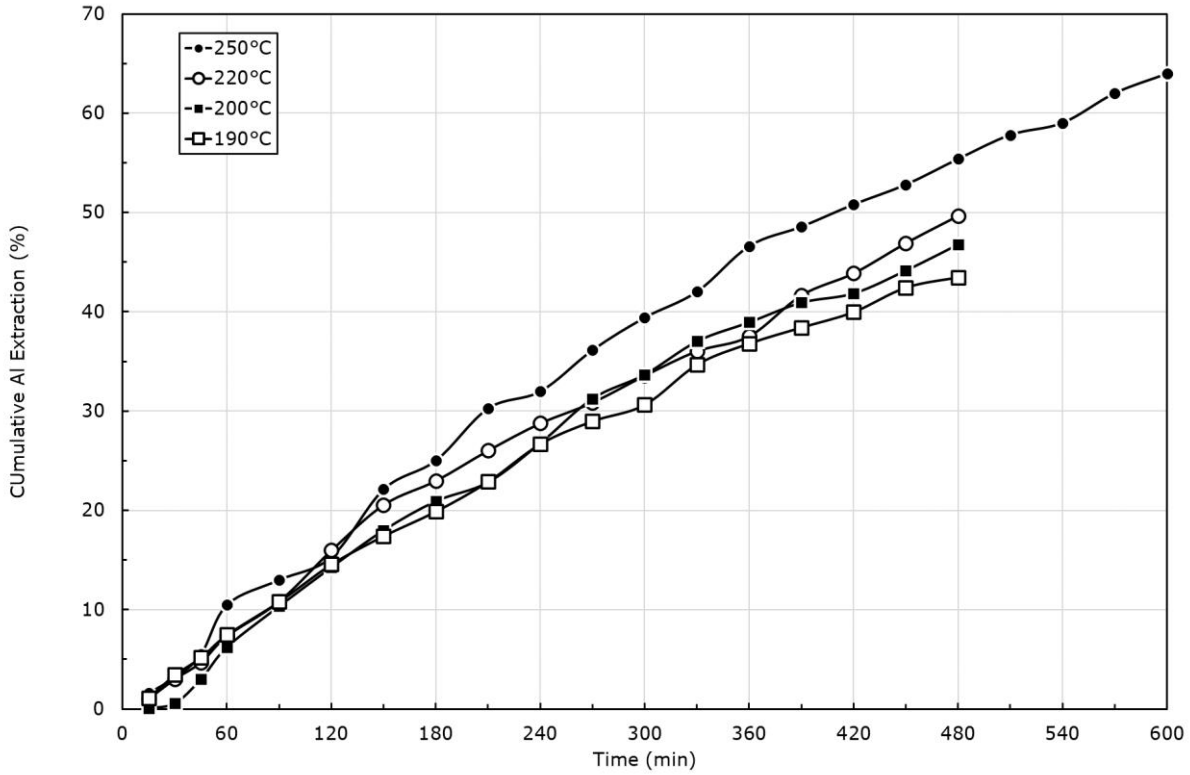


Figure 3: Effect of temperature on the cumulative extraction of aluminium from synthetic alumina (Mpana 2012:37)

The selection of kinetic models

The choice of model made to explain reaction kinetics—the shrinking core (Mariba 2010:81)—was unsuitable. Had the product which was proposed formed, it would have been in the vapour phase. Thus, the shrinking core model would not have been appropriate as the basis of this model is the formation of an ash layer around a core of unreacted material that shrinks as reaction proceeds. If a shrinking core had formed, it would have been easy to verify by backscattered-electron (BSE) imaging, and would have negated the basis of the work, for then the product would in fact have been a solid. The apparent fit of this model to reality may simply be an artifact of diffusion limiting the reaction owing to a lack of fluidization; there could have been channelling of the vapour reagent and diffusion into the bed from these channels would be the rate-limiting step. This could have imitated the diffusion effect observed through the ash layer in the shrinking core model. Unfortunately, some of the later studies also drew on the shrinking-core model to describe the kinetics of reaction.

Mpana (2012:20–25), on the other hand, developed a kinetic model of greater credibility. He did not assume a shrinking core and did not mention the formation of an ash layer. Mpana considered amorphous alumina more likely to react and that $Al_6Si_2O_{13}$ (mullite), which contained much of the aluminium oxide, in being resistant to acids would, by extension, also be unreactive to an organic ligand. That said, the model assumed that the resistance owing to mass transfer was negligible (*ibid.*:23). This assumption may be reasonable in a fluidized bed. There is evidence, however, that the beds tested in the laboratory were not truly fluidized. This discrepancy in conditions will be addressed in chapter 4.

Subsequent studies at Wits drew uncritically on the shrinking core model. Tshofu (2014:49–51) postulated diffusion through a product layer. One might have thought it feasible that a residual ash layer of unreacted material could also justify the choice of a shrinking-core model. No attempt was made to study the particles after the reaction to determine the reaction model, nor to determine what the supposed solid product was, and what products were formed and what phases they were in. The belief that a passivation layer was forming on the surface of the iron ore fines was posited on the significantly lower extraction which was achieved as compared to previous studies (*ibid.*:35–36, 40–41). The extraction was performed at three temperatures, 160, 250, and 275°C. The extent increased at the higher temperatures but was still low overall, under 2%. However, at the two lower temperatures the rate of extraction decreased significantly around the two-hour mark. This is attributed to the formation of a passivation layer. However, this trend was not observed at 275°C. At 250°C, the decrease in rate, whilst significant, does not cause such a severe plateau as seen at 160°C. As these temperatures are all above the temperatures at which the complex volatilizes significantly, it seems odd to assert that a solid product layer would form. It is more likely that the complexes were decomposing at the higher temperatures, and the new volatile components were more reactive with the iron, and as higher temperatures resulted in greater decomposition, the extent of extraction increased. Tshofu then asserts that the passivation layer was not a product of the reaction with iron, but rather with impurities, contrary to what he states earlier in the dissertation. He adduces a passivation layer to account for lower extractions

from the natural iron ore than from synthetic haematite. However, differences in extraction can be attributed to structural differences between phases, such as between phases which are amorphous and crystalline.

Tshofu also asserted that a solid product layer existed to justify the choice of model rather than assessing the choice of model. It was mentioned that the iron ore particles were shrinking (*ibid.*:51), which directly goes against the premise of the shrinking core model. Szekely and co-authors (1976:65–66) propose three geometrical groups to classify gas-solid reactions. The first is a shrinking particle, which would have either gaseous products or solid products that do not adhere to the surface of the particle. This seems the most obvious choice when selecting a model, particularly as Tshofu noted that the particles were shrinking. The second model is the shrinking unreacted core, which has a solid, sometimes inert product forming a layer around the reacting material, with the overall size of the particle not changing significantly. The final group includes particles that undergo a change in size owing to the difference in densities of reactants and products (*ibid.*:66).

Olehile (2017:8–11) listed several reaction models but did not include the shrinking particle. He noted that Szekely "highlighted that the unreacted core model approximates most real gas-solid reactions, and is attractive for its mathematical and conceptual simplicity" (*ibid.*:9). No page number was given in the citation for this assertion, and I expect that it may be a misinterpretation as I am unable to find support for this statement in the source cited. Szekely and co-authors (1976:65) stated that in many such systems the solid is nonporous before the reaction begins. They further stipulate that many gas-solid reactions result in both solid and gaseous products (*ibid.*:125), and in such cases the particle size may increase or decrease depending on the densities of the reactants and products. The change in size tends to be small so the overall size can often be considered constant; in other words, the shrinking-core model can be employed. This is of course if both gaseous and solid products are present. They add that the "simplest system in fluid-solid reactions is that of a shrinking non-porous particle forming no solid product layer" (*ibid.*:66). This seems to contradict the statement that the shrinking core model is attractive for

its simplicity, as this model is even simpler, as well as being more appropriate for the system in question.

None of the authors commented on the apparent discrepancy of using the shrinking core model with a vapour phase product, or sought to justify or clarify the choice against the apparent discrepancies. This phenomenon was captured well by Iain McGilchrist (2019:xvii):

> In science you can be as perfunctory as you like as long as you are saying what everyone else is saying, but if you are saying something different, you need, reasonably enough, to be as explicit about your evidence and as empirically based as possible. That way you are open to challenge, and that is how science progresses.

That is to say, it seems that the approach in these studies was somewhat careless. This went unnoticed as they all reported and found the same trends, seeming to verify an apparent phenomenon.

Another example of this is when Olehile (2017:12) commented that Tshofu found that the "minerology [read phase type] of the mineral-containing matrixes also plays a key role [in] the extraction process." There was no further mention of the importance of the phases or how they could affect the extraction. This is in contrast to the preceding statement of its having a "key role". If it had been considered then the lack of extraction may have been attributed to the type of phase. Instead, Olehile immediately follows the statement above with another which attributes the poor extraction found by Tshofu to the hypothesized passivation layer. Surface passivation had never been mentioned prior to Tshofu and, as explained previously, is not expected in these systems unless the reaction mechanisms present are vastly different from what is desired, an outcome that would invalidate the use of the technology. Perhaps previous researchers in the group recognized this and that is why it was never mentioned at all. However, once it had been suggested, subsequent studies simply accepted its existence and did not consider it or other alternatives any further.

Chapter 4
Fluidization of the Beds

Mariba (2010:63) and Olehile (2017:45) found that extraction was lower from beds that contained a higher mass fraction of the oxide containing the species of interest. This seems counterintuitive, but Mariba (2010:72) reported measurable iron extraction from a system with no Fe_2O_3 charge. This was attributed to impurities in the silica used, with a haematite content of 0.6%. It is unclear whether impurities were taken into consideration when charging the bed to the desired ore concentration.[7] This could further explain why the extraction percentage was 'higher' when the overall composition was lower, as the portion of haematite not accounted for in the impurities became less significant than the quantity which was added to the bed. Another factor that could contribute to this phenomenon is the overall bed density. Fluidization is reviewed in this chapter as it is unclear if the beds were properly fluidized.

Poor contact within the bed and channelling of the particles would affect the rate of reaction that was measured. Mariba recommended improving the experimental setup to counteract poor contact (*ibid.*:94). He does not make clear what aspect of the design needed improving, but poor contact may indicate challenges in fluidizing the bed. Had the bed been truly fluidized, there would have been no need to improve contact between the vapour phase reagents and the magnetite particles. If the magnetite were locked within another phase, which was not the case as this study used a synthetic sample, then changing the setup would not have addressed this issue as the reagent would still be unable to reach the target species regardless of the

[7] This could have a significant impact when calculating the total extraction percentage. With a bed weighing 50 g (Mariba 2010:49), 1% oxide corresponds to 0.5 g; silica weighs 49.5 g. A haematite impurity level of 0.6% in this silica corresponds to roughly 0.3 g haematite. Thus, the bed may have contained 60% more haematite than expected, which would inflate the reported extraction by 60%.

base setup. That is, I cannot see another explanation for poor contact aside from poor fluidization.

Fluidization was overlooked in all of the studies. It may have been an issue. Of the studies mentioned thus far from Wits, Mariba's was the only one that reviewed literature and discussed fluidized beds and the concept of fluidization. Mariba identified minimum fluidizing velocity (U_{mf}) as a significant variable when using fluidized beds (*ibid.*:28–40). It was calculated in Appendix A (*ibid.*:102–3) where the minimum flow rate required to achieve the U_{mf} was calculated to be 128.4 cm^3/min. The velocity of the gas flow through the beds in the experiments was not calculated and compared with the calculated U_{mf}. It was "assumed [that] the ligand expands so much that its flow rate into the FBR is higher than the minimum fluidization velocity" (*ibid.*:103). It would have been preferable had the velocity been calculated as this would have ensured that U_{mf} was achieved and eliminated a potential shortcoming of the work.

The next section discussed the behaviours of fluidized beds, as well as Geldart's fluidization classification of particles. Geldart (1973) established four particle classifications which can help predict if and how a bed will fluidize (see Figure 4). Owing to the absence of information on particle size distributions in the studies, the average particle size, where available, is taken here, or the midpoint in a size range reported, rather than the Sauter mean diameter as would usually be used when doing such classifications.

Particles falling in Group C are typically cohesive—van der Waals forces of attraction dominate when particles are very fine—and as such bubbling fluidization is difficult, if not impossible. Beds of groups A and B particles fluidize well. Group A particles are small and/or have low-densities, which promote smooth fluidization. Particles in Group B are sand like, having slightly larger sizes (40−500 μm), and higher densities (1.4−4 g/cm^3, *ibid.*). Group B beds bubble vigorously. Large and dense particles fall into Group D. Beds are shallower and spouting is typical.

None of the studies classified the particles being tested. Mpana (2012), Tshofu (2014), and Olehile (2017) make no mention of the Geldart classification. Mariba

(2010:46–47) used iron(III)oxide particles with a density of 5.12 g/cm^3, and chromium(III)oxide particles of 5.21 g/cm^3. Various sizes of Fe_2O_3 particles were tested, ranging from 45 to 300 µm. The sizes of the chromium sesquioxide particles were not specified, but it is likely that they would have been similar to those of the haematite particles tested. The bed of heamatite particles sits comfortably in Group B (see Figure 4).

Mariba did not specify the sizes and densities of the silica particles, but it is expected that they were the same as the silica sand used in a subsequent study within the research group, as the compositions are nearly identical (Mariba 2010:47; Mpana 2012:44). Mpana gives the size of the silica as 53−75 µm, which along with a typical density of 2.65 g/cm^3 places then in Group A (see Figure 4). As these particles made up most of the bed, one can expect that they would have determined the behaviour of the bed.

The characteristically smooth fluidization of Group A, or bubbling at higher vapour velocities, provides thorough mixing of vapour and solids, which guarantees intimate contact between vapour and particles. This seems at odds with the poor contacting mentioned by Mariba. Because the particles were most likely fluidizable, the next likely parameter which could cause poor fluidization was the velocity of the vapour through the bed, which was overlooked as discussed above.

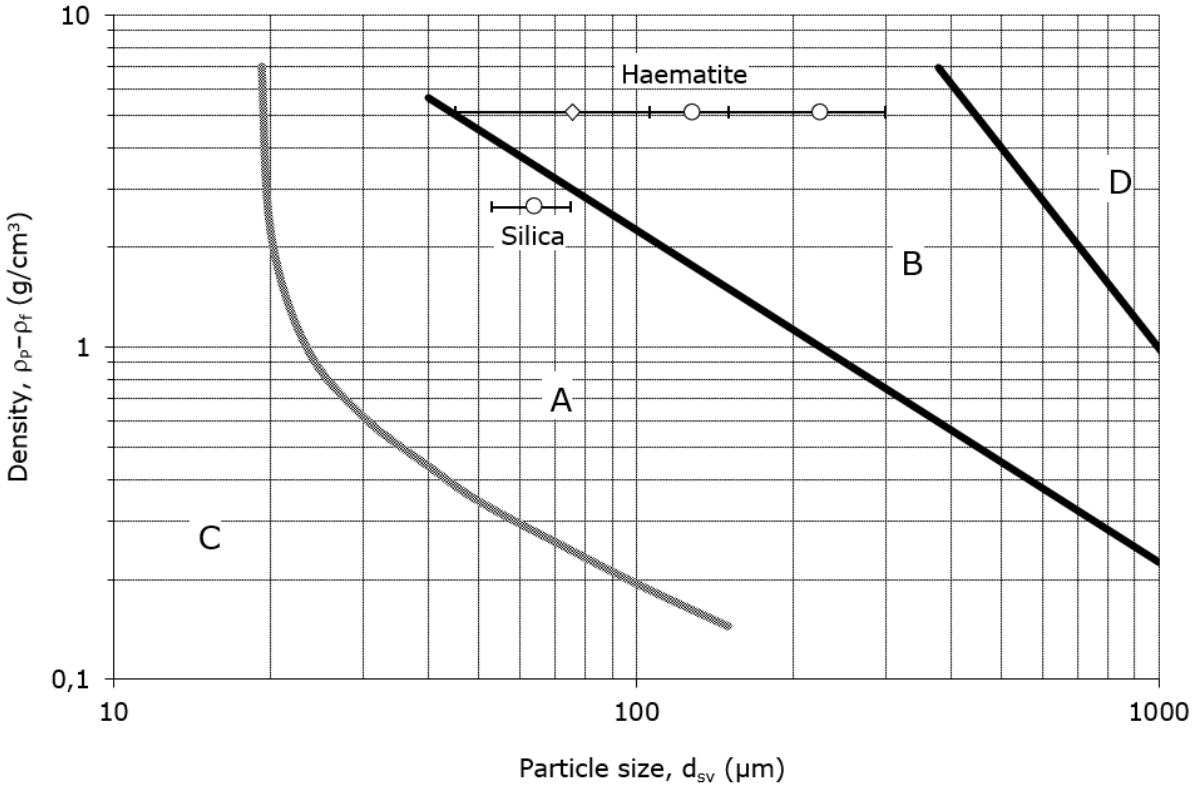


Figure 4: Geldart classification of the haematite and silica used by Mariba (2010)
Legend: points indicate midpoint values; bars indicate the size range;
ρ_p denotes particle density; ρ_f denotes fluid density; here $\rho_p - \rho_f \approx \rho_p$

There are two other indications that the beds were not fluidized. The first is decreasing extraction as the particle size increases. This can simply be attributed to the expected phenomenon of increased reactivity by increasing the surface area. However, this effect may be exacerbated by a lack of fluidization. Larger particles could have defluidized the bed, hence poor contact, resulting in lower extraction. The results for the different size distributions were not included in the appendices.

Figure 5 shows Mariba's graphs depicting this relationship. Graph A depicts the extraction data of the smaller size fractions at 230°C, with Figure 5 B the larger at 210°C. The change in extents of extraction is not proportional to the change in size for the particles.[8] This implies that another factor is contributing to the decrease in extent. The increased particle size without a corresponding increase in reagent flow

[8] The percentage increase in size for the lower limit in the first graph is by 236% and 142% for the upper limit. The associated decrease in extent is from 28% to 10% (Mariba 2010:65), a relative decrease of 64%. The percentage increase in the lower limit for the second graph is 142% and 200% for the upper limit. The corresponding decrease in extent is from 13% to 9% (*ibid.*:66), a relative decrease of 31%. Whilst the proportional increase in particle size is quite similar, and thus the corresponding increase in surface area, the relative change in extent is not.

rate, with the examples in Figure 5 both being at 3 ml/min, the bed will be less likely to fluidize, or have a denser fluidized bed more prone to channelling. This reduces diffusion through the bed and thus further reduces the extent of reaction.

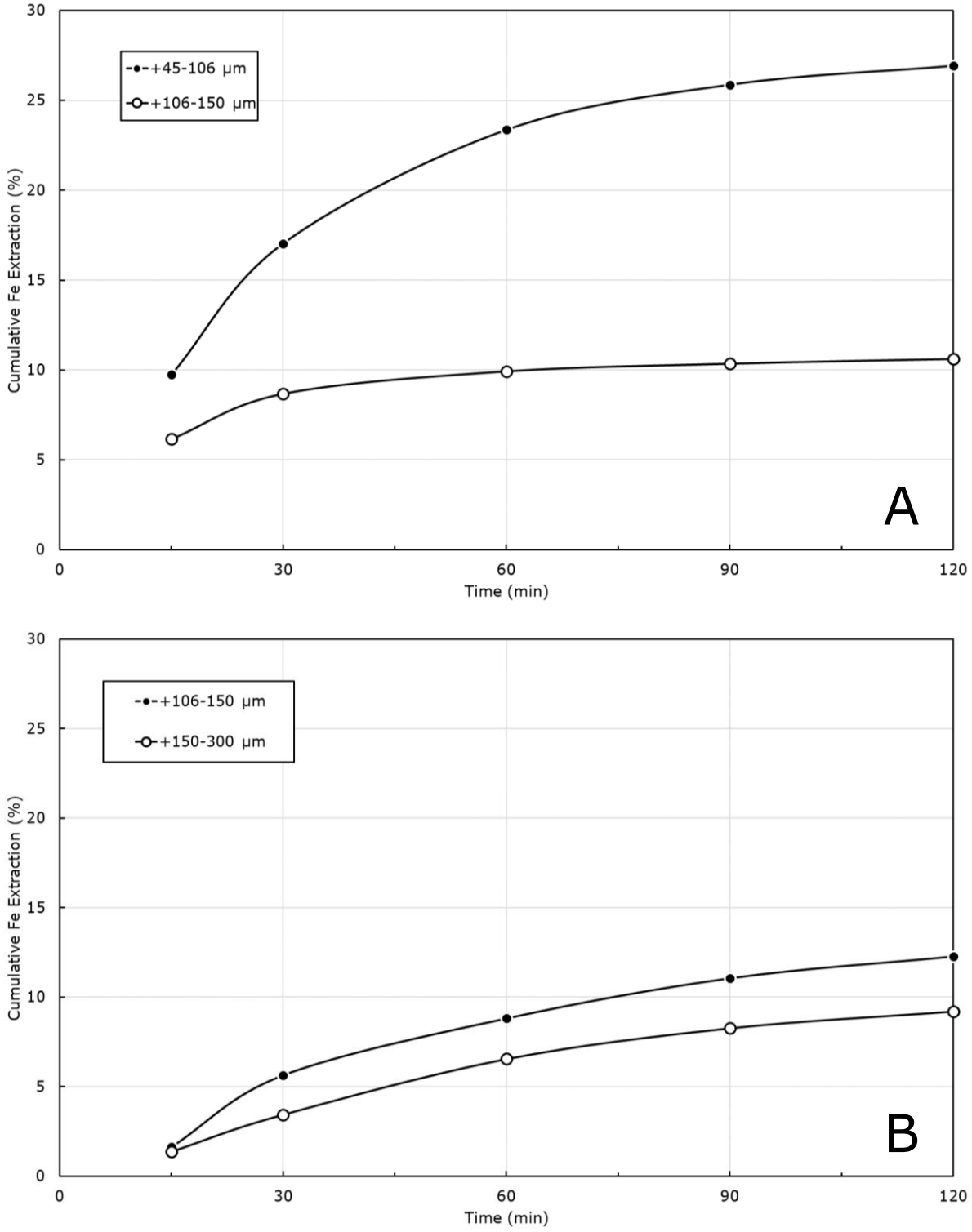


Figure 5: Effect of size distribution on extraction of iron (Mariba 2010:64–65)

Extraction decreased with an increased proportion of haematite in the bed. A contributing factor could be an error when determining the charge owing to impurities in the silica, as explored before, but another plausible explanation is that haematite is denser than silica, and the particles used were larger than the silica. Incorporating more haematite in the bed increases the minimum fluidizing velocity, which if not overcome, would prevent fluidization. Mariba (*ibid.*:61) refers to Figure 6 as the effect of ligand concentration, but it may also reveal another interesting possibility. 'Pairs' of extraction curves are grouped together. One can, as Mariba did, think of this as an effect of similar concentrations, with a proportional increase of reagent and reactant resulting in a similar extraction. It may also imply that an increase in bed density and proportional increase in vapour flow rate would result in similar fluidizing regimes being achieved. It is probably due to reactant starvation, *i.e.*, low concentration, but fluidization may well be a contributing factor, albeit a minor one in this particular instance.

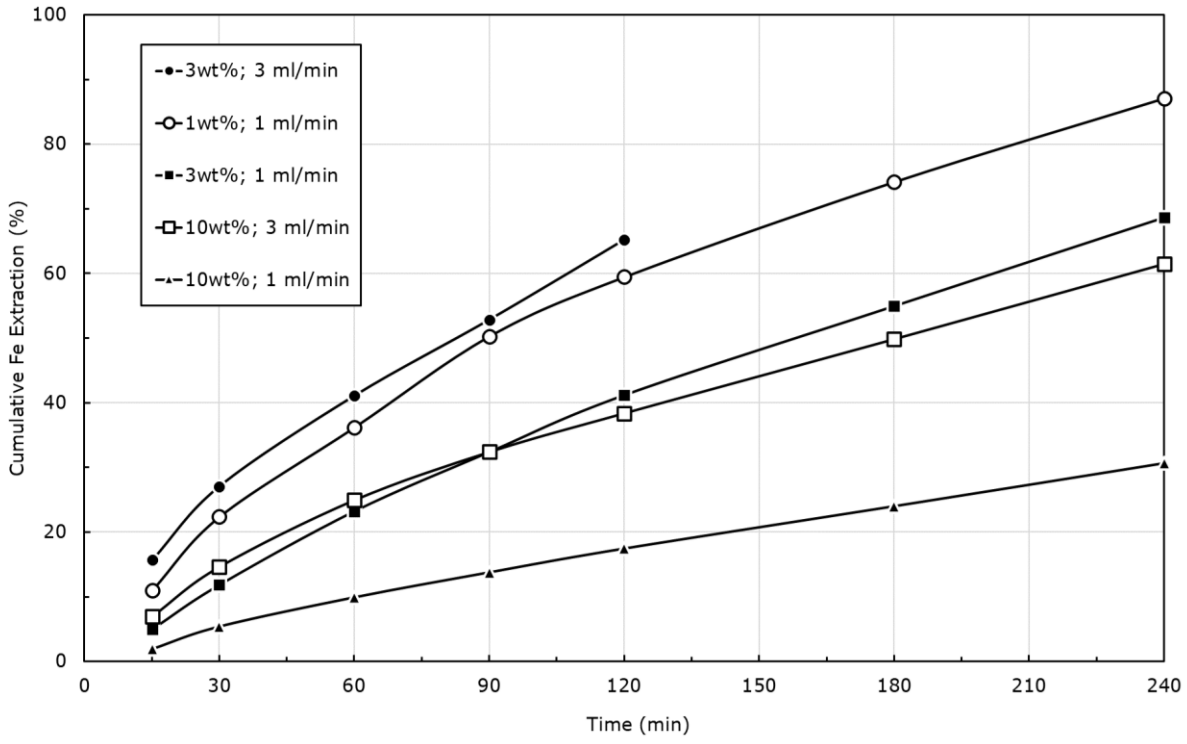


Figure 6: Relationship between ligand flow rate and weight percentage of haematite in the bed (Mariba 2010:61)

Mpana (2012) ran tests with a fly ash bed from the Kendal Power Station and a synthetic sample bed that imitated the chemical composition of the fly ash (*ibid.*:ii).

The synthetic sample contained 31% Al_2O_3 (corundum), the rest being silica (*ibid.*:29). The density of Al_2O_3 was given as 3.97 g/cm^3 (*ibid.*:27) and an average size of 112 µm (*ibid.*:48). The range of particle sizes of the alumina was not specified, so it was taken as being 75−150 µm as these standard screen sizes were used elsewhere in Mpana's study, and 112 µm is close to the midpoint of these limits (see Figure 7). The synthetic bed was likely to have fallen in Group A, as with Mariba, but may have behaved more like a Group B bed as there was a greater proportion of alumina in the bed. The bed would have been fluidizable regardless of which group it was in, as these groups fluidize easily if the superficial velocity of the gas is sufficient.

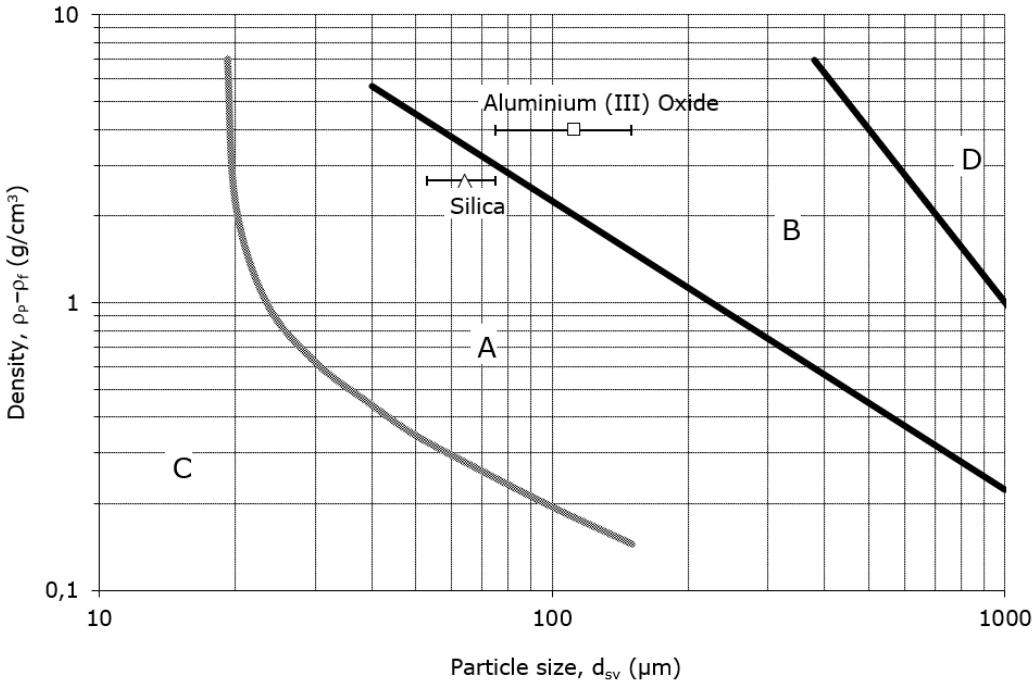


Figure 7: Geldart classification of the Al_2O_3 and SiO_2 (quartz) used by Mpana (2012)

On the other hand, the fly ash sample was finer. Two size distributions from the sample were tested, one of them in the range 75−150 µm, the other finer than 75 µm (*ibid.*:47). About 94% of the ash passed 150 µm, with 75% finer than 75 µm. This is the extent to which the distribution was described. Li *et al.* (2014:1181) and Lind *et al.* (2003:2842) note that fly ash often demonstrates a bimodal distribution with respect to number of particles. The fly ash size distribution of the sample was similarly bimodal (see Figure 8). In this sample, 90% of the material passed 75 µm and half the sample was finer than 28 µm; 10% was finer than 5 µm. The median diameter, at

40 µm compared with a d_{50} of 28 µm, shows how skewed the PSD was towards fine particle sizes.

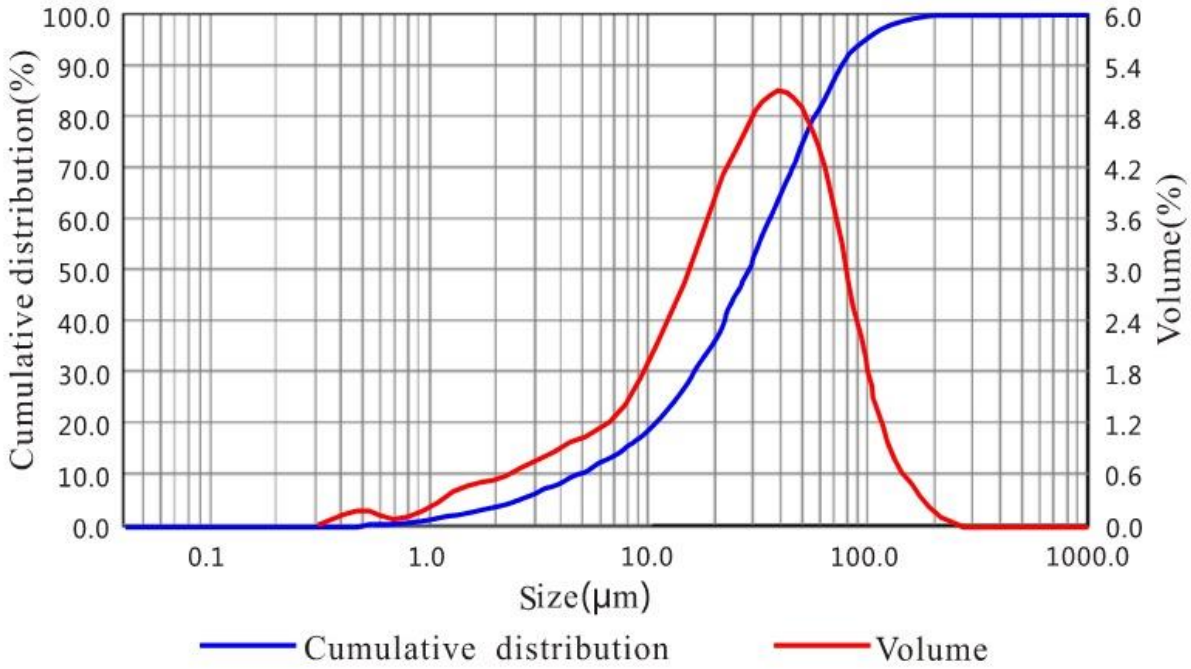


Figure 8: Fly ash particle distribution from Li et al. (2014:1182)

Therefore, as is quite typical of fly ash samples, the sample used by Mpana may well have consisted primarily of very fine particles. Furthermore, Mpana (2012:66) did not determine the density of fly ash correctly. The density was calculated by assuming that it was additive for each species, and that it was proportional to the composition. This may not be the case for fly ash, as will be discussed shortly. Even if this had been sound, the calculation only accounted for the two most abundant components, silica and alumina. Assuming that this 87% is representative of the entire sample, that would give a density of 3.12 g/cm^3, as compared to the 2.70 g/cm^3 that she had calculated. However, the density was most likely lower. When Mpana calculated density, she took the densities of SiO_2 (quartz) and Al_2O_3 (corundum). Fly ash would not comprise these phases. Lind *et al.* (2003:2843) found that very fine particles of less than 1 µm were typically single particles, or agglomerates consisting of a few particles. As such, they were often nearly spherical and dense; their densities would approximate the density of the phase. Larger particles (> 1 µm) tended to be agglomerates of finer particles. They were porous; particle densities would therefore be less than the skeletal densities.

It is worth noting that although the study had a smaller overall size distribution than that of Mpana, the characteristics (particle size distribution, density, and phase-chemical composition) are typical of fly ash, with Lind and colleagues stating that their findings were consistent with other unrelated fly ash samples (*ibid.*). When classifying the ash according to Geldart's classification, with fine particles being the most dense, and porosity increasing with size, it is possible that they would have been Group C particles—*i.e.*, cohesive and difficult to fluidize. Colleagues have confirmed this empirically (Luckos and Den Hoed, pers. comm.) Poor fluidization could prevent the ligand from reaching the targeted species.

Mpana (2012:47–48) found that the coarser ash resulted in a slightly higher extraction. This is unexpected, as increased surface area tends to increase extraction, and for a given mass smaller particles would have a larger surface area. Mpana (2012:48) suggested the possibility—unconfirmed—that more of the amorphous alumina particles reported to the larger distribution. However, small particles tend to constitute only one phase, as mentioned previously, with larger particles being agglomerates of multiple phases. A more plausible explanation perhaps is that diffusion was more limiting in the smaller distribution owing to poor fluidization, whereas the coarser bed allowed for better mixing. This suggests that the bed behaved as Group C particles.

Graph A in Figure 9 may also imply that the bed was not fluidized. The step change from 2 to 6 ml/min may have occurred because the reaction was starved and the increased flow rate provided reagent beyond the starvation threshold. The lack of considerable change when the flow rate was increased to 9 ml/min indicates that the rate-limiting step changed. Such a step change is expected if diffusion were limiting initially rather than the reaction, and the increased flow rate allowed the bed to become fluidized, with diffusion then no longer being the limiting step. The change indicates that the bed was not consistently fluidized.

Graph B shows a similar relationship, except here the three curves flatten out after roughly two hours. Perhaps these reactions were somewhat complete—they still increase slightly—as the active phases becomes depleted, as compared to the

alumina which did not constitute different phases. All things being equal we can conclude that phase, its structure and composition, has a bearing on the rate of reaction, for the rate of extraction from Al_2O_3 was greater than that from fly ash (*ibid.*:42). The aluminium in the fly ash likely occurred as a silicate—$Al_6Si_2O_{13}$ (mullite). Pure droplets are accessible to reagents, hence the similar rates of extraction from Al_2O_3 and fly ash. This highlights the importance of identifying phase in describing any process using gas-phase extraction.

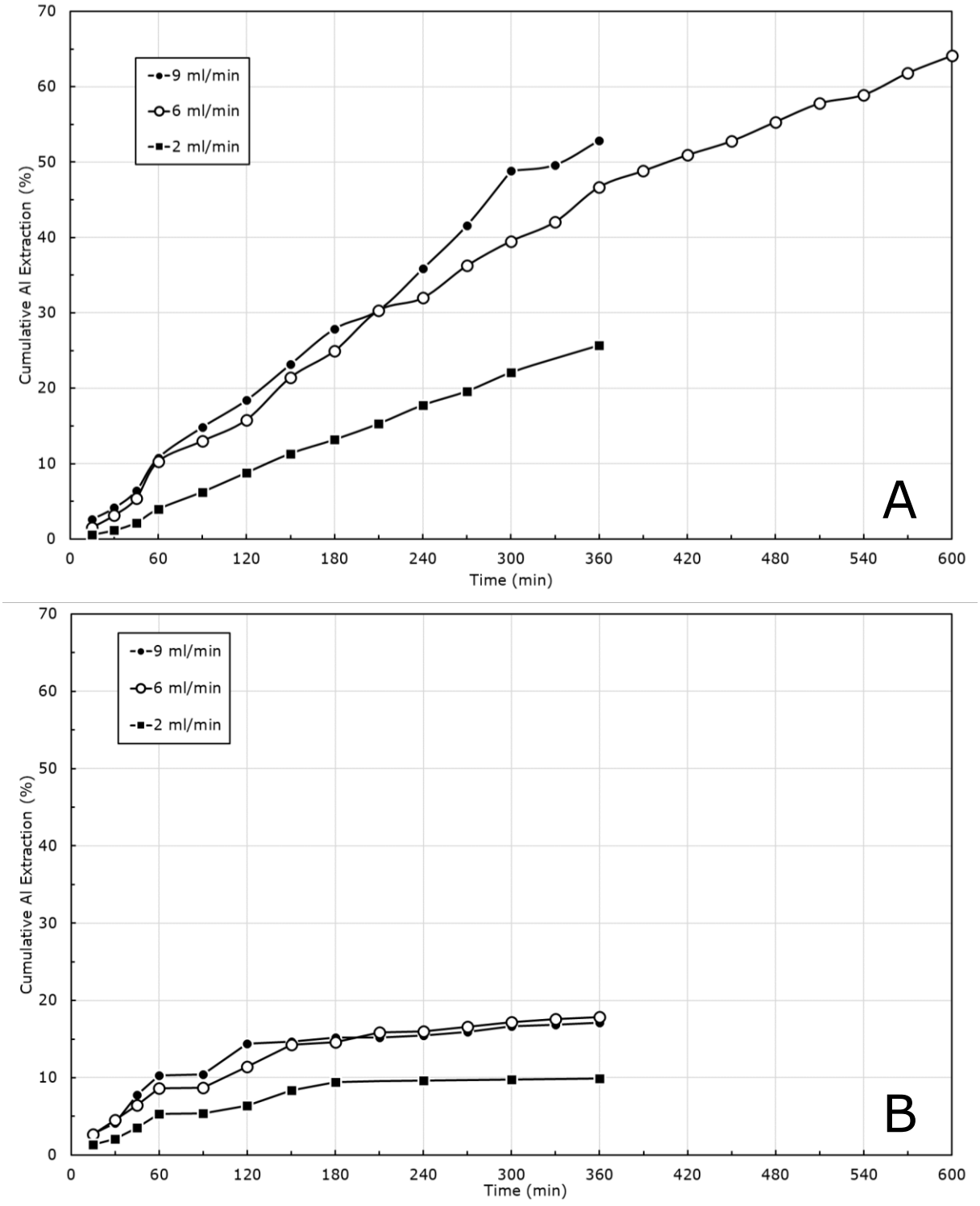


Figure 9: Effect of ligand flow rate on the cumulative extraction of aluminium from (A) alumina and (B) fly ash (Mpana 2012:40)

Mpana's increasing the gas flow rate, and therefore the superficial velocity through the reactor, by introducing a carrier gas had little or no effect on extraction, which agrees with the findings of earlier studies (*ibid.*:44). Mpana added that a lower partial pressure of ligand in the gas phase could reduce the extraction. Arbitrary tests such

as increasing the bed mass without increasing the ligand flow rate were also performed. The predictable result of this test was that extraction decreased with an increasing bed mass. Increasing the mass of the bed likely hindered fluidization and thus contact between vapour and solid. The effect on fluidization is evident as increasing the bed mass proportionally with the ligand flow rate results, within the limits of uncertainty, in similar extraction curves (see Figure 10), which mimics a pattern evident in Figure 6. By changing these factors together, it merely demonstrates proportionality. However, it can also be attributed to ligand starvation. The test does not inform on the effect of ligand concentration, or flow rate, as there is no change in the extraction, and it would not have been possible to attribute any change in the system to any one factor. It also does not inform on the scalability of the process, as the largest bed was 100 g, which cannot be considered as a scalability test as it was not significantly greater than the lightest bed, which weighed 25 g.

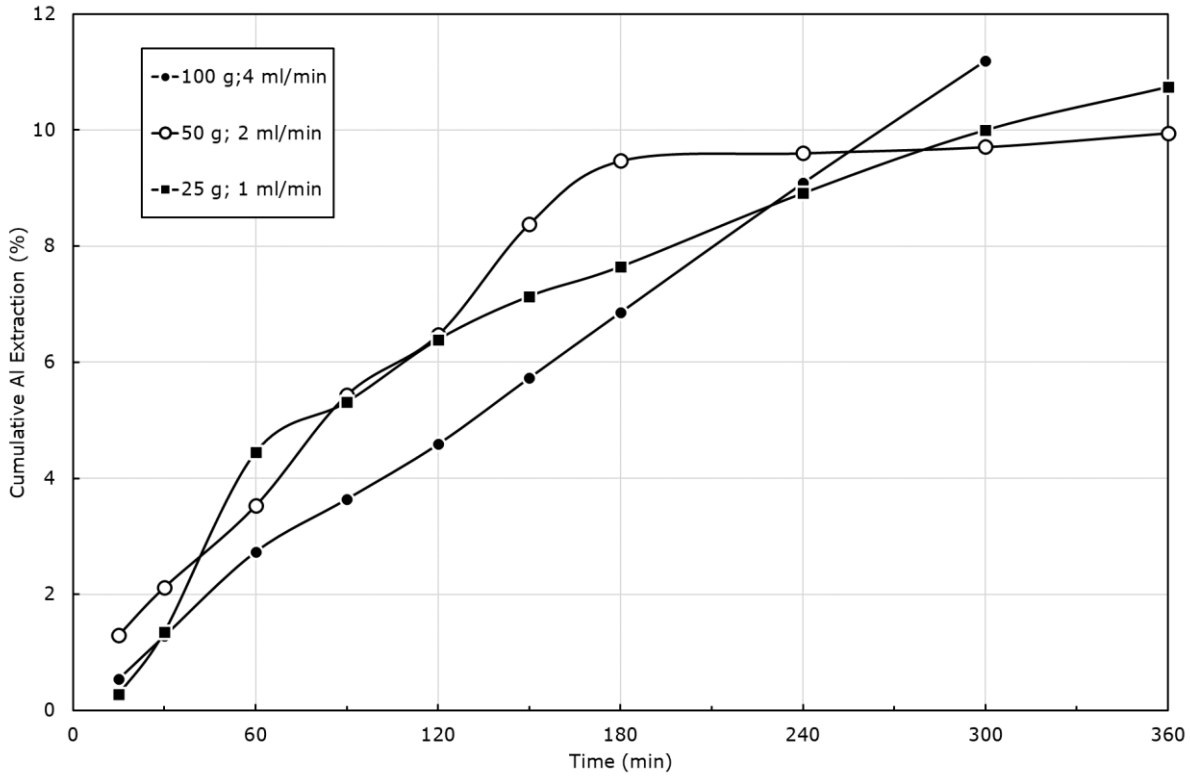


Figure 10: The effect on extraction of increasing bed mass and ligand flow rate proportionally (Mpana 2012:46)

The extraction of iron from iron ore fines by gas-phase extraction was studied next. Tshofu (2014:31–32) measured the particle sizes. The d_{50} was 2.5 mm and Tshofu

notes that most agitation leaching operations use particles that are smaller than 500 µm owing to larger particles having high settling velocities, and thus not remaining in suspension. This is describing a system where the contacting fluid is a liquid. He makes no mention of the Geldart classification, and that the particles used in a fluidized bed using a vapour/gas medium would be more difficult to suspend than in a liquid agitation system.

The surface areas (by BET analysis) of three size fractions—106 to 150 µm, 300 to 400 µm, and 1180 to 2000 µm—were measured. These are not the size fractions that were used in the experiments, but it provided a good overview of the surface areas one could expect to see in the test samples. In one test, which compared the extraction from synthetic iron oxide with that of the fines, a size distribution ranging from 106 to 1150 µm was used. Other tests used ranges of 106 to 150 µm and 400 to 600 µm. The Geldart classification for these two ranges, using the density provided in the report of 4.85 g/cm^3, is shown in Figure 11.

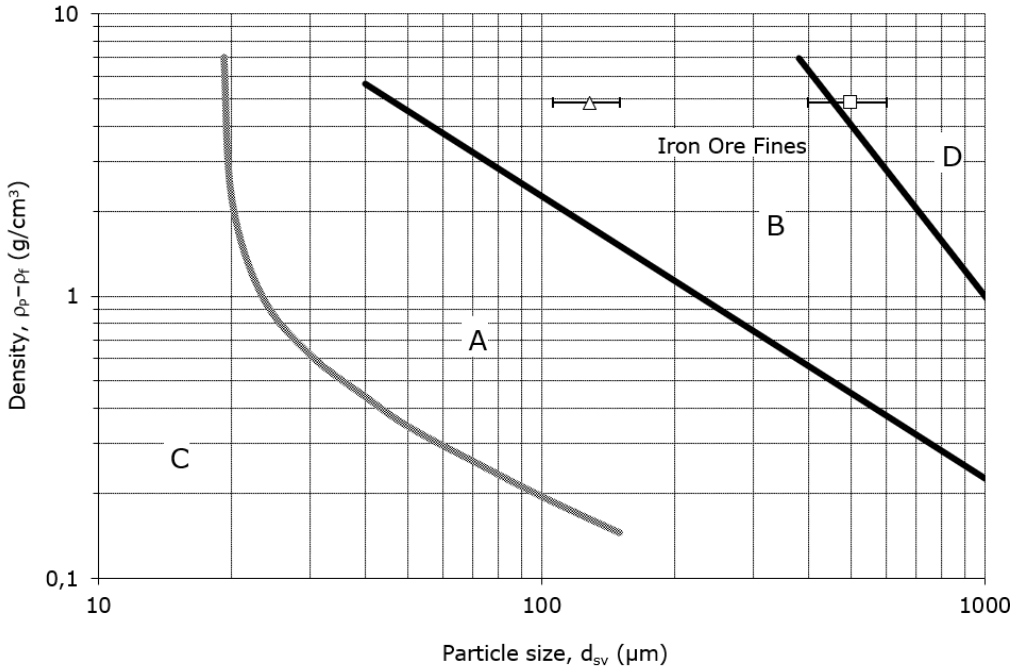


Figure 11: Geldart classification of the iron ore fines used by Tshofu (2014)

The smaller size distribution, 106 to 150 µm, would behave as Group B particles, with the larger distribution, 400 to 600 µm, crossing into Group D. Kunii and Levenspiel (1991:77–79) describe how beds of Group D particles are difficult to fluidize, with particles above 500 µm usually behaving in this way. The beds are erratic,

characterized by large, exploding bubbles, channelling, and spouting. They require "an enormous amount of gas" (*ibid.*:79) to fluidize, without which spouting and channelling occurs, and contacting is poor. This turbulent action results in attrition, and with the associated high gas flow rates the small particles that are produced are elutriated (Geldart 1973:287).

Given that this is how the bed was expected to behave, the statement by Tshofu (*ibid.*:37) that the maximum flow rate was 9 ml/min—which can hardly be considered an 'enormous' quantity—and that no elutriation was observed indicates that the bed was not fluidized. This is also the first of the studies to mention elutriation. Elutriation refers to the separation of finer and larger particles in the bed and freeboard, and may or may not include removal (*i.e.*, entrainment). Entrainment refers to the carry-over of solid particles from the bed out of the reactor by the gas (Kunii & Levenspiel 1991:165–66). Given the context, Tshofu likely meant 'entrainment' rather than 'elutriation'; not having either indicates that there was no fluidization.

Olehile (2017) does not mention the densities of the materials used. For the synthetic tantalum oxide ore mixture, he provides no information on particle sizes of tantalum oxide or silica. For the spent vanadium pentoxide catalysts there were three size fractions used, 250−500 μm, 500−1000 μm, and 2000−4000 μm (*ibid.*:24). Regarding the gap between 1000 and 2000 μm, he states that greater extraction is achieved at smaller size ranges This would explain why sizes from 1000 to 2000 μm were not tested, but then why test the larger sizes, 2−4 mm? Ksibi and colleagues (2003:106), whose study was cited by Olehile, give the constituents of a deactivated V_2O_5 catalyst. Silica constitutes 48.7% of particles. If we use the density of silica, we see that the catalyst particles straddle the divide between groups B and D in Geldart classification (see Figure 12). Therefore, the bed would not—*could not*—have fluidized.

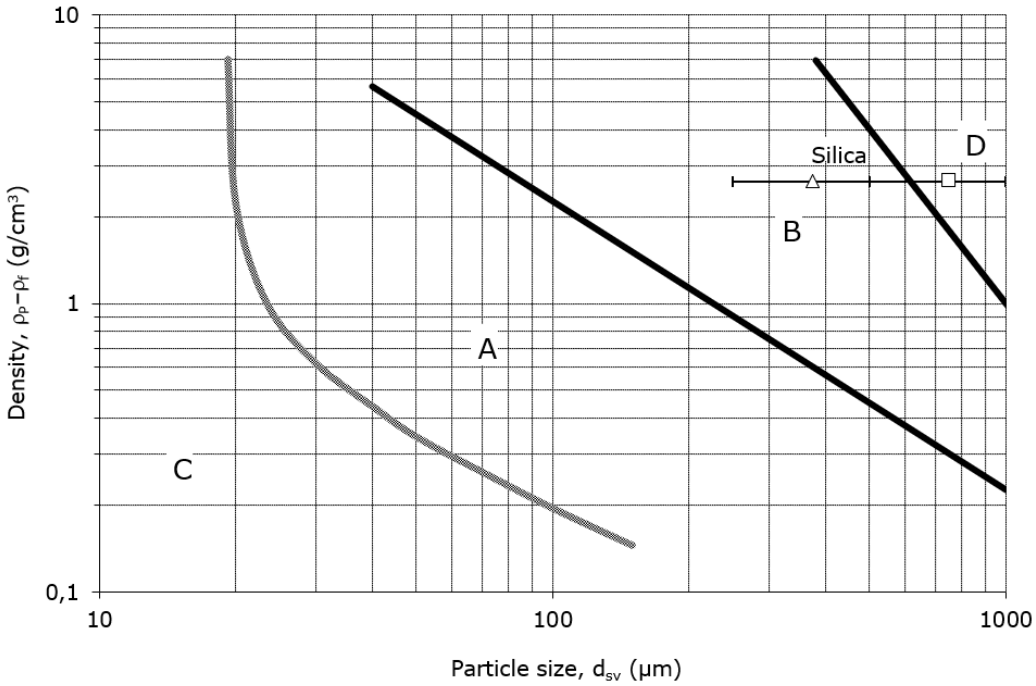


Figure 12: Geldart classification of silica particles in the size ranges specified by Tshofu (2014)

Olehile (2017:37) likewise mentioned an "elutriation phenomenon" when using higher flow rates with smaller size distributions. He selected flow rates that were low enough for there to be no elutriation, but as mentioned above, elutriation is quite characteristic of Group D beds. Thus, it is not clear that they were fluidized, as the fluidization was not mentioned, let alone characterized. Evidence points to the beds not having been consistently fluidized. In one series of tests (*ibid.*:31, 35) the effects of temperature, particle size, gas flow rate, and bed load were tested. Some of these tests, particularly changing bed load, seem quite arbitrary. Two loads were tested, 5 g and 15 g. It is not made clear what the author sought to understand by performing these tests, and what significance the results of such small beds with such small masses would have. The tests were conducted at 150 and 200°C, with particle size distributions of 0.5−1 mm, and 2−4 mm. Flow rates of 1 and 5 ml/min were used. One cannot comment on trends with only two data points for each variable. Olehile noted that the interaction between flow rate and particle size has a significant effect in the larger bed, whilst temperature has the greatest effect in the smaller bed. Thus, the author concluded that the chemical reaction controlled the reaction rate in the lighter bed, with diffusion controlling the rate in the larger bed. However, in a subsequent series of tests—with particle sizes of 0.25−0.5 mm and 0.5−1 mm, flow

rates of 5 and 7 ml/min, and bed loads of 15 and 50 g[9]—Olehile concluded that reaction in the smaller bed was limited by diffusion owing to the effect of flow rate, whereas a topochemical reaction limited the rate in the larger bed as gas flow rate did not affect the observed overall rate significantly. This is the inverse of what he had found in the first set of tests, and thus a contradiction.

As mentioned above, one would need more observations (data points) for each factor considered to plot any trends and infer reliably rate-limiting processes. A temperature of 200°C, for example, might have been high enough for acetylacetonates to decompose, with products of decomposition possibly being more reactive. As the only other temperature tested was 150°C this cannot be said for certain, but neither can it be said that a topochemical chemical reaction is rate limiting purely on the basis of temperature. The fact that the flow rate and particle size together were significant, and not by themselves, and particularly in the case of the lighter bed, is indicative that the bed was not fluidized and contact was limited, as stated above. However, it was probably because a lighter bed with smaller particles with a greater flow rate may have been fluidized. In the heavier bed, it should be noted that temperature causes only a slight increase at a flow rate of 1 ml/min, with a maximum extraction of 11.3% (*ibid.*:32). At a flow rate of 5 ml/min the smaller particles result in greater extraction, which may imply that these particles were fluidized. That said, the extraction achieved with the large particles was not insignificant, but with such larger particles the voids between particles may be large enough for the gas to permeate through the bed, allowing the ligand to reach the material without the bed being fluidized. In the second set of tests, the curves are all similar, perhaps so much so to say with confidence that trends (see Figure 10) can be inferred. In the 50 g bed, the lowest extraction was 31.0%, and 35.3% in the highest. In the 15 g bed, the highest extraction of all the experimental runs was achieved, 55.1%. This occurred with a flow rate of 7 ml/min and particle size of 0.25−0.5 mm. Perhaps the increased flow rate and decrease particle size contributed to the bed being fluidized and unhindered diffusion taking place. Olehile did not seem certain

[9] I have corrected an obvious mistake: the sizes run from 0.5 mm to 1 mm.

how to explain this, not accounting for fluidization and by extension a radically different diffusion model. This disjointed statement illustrates the author's apparent confusion:

> The adjustments could have been such that, [*sic*] the initial reaction rates are very rapid compared to the diffusion rate of product to the bulk gas, subsequently causing an increased diffusion barrier attributed to the [*sic*] both the ash layer and the gas film layer, thus contributing to the significant slowing of the reaction, resulting in low degrees of extractions. (*ibid.*:38)

As has been discussed previously, no ash layer could exist, particularly if the bed is fluidized. It is unclear how a gas film layer would be limiting in this situation. It is particularly unlikely for such a barrier to exist in a fluidized bed. The trends, or lack thereof, can be better attributed to the beds not being fluidized. With a larger bed, 50 g, perhaps the bed did not fluidize in any of the experimental runs. This would have resulted in a similar extent of extraction among all the tests, with seemingly random patterns which would be difficult to describe. This would simply be a result of uncertainties, which are always present in any experimental work, and should be accounted for. This phenomenon can perhaps be observed in Figure 13. With the extractions being so similar, it is reasonable to think they could be approximately the same. This indicates that fluidization, and by extension actual contact of the ligand with the particles, is the most important factor. If there is no contact, the reaction cannot take place, and testing other conditions becomes irrelevant. There will still be some level of contact with the particles, but it may not permeate through the bed as channelling occurs. Owing to these shortcomings, in addition to the choice of kinetic model being inappropriate for the reaction that was expected to take place, the kinetic study of the vanadium extraction will not be considered further.

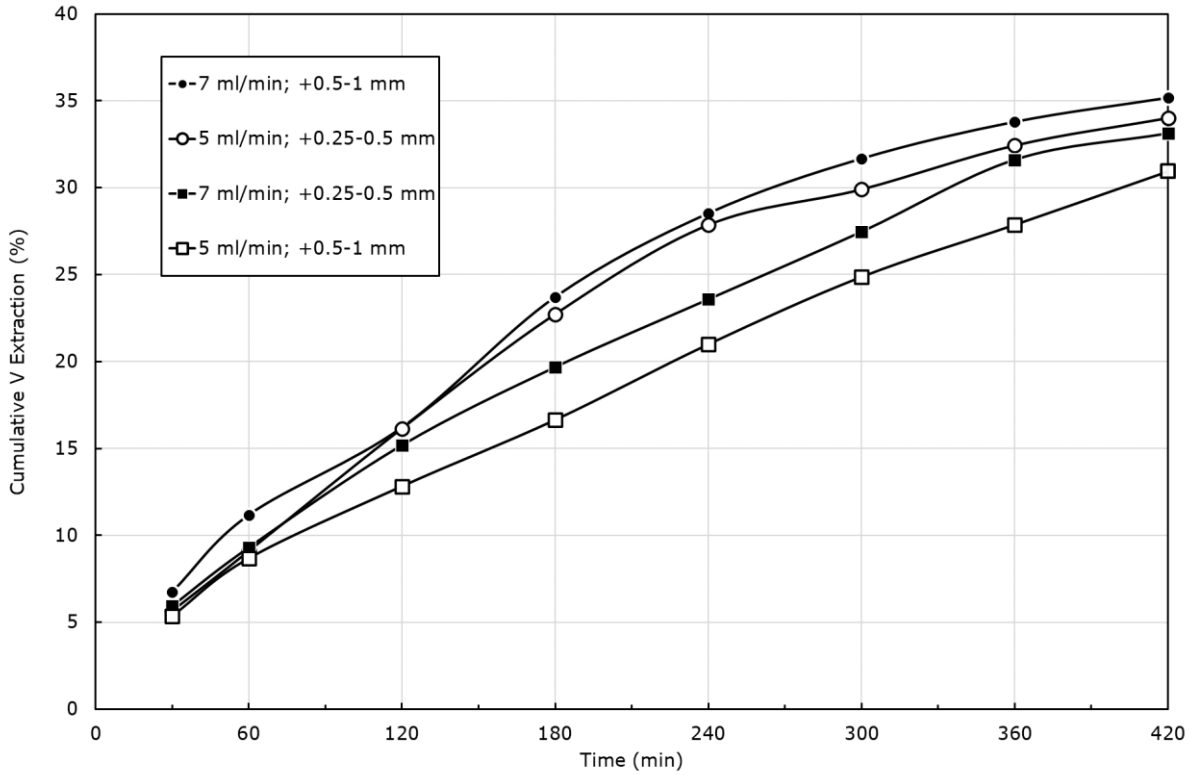


Figure 13: Vanadium extraction from a 50 g bed (Olehile 2017:39)

Chapter 5

Extracting Gold with the SERVO Process

The subsequent three projects that followed at Wits University studied the VPE of gold with acac. This was the first time that the group focused on one particular metal or source for multiple studies. The first of the studies repeated the algorithmic approach taken previously by the studies on the other metals. However, as this had been done in the first study, the following studies sought to understand and develop the process further. Wood (2022) then discovered that some of the results and trends that had been recorded previously may have been anomalies.

Comparison between Machiba and previous work

A cursory examination of Machiba's dissertation revealed that it too followed the poorly set precedents, *i.e.*, that VPE falls outside of the scope of pyro- and hydrometallurgy, use of the shrinking core kinetic model, *etc.* He included a review of the cyanide process which is used to extract gold, but aside from stating that it is harmful thus providing motivation to replace it, this section is irrelevant when studying vapour-phase extraction. No literature was provided that discussed acac complexes with gold or that indicated its viability. A deeper analysis revealed that Machiba's literature review did not otherwise extend beyond looking at the work done within the group itself, particularly that of Mariba (2010). This led to the discovery that the dissertation was heavily plagiarized, with most of the literature review being copied almost verbatim from Mariba's work, and with some sections being copied from other sources. There are also striking similarities to the results in Mariba's dissertation, which may indicate that the results are not authentic. The analysis of these results was copied as well (Machiba 2020:40; Mariba 2010:55). This casts further doubts on their authenticity, given that most of the dissertation was in

fact plagiarized. Thus, this project cannot be considered as evidence for a viable process.

The project had sought to react acac with tailings from DRDGOLD's Ergo plant using the same experimental setup as the previous studies in the group as outlined in chapter 3. The objectives included understanding the chemical reaction (Machiba 2020:4). He asserted that the β-diketones—particularly acac—had been selected to extract gold. He gives no evidence in support of this decision, aside from the fact that it had been used previously in the group for other metals. He notes that gold "is one of the least reactive chemical elements" (*ibid.*:11), yet does not make clear why he or anyone else believed that acac would react with it. As with tantalum in the work by Olehile, gold does not complex directly with acac. Moshier and Sievers (1965:141) give two possible complexes, namely, Au(III)bis(methyl)acetylacetonate[10] and Au(III)bis(ethyl)acetylacetonate[11]. Other studies show that it is possible to substitute acac into a complex constituting gold (Wunsch *et al.* 2022), but I have not yet come across any outside of Wits that claim to have produced a direct complex constituting solely gold and acac.

Given the lack of useful analysis, the high degree of plagiarism within the dissertation, and the doubts as to the authenticity of the results, there can be no benefit in discussing the work done by Machiba any further. This brings us to the work undertaken by Ali (2021). He tested the gold extraction from the DRDGOLD tailings using the techniques and setup previously established in the group. He reported a gold extraction of up to 50% at 250°C. He did, however, state that the results obtained were inconsistent and thus unreliable (Ali, pers. comm.). The 'best' results, *i.e.*, those that produced the desired trend, were selected. It cannot be said with any certainty then that gold was actually extracted and that the selected results have any bearing on reality, particularly in light of other sources' indicating that such a reaction is unlikely (Moshier & Sievers 1965:141). As such, he made the focus of his study Density Functional Theory (DFT), which had not been applied before.

[10] $(CH_3)_2(C_5H_7O_2)Au$
[11] $(C_2H_5)_2(C_5H_7O_2)Au$

Density Functional Theory

DFT, the most commonly used tool in quantum mechanics, can predict various ground-state properties of molecules, a consideration in theoretical chemistry (Li *et al.* 2019:55). Ali (2021) and Wood (2022) modelled various theoretical gold-acac organometallic complexes, including various substitutions on the acac molecules and used DFT to optimize them. The underlying assumption is that if the solution converges with a negative Gibbs free energy of formation, then the complex can exist. This could be the case, but I believe that the value of such a technique is more comparative, not predictive.[12] Other complexes may exist which are thermodynamically favoured, complexes that DFT in an exercise does not predict. However, if the user had predicted them and simulated their states, the comparison between the results would be valuable, and could be further used to predict which of the simulated complexes is the most likely to form. The value of such an approach was recognised when Ali (2021:43) simulated various β-diketones and concluded that their stabilities were similar enough so as not to warrant using a ligand other than acac, which would be the cheapest and most accessible of the β-diketones simulated. However, this comparison did not account for decomposition products which may be more stable, or if the reactants themselves were more stable—*i.e.*, whether a reaction would take place at all. As with all tools, there are limitations. The analogy of a calculator illustrates the limitation: computation generates more often than not an answer; whether the answer is correct depends on the applicability of the tool and on the input from the user. Often an unquestioned assumption when using simulations or modelling techniques is that convergence to an answer implies that the solution is meaningful. However, it is appropriate to think of them as advanced calculators. Just because a solution was generated, it does not necessarily have any bearing on reality.

The DFT work done on gold VPE did not provide sufficient clarity on the structure of the hypothesized complexes. If the studies and development of a process were to

[12] This is specifically regarding whether or not a complex will form, as the ground state properties would still be predicted.

progress any further, the complexes would need to be understood more fully. Thus, together with the work involving DFT, Wood (2022:30–35) attempted to synthesize the complex directly. When he failed, a critical test was undertaken—pure acac vapour was passed over a nugget of pure gold—to see if such a complex would form under the conditions that had been documented. No evidence of any reaction was forthcoming (*ibid.*:42–43). To account for the familiar patterns and trends documented, Wood then proposed a mathematical model which demonstrated that these 'results' could be reproduced by noise or uncertainties in the experimental readings (*ibid.*:83–86).

Possible contributing factors to the anomaly

Two factors were seemingly overlooked in the previous test work undertaken. As it is the only reliable study on gold, I have based my analysis on the work Ali did. The tests used the same experimental procedure and setup used by the studies discussed before. The "fluidized" bed was 20 g of gold tailings obtained from DRDGOLD. The grade was given as 0.3 ppm. The significance of this is that—assuming that the sample tested was representative of the bulk—there would have been 6 µg of gold in the sample. As the condensates collected in any interval (30 minutes or 1 hour) tended to be about 30 ml (Ali 2021:65–67); I have based my assessment on a conservative 30 ml. Thus, if 100% of the gold were extracted in any interval, this would produce a condensate containing 0.2 µg of gold per ml. The condensate was then made up to a fixed volume (very likely 50 or 100 ml as these are standard flasks in the laboratory) in a volumetric flask for analysis using atomic absorption spectrometry (AAS), a procedure that dilutes the concentration of gold. Some of the condensates collected exceeded 50 ml. Thus, it is likely that all samples of condensates were diluted to 100 ml. The concentration of the diluted sample would then be 0.06 µg/ml. The significance of this is that the finest recommended working range of the AAS used, an Agilent Technologies 200 Series AA, by the operational method guide is 0.1−30 µg/ml, the other being 0.2−60 µg/ml (Anon. 2021:12). It is not certain what going outside of this range would do, but it is possible that it would simply result in greater uncertainties, *i.e.*, noise, as suggested by Wood. Another factor mentioned in the guide is that iron may suppress gold readings. The acac may

well have extracted some iron from the sample which could also have affected the outcome. Thus, the critical test undertaken by Wood is the only reliable test. Importantly, it determined that no extraction occurred. He considered the detection limits and used a large enough quantity of gold to ensure that had extraction occurred it would have been within the detection limits. This is the first of the factors that was overlooked, namely, the detection limits of the instrumentation used.

The second factor that was overlooked is whether the sample was large enough—in other words, was the 20 g of sample (tailings) tested representative of the bulk material for which 0.3 g Au/t obtains. It is possible that with the distribution of gold within the tailings dam, particularly with a gold concentration as low as 0.3 ppm, that there was less gold, if any, in a sample of 20 g. Thus, sample size needs consideration, and should not be arbitrarily selected. Pierre Gy developed a system to quantify sampling uncertainties—which he referred to as sampling errors—which can be used to determine an appropriate sample size (Wills & Finch 2016:44–45). Gy proposed Equation 10, which reduces to Equation 11 in the case where the mass of the entire body (M) is significantly larger than the sample mass (m_s). In the tests described, the 20 g sample was taken from a bag of tailings meant to be representative of tailings dams to the west of Johannesburg; hence, the simplified equation applies. The standard deviation (σ_f) represents the fundamental sampling error, which can be understood as an uncertainty percentage; d is the nominal particle size in the sample; and C is a particular constant for the material to be sampled. C is the product of a shape factor (f), a granulometric or particle size distribution factor (g), a liberation factor (l), and a mineralogical composition factor (c).

$$\sigma_f^2 = \frac{(M-m_s)}{Mm_s} C d^3 \qquad \textit{Equation 10}$$

$$\sigma_f^2 = \frac{Cd^3}{m_s} \qquad \textit{Equation 11}$$

I used Equation 11 to provide an indication of the sample mass which would be required to reduce the sampling uncertainty to a satisfactory limit. Minnitt and his colleagues (2007:507) stipulate a shape factor of 0.2 for fine gold ores. The

granulometric factor is given by a corresponding ratio of the nominal top size to the lower limit size, which in the case of the tailings are 300 and 3.3 µm, respectively. Such a large size distribution corresponds to a g value of 0.25. The mineralogical composition factor can be determined from Equation 12. However, in the case of low-grade materials, such as gold tailings, it can also be taken as the ratio of the density of the material to the grade in parts per million (Wills & Finch 2016:45). In this case, that would be 6.4×10^7 g/cm^3.

$$c = \frac{(1-a)}{a}[(1-a)r + at] \qquad \textit{Equation 12}$$

$$l = \left(\frac{L}{d_{95}}\right)^b \qquad \textit{Equation 13}$$

Equation 13 is used to determine the liberation factor, where L is the liberation size (cm), d_{95} is the nominal particle size. Gy typically used a value of 0.5 for b, but it can vary from 0 to 3, and is usually 1.5 for gold ores (Minnitt *et al.* 2007:508). In this case, the liberation size is in the range 1−5 µm. This corresponds to a fundamental uncertainty in the range of roughly 3−10%. This can be considered a tolerable uncertainty, but should 10% be considered too high, a larger sample would be required, particularly when samples are close to the detection limits of the techniques employed, as was the case here. The liberation size range quoted here would require a sample size of 170−1900 g if one sought an uncertainty of 1%. However, the total uncertainty is larger than this fundamental uncertainty, so it is recommended to double the sample mass given from Gy's relationship (Wills & Finch 2016:45).

Takeaways on gold extraction

Although the sampling size was sufficient to be considered representative, there was still too little gold in the sample for the concentration to lie above the testing limits of the AAS instrument. Even had all the gold been extracted, the detection level would not have been in the operating range recommended by the instrument manufacturer, and in practice less than all the gold would be extracted in any one interval of sample collection (30 minutes or 1 hour). Thus, the model proposed by Wood which attributes the regular trends observed to cumulative noise generating non-existent trends is a probable explanation. This agrees with other studies, which demonstrate

that gold does not complex directly with acac. All the evidence points to the VPE of gold using acac as an impossibility. Any other reagent which reacts with gold will likely react with many other species in an ore sample. This negates the principle of selectivity in extractive metallurgy and, in all likelihood, would make the costs of such a process prohibitive. Further endeavours in this direction should be abandoned.

Epilogue

Vapour phase extraction is a process in which an organic ligand reacts, ideally selectively, with an element of interest; the product, an organo-metallic complex, reports to the vapour/gas phase and so is separated from the bulk material. Contacting with the solid particulate material occurs in a fluidized bed (preferred over a rotary kiln). The stable organo-metallic complexes, being removed, are condensed. The ligand is regenerated in a hydrogenation reaction and the metal is precipitated. This is the basis of the SERVO process. VPE seems a promising technology as the reaction aspect of extraction directly causes separation of the phases. Elevated—but not high—temperatures reduce energy requirements. It presents further advantages particularly when used to recover metals from low-grade sources such as tailings. Reacting the ligand directly with the targeted species reduces reagent consumption. Added advantages to treating waste materials such as tailings include land remediation and reclamation from reprocessed tailings dams and the mitigation of associated environmental and health risks.

The potential of the technology has therefore been explored. Wits investigated using acetylacetone to extract several metals from various sources. The extraction of iron from iron ore fines and synthetic sources was investigated, as well as chromium and tantalum from synthetic samples. Aluminium extraction from fly ash and synthetic sources was studied; vanadium from depleted catalysts; gold from tailings (gold mine dumps). Acac is not selective when extracting metals, but vapour fractionation can be used to isolate the target species. However, only the complexes of aluminium, beryllium, chromium, and vanadium are sufficiently stable to be removed and treated in this way. Several other metals can react with acac, but above 200°C complexes are prone to decomposition, which is an economic barrier for the process as ligand cannot be recovered and recycled. Gold and tantalum cannot be extracted by acac at all; species that could be extracted and the phases in which they occur

were not considered. Without understanding the reaction, and what complexes are formed, analytical techniques such as DFT cannot be employed. DFT should be used to gain a further understanding of complexes which had formed or are known to exist, rather than to predict hypothetical complexes. This is evident from Ali's (2021) and Wood's (2022) modelling supposedly stable complexes—comprising gold and acac—which does not exist.

Ligands such as TFA and HFA can form complexes with more metals than acac, and these complexes are also stable at higher temperatures, reducing the risk of decomposition. However, TFA and HFA are prohibitively expensive in the context of an industrial process. This is what motivated the use of acac. Future studies would need to identify ligands that can form stable complexes with the desired species and would be cheap enough for the process to be economically viable. Ligands may also not react with—or react with in the same way with—different polymorphs of a compound or a species occurring in different phases—amorphous, crystalline, silicates, *etc.*

The effect of different phases has not been properly explored beyond Mpana's (2012) and Tshofu's (2014) mentioning that higher extractions were obtained from synthetic samples. The underlying causes were was not adequately considered. Essential properties—such as phase and composition—were not identified, much less characterized. The ligand might have a capacity to extract an element, but not necessarily from the phase in which they occur; the element might occur in a phase—or locked in another phase—that does not react with the ligand. Overcoming this obstacle may require pretreatments such as roasting to convert sulfides to oxides. This would make treating low-grade materials significantly more expensive.

Other limitations in an industrial application of the technology include fractionation and fluidization. If the grade of the material is very low, there may not be sufficient metal recovered to isolate it by means of fractionation. This would require the process to be highly selective, which precludes the use of acac. Regarding fluidization, if the material is not fluidizable, contact with the ligand will be inhibited. If particles are fluidizable, in an industrial process, the stream would

require a carrier gas. If not, then the quantities of ligand required to fluidized beds would be enormous and exorbitant.

All the evidence indicates reagent starvation during extractions tested. It is possible that starvation was caused by a lack of fluidization and thus the reagents could not reach the target species. Without proper fluidization, the conditions needed to undertake kinetic studies were not met, which invalidates the tests and their findings. The measurements are unreliable owing to poor test work, *viz*., that the beds were not fluidized. There is no potential to develop a process using acetylacetone to extract gold or tantalum in the vapour phase. The work that reported success has been shown to be adversely affected by experimental anomalies. However, given the shortcomings of the investigations, the possibility of using such a process cannot be ruled out altogether. There may be alternative ligands that can be considered, but only if they can be shown to react with a target species in the phase in which it occurs. The mechanisms involved in the process—such as fluidization—need to be properly understood and employed.

In science, one does not chart a way forward with reckless abandon, but carefully considers one's work and that which precedes it so as to make a meaningful contribution in the pursuit of knowledge and understanding rather than the accruement of senseless data.

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