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CARBOTHERMIC REDUCTION OF ALUMINA INTO A METALLIC SOLVENT PHASE

BY DEREK CAIZERGUES

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

Johannesburg, 1998

ABSTRACT

Experiments have been conducted at around 1700^{0}C to determine the whether carbothermic reduction of alumina is possible at these temperatures. Total pressure of the system was reduced to around 30 kPa and various metallic solvents such as copper, nickel, iron and tin were used to dissolve the metallic aluminium produced. The use of a solvent (and hence decreasing the activity of metallic aluminium) and a lower pressure are thermodynamic requirements to increase the extent of reduction under a given set of conditions. This enables the use of lower temperatures than are required under atmospheric conditions.

The highest recovery of aluminium was achieved with the nickel solvent decreasing in order from iron, copper and tin. This ranking was also in accord with the extent of deviation from ideality in the respective binary solutions of these solvents with aluminiur . The nickel-aluminium system displays the largest negative deviation from ideality whereas the tin-aluminium system showed a positive deviation.

The rate and extent of the reduction was found to be highly dependent on temperature and pressure. The pseudo first order reaction rate was found to be the primary order for the reduction of aluminium in all the solvents used. It is also suggested that the reduction rate was controlled primarily by chemical reaction rate rather than by transport processes. This is due to the extreme sensitivity of the rate and extent of the reaction to temperature.

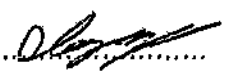
ACHIEVEMENTS

Confirmation that the solubility of aluminium in the four solvents used namely nickel, iron, copper and tin, follow thermodynamic and solubility principles defined by their deviation from ideality. i.e. The varying deviations of the solvents from Raoult's rule of ideal solutions.

Lowering system pressure and use of a solvent metal does in fact assist in the carbothermic reduction of aluminium.

DECLARATION

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



Derek John Caizergues

29 January 1999

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LIST OF SYMBOLS USED

(s) = Solid

(l) = Liquid

(g) = Gas

(aq) = Aqueous Solution

$\underline{X}$ = Element X in Solution

ΔG^{o} = Free Energy of Formation

k = Reaction Rate Constant

τ = Time constant of Reaction

μ_{Mg} = Measure chemical potential

μ_{Mgl} = Chemical potential of monomeric magnesium

χ_{Mg} = apparent mole fraction

γ_{Mg} = Usual apparent activity coefficient

z_{Mg} = True mole fraction of monomeric Mg

α_{Mg} = true activity coefficient of Mg

= Activity of a Component

f = Fugacity of the Substance

f^{o} = Fugacity of a Substance in its Standard State

P_i = Partial Pressure of Component *i*

P_i^{o} = Partial Pressure of Component *i* in its Standard State

x_i = Fraction of Substance *i*

γ = Activity Coefficient

1 INTRODUCTION

Aluminium has led a very varied existence, from being one of the rarest materials in the middle ages being found only in the richest of houses, to being one of the most commonly used metals available today. Its physical properties enable it to be used for a large range of products. Its malleability and resistance to corrosion make it ideal for eating and drinking utensils, its low density is a great advantage in the construction and aviation fields. Napoleon pushed for research into the metal as he foresaw immense potential for its use in light weight armour for his troops.

It is currently relatively cheap to produce for its class of material. This does not however make it perfect, or even particularly easy to process. Any increase in production or drop in the production costs of aluminium by traditional methods, will be beneficial to the industry and open up new avenues.

The principle of carbothermic reduction of alumina into aluminium has been around for many years. It is one of the simplest, and theoretically the most effective way of aluminium production. The "waste" products from the reaction can be controlled and even used for other commercial purposes. The simplicity of this process has several complications, so current fused salt electrolysis production methods still dominate the industry. The production of aluminium in the modern age is electrically very energy intensive. Environmental concerns and the rising cost of electricity are making production, especially on a smaller scale, very difficult. Countries such as Japan have very high penalties for high usage of electricity during peaktime. This has forced factories and other large power consumption facilities to operate at off-peak times. Current processes are reaching the peak of their efficiency, and thus new processes may be needed to diminish the adverse affects of current aluminium production.

Various new processes have been tested with fair to limited success. It is the aim of this project to investigate and test various procedures whereby the rather unfa ourable thermodynamic and environmental effects of direct carbothermic reduction of alumina could be minimised. Most of the investigations carried out have dealt with attempts to decrease reduction temperature. They have had limited success due to inadequate knowledge of the thermodynamics involved at the elevated temperatures.

The direct carbothermic reduction of alumina has proved to have a multitude of problems associated with it. The temperature required to effect reduction is in the region of 2200 °C and is currently one of the major problems. At this temperature the attack on the lining of any vessel used to contain the reaction would be severe, as well as the excessive energy requirements to maintain this temperature. In principle, reducing the temperature of the operation should be possible by lowering the total pressure of the system i.e. operating under a vacuum. This is because the total pressure of the system is equal to the partial pressure of carbon monoxide, which along with aluminium metal is a product of the carbothermic reduction reaction. Another major problem in carbothermic reduction of aluminium, is the formation of aluminium carbides and oxycarbides, as reaction products, rather than aluminium metal. According to thermodynamics the decrease of the thermodynamic activity of aluminium in the product metal phase will increase the extent of the reaction, and will decrease the extent of carbide or oxy-carbide formation. This is possible by conducting the reduction process in the presence of a metallic solvent, which favours a high dissolution of aluminium.

Such a carbothermic reduction under vacuum and in the presence of a solvent phase might well be suitable for smaller scale production of aluminium metal or aluminium alloys, using much smaller and much less capital intensive reactors.

Current electrical based aluminium smelters are inflexible in terms of material input and products.

In order to develop a process based on the carbothermic reduction of alumina, along with thermodynamics, the kinetic aspects must be examined as well as recoveries of the metal. Therefore the objective of this investigation is to examine on a laboratory scale, the feasibility of carbothermic reduction of alumina at a reduced pressure (under vacuum) and in the presence of a metallic solvent phase.

The experiments have been designed in such a way as to gather information on recovery, along with continuous recording of the changing system pressure, which will also shed light on the kinetics of the reactions, and possibly on thermodynamic equilibria.

2 LITERATURE SURVEY

2.1 Bayer Process

2.1.1 Introduction

The initial production of aluminium (Al) was very slow and very expensive due to the high stability of the metal oxide alumina (Al_2O_3). The production of the oxide was not very difficult but the purification process was very slow. Karl Bayer developed a method for high purity alumina to be produced on a large and much more economical scale.

This process was patented by Karl Bayer in 1888 and comprises the two following reactions:

$$Al_2O_3.3H_2O\ (s) + 2NaOH\ (aq) \Leftrightarrow 2NaAlO_2\ (aq) + 4H_2O\ (aq) \qquad \textbf{(2.1 a)}$$

Extraction of the alumina into an aqueous solution is the forward reaction proceeding to the right, while the next step, decomposition of the aqueous solution formed, is in the reverse direction.

The calcination step is the second process and is represented as follows:

$$Al_2O_3.3H_2O\ (s) \Leftrightarrow Al_2O_3\ (s) + 3H_2O\ (g) \qquad \textbf{(2.1 b)}$$

2.1.2 Technical Overview

Most of the alumina in the world at the moment is not very pure in its raw state. Various compounds of silicon, calcium, iron and tin, to mention a few, represent impurities that impede the use of alumina in industrial processes. Bauxite contains about 55-65% Al_2O_3, 1-27% Fe_2O_3 and 1-10% SiO_2, together with TiO_2, vanadium, manganese, galium, zinc, calcium etc. [1,2]

Karl Bayer perfected a process whereby alumina with various impurities could be purified to a stage where further processing was made easy. Patented in 1888 Bayer proposed that by adding the bauxite to a solution of NaOH at temperatures up to about 240 °C and under a pressure of 6 atmospheres, the bauxite would react with the caustic soda to produce a solution of sodium aluminate. The various forms of bauxite found around the world are treated in different ways to effect good extraction of the alumina.

Specifically the extraction of the trihydrate alumina takes place within one hour. This gives the liquor containing 140 g/l total Na_2O and 90 g/l free Na_2O, with a molar ratio Na_2O / Al_2O_3 = 1.6 to 1.8. Compounds such as monohydrate bauxite on the other hand are treated for 2 to 8 hours to get a concentration of 300 g/l to 350 g/l total Na_2O and 270 g/l to 315 g/l free Na_2O. The molar ratio is still 1.6 to 1.8. Before the separation takes place, the leached slurry composition is adjusted, by dilution to the concentration required for the decomposition of the leach liquor. [3,4]

The high pressure leaching vessels used for the leaching steps, dehydrate the iron hydroxides found in bauxite and produce an α-Fe_2O_3 solid solution, which contains about 10% Al_2O_3. This then crystallises out forming the bulk of the "red mud". The silicon impurities present in the liquor are converted to sodium alumino-silicate, which also precipitates out in the red mud. The process does

not however remove all the silicon from solution. A small percentage remains in the final liquor as an impurity. This is due to the physical and thermodynamic similarity between the alumina and silica. This red mud is an insoluble finely sized precipitate that is filtered out, with the residue and sand, of the circuit by counter current decantation, and discarded as a waste product of the process.

A typical composition of red mud is shown in Table 2.1 [1]

Table 2.1 Typical Composition of Red Mud

Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	Na_2O	TiO_2
56 - 60 %	16 - 18 %	5 - 8 %	2 - 3 %	0.5 - 1.5 %	0.4 - 6 %	6 - 8 %

The primary chemical reaction can also be represented by:

$$Al(OH)_3 + NaOH \Leftrightarrow NaAlO_2 + 2H_2O \qquad (2.1\ c)$$

Not all the impurities can be removed in the leaching process. Small amounts of the silicate and iron oxide pass through the filtration stage and contaminate the final liquor. The concentrations of these impurities depend on the process being used and on the control over the process.

The precipitation of the final and clarified liquor to form a crystalline precipitate is carried out in batches. The solution is then cooled and pumped into a decomposer, which contains a crop of alumina seeds from the previous batch, and is stirred for two to four days until the Na_2O / Al_2O_3 ratio has risen to about 3.5 to 4.5. The precipitated, $Al(OH)_3$, is washed and then calcined in a rotary kiln at about 1200 °C to remove water and produce a product comprising

α-Al_2O_3 in a fine powder form. The alumina produced during the calcination must be free from any hydrated alumina compounds to prevent any furnace damage.

The old liquor from the dissolution step is recycled, concentrated by evaporation and causticised, either in a separate operation, or during the next leaching cycle. The impurities that are still in the liquor contaminate the recycled liquor as well contaminating the alumina pr ..

The industrial Bayer process is very closely integrated, and any changes made to one step in the circuit affect the whole system. The extraction depends more on the feed material being supplied, specifically the purity of the feed, resulting in an optimised alumina recovery.

The physical and structural form of alumina has a bearing on its use as well. In the furnace, during the Hall-Héroult reduction, the cryolite together with the alumina forms a hard thermal insulating crust over the top of the furnace. A coarse sandy type of feed is needed to ensure the crust is formed, a finer size distribution does not give the desired result.

The chemical specification for metallurgical grade alumina is given in Table 2.2.

Table 2.2 Typical Analysis of Metallurgical Grade Alumina

Constituent	Percentage
Silicon	0.02 % SiO_2 max.
Titanium and Zircon	< 0.01% ($TiO_2 + ZrO_2$) max.
Iron	0.02% Fe max.
Sodium	< 0.5% Na_2O acceptable
Zinc	0.0001% Zn max.
Calcium	0.05% CaO max.
Phosphorus	0.01% P_2O_5 max.
Loss on Ignition	0.25%
Aluminium	Remainder

The high purity is required for the following reasons:

1) All other impurities in the alumina, except the alkalis, are reduced to the metallic state in the electrolytic cells, and would thus contaminate the products.

2) Potassium forms potassium cryolite, which attacks the cathode linings of the electrolytic cells.

3) Titanium and phosphorus reduce the current efficiency of the electrolytic cells.

2.2 The Hall-Héroult Process

The discovery by Charles Hall as to how alumina could be reduced into metallic aluminium on a commercially viable basis was made in 1886. Hall correctly analysed the problem of aluminium production at around the same time as Héroult did across the Atlantic in France. Alumina was available in a high purity form at a low cost, but its high melting point (2040 °C) and low electrical conductivity made its electrolysis very difficult in the oxidic form. The use of a fused salt that allowed the dissolution of large amounts of alumina at reasonable temperatures would make electrolysis of the aluminium in solution possible. The fused salt would have to have a higher stability than the alumina to prevent decomposition before or during the reduction.

The fused salt that was chosen was cryolite (Na_3AlF_6) as it had the desired properties. Cryolite has a relatively low melting point and a low operating voltage is required for the electrolysis. Bath temperatures are at around 950 °C. The lower density of cryolite means the aluminium produced will sink to the bottom of the crucible where it is protected from re-oxidation.

A typical electrolyte today contains about 80 - 90% cryolite, the balance being mainly alumina and a small amount of additives such as aluminium and calcium fluorides. [1]

After finding that the type of pot used in the experimentation would have to assist in the reduction, Hall built a carbon crucible for the experimentation. The crucible acted as the cathode, and a carbon rod was inserted as the anode.
Figure 2.1 [4] depicts the typical section of a multi-anode production cell. The cell is lined with baked carbon or graphite bricks that act as insulation, a cathode and to collect the molten aluminium.

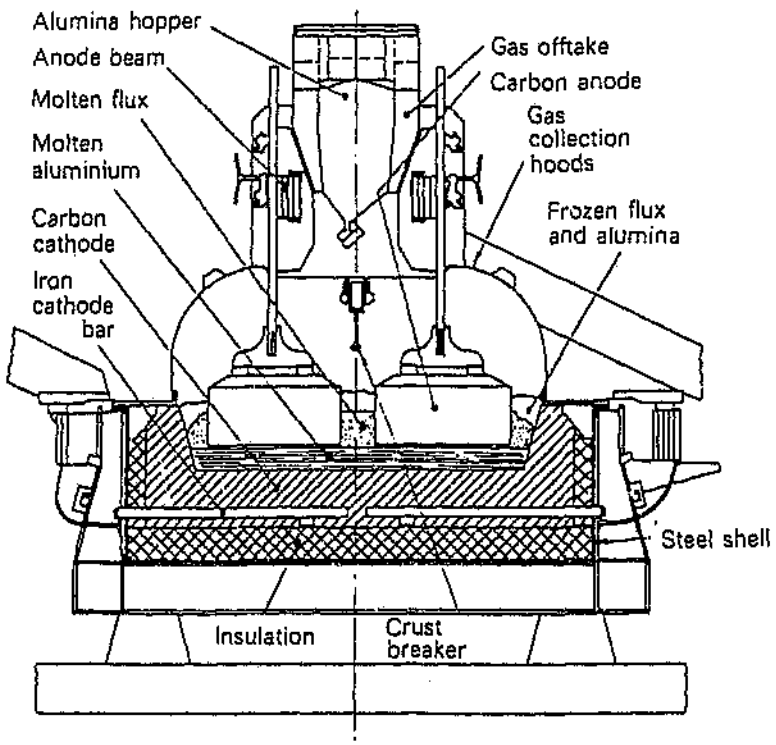


Figure 2.1 Section of a Multi Anode Production Cell

The anode can be one of two types. The first type is a single electrode or "Soderberg" electrode, in which anode carbon paste is added in situ, and baked by the waste heat of the cell and gradually consumed. Alternatively, pre-baked carbon blocks are used which dip into the electrolyte and are also gradually consumed. [4]

Cell voltage drops are in the region of 5 V and current consumption is high, up to 250,000 amps. The cells are arranged in series or "potlines" with the aluminium being tapped at regular intervals, and the purified alumina added as required.

The ionic transfer is believed to be by various ions including, Al^{3+}, O^{2-}, Na^{+}, AlF_4^{1-}, AlF_6^{3-}, all having the neon configuration, other ions such as $AlOF_3^{2-}$ are believed to assist in ionic transfer. At the cathode the aluminium fluoride ions are discharged to produce aluminium metal and F^- ions, while at the anode the ions dissociate to produce carbon dioxide. [1]

Figure 2.2 shows a typical integrated production flow diagram for aluminium production from the Australian Aluminium Development Council. Production of one tonne of aluminium for only the Hall Héroult process takes a massive amount of electrical energy, in the region of 15,000 to 16,000 kWh. By contrast the thermodynamic energy required for the same total production tonnage would be of the order of 6,500 kWh.

To gain an idea of the costs involved in the production of aluminium metal from the mining of the raw economical grade bauxite we can compare aluminium production with iron production. Aluminium production from raw bauxite consumes about 22,000 to 25,000 kWh electrical energy per tonne, whereas the processing iron ore only requires 4,500 to 5,500 kWh of electrical energy per tonne of product. [1]

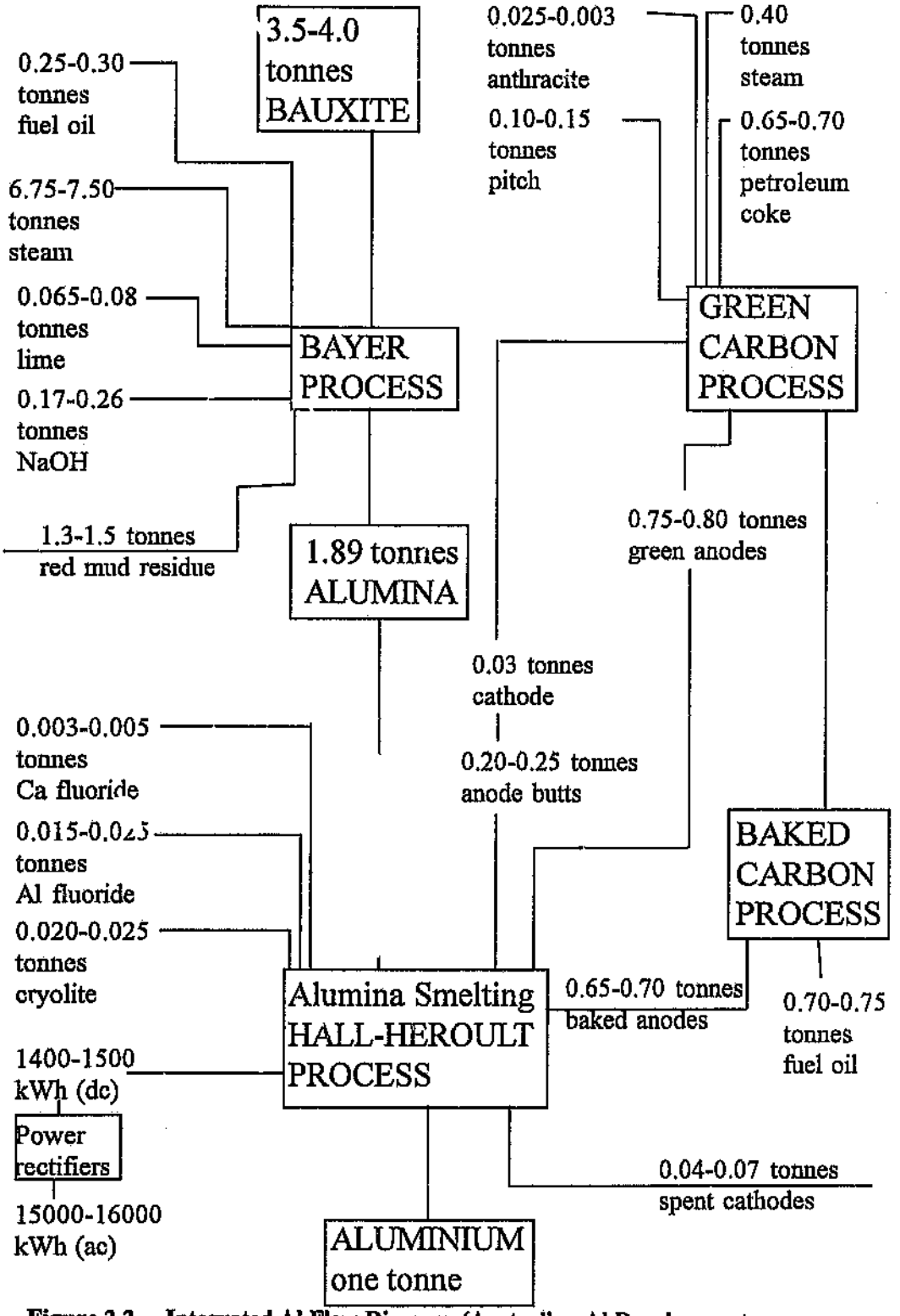


Figure 2.2 Integrated Al Flow Diagram (Australian Al Development Council)

2.3 CARBOTHERMIC PRODUCTION OF ALUMINIUM

2.3.1 Introduction

Classical carbothermic production of metals from oxides at elevated temperatures is as follows:

$$Me_xO_y\,(s) + yC\,(s) \Leftrightarrow xMe\,(l) + yCO\,(g) \qquad (2.3\ a)$$

For oxides lower down on the Ellingham diagram, carbothermic reduction is not a viable option at lower temperatures as the oxide is too stable. In addition for the metals lower down on the Ellingham diagram, the refining of the metal produced, which is saturated with carbon, becomes problematic. Aluminium falls into this category and solutions are being sought to both of these problems.

The history of understanding the chemistry and kinetics of the reactions between the three major elements, carbon, oxygen and aluminium has been very slow and tedious. The process has not yet evolved into a viable process that can be rationalised from the product side. The actual steps that take place are still not completely understood.

The reactions that were thought to be the primary reactions involved are as follows: [8]

$$2Al_2O_3(s) + 9C(s) \Leftrightarrow Al_4C_3(s) + 6CO(g) \qquad (2.3\ b)$$

$$Al_2O_3(s) + Al_4C_3(s) \Leftrightarrow 6Al(l) + 3CO(g) \qquad (2.3\ c)$$

$$Al_2O_3(s) + 3C(s) \Leftrightarrow 2Al(l) + 3CO(g) \qquad (2.3\ d)$$

$$Al_4C_3(s) \Leftrightarrow 4Al(l) + 3C(s) \qquad (2.3\ e)$$

Foster Long and Hunter [6] performed experiments, which allowed analysis of various samples during the reaction. The results showed that various intermediate compounds existed that changed reaction processes and equations to explain them. The primary intermediate compounds identified were Al_4O_4C and Al_2OC, both belonging to the pseudo binary system Al_2O_3-Al_4C_3.

Foster changed the carbon content of his system to produce the two different compounds according to the following reactions:

$$4Al_2O_3(s) + Al_4C_3(s) \Leftrightarrow 3Al_4O_4C(s) \qquad (2.3\ f)$$

and by increasing the carbon content further the following occurred:

$$Al_4O_4C(s) + Al_4C_3(s) \Leftrightarrow 4Al_2OC(s) \qquad (2.3\ g)$$

Cox and Pidgeon [7] proposed various reactions for the production of aluminium utilising the intermediate products of Al_4C_3 and Al_2OC. The reactions are given below:

$$Al_2O_3(s) + 3C(s) \Leftrightarrow Al_2OC(s) + 2CO(g) \qquad (2.3\ h)$$

$$2Al_2O_3(s) + 3C(s) \Leftrightarrow Al_4O_4C(s) + 2CO(g) \qquad (2.3\ i)$$

$$Al_4O_4C(s) + 6C(s) \Leftrightarrow Al_4C_3(s) + 4CO(g) \qquad (2.3\ j)$$

$$Al_4O_4C(s) + Al_4C_3(s) \Leftrightarrow 8Al(l) + 4CO(g) \qquad (2.3\ k)$$

They also proposed that the compound Al_2OC was formed before Al_4O_4C, against what would be expected in the equilibria. Motzfeldt [8] expressed concerns that their system was contaminated with nitrogen gas. Motzfeldt's hypothesis was that Al_2OC was a nitrogen stabilised compound that does not occur naturally, and thus can not be considered to be a stable product under the strict conditions applied during experimental test runs. The nitrogen stabilised Al_2OC, may be a compound which proves necessary for easier processing, but research has not shown this.

Experiments conducted by Komarek, Coucoulas and Klinger [9] and Prescott and Hincke [10] confirmed the production of the two intermediate oxycarbides. It was concluded that the formation of aluminium by the direct reduction of Al_2O_3 was not possible, and that various other intermediate reactions take place instead.

Excessive product loss during experiments of aluminium has led researchers to believe that there is substantial volatilisation of aluminium and aluminium oxides during high temperature reduction. The compound primarily believed to be responsible for the loss is gaseous Al_2O. [8]

$$Al_2O_3(s) + 2C(s) \Leftrightarrow Al_2O(g) + 2CO(g) \qquad (2.3\ l)$$

Al_2OC was found in cooler areas of the furnace, but not in the charge and also added to product loss. The following back reaction has been proposed to account for product loss. [5]

$$2Al(g,l) + CO(g) \Leftrightarrow Al_2OC(s) \qquad (2.3\ m)$$

This is not a reaction that assists in reduction but rather a relocation of aluminium within the system. Recovery of this material from the furnace may prove to be problematic.

Herstad [11] tried to produce the compound by reacting Al(l) and CO(g), but only produced the carbide Al_4C_3 and Al_4O_4C. By the addition of nitrogen into the CO stream, he did manage to produce a compound corresponding to the Al_2OC EDX spectra. When the nitrogen contaminant was removed only traces of the compound were found. A white fluffy condensate was however recovered from colder parts of the furnace, which produced the diffraction pattern of Al_2OC. The conclusion was drawn that it is not a thermodynamically stable compound in the system at temperatures of 1400 °C and above. The precipitation of this compound in the cooler areas of the furnace tends to indicate that further reactions can take place under different thermodynamic conditions throughout larger and more complicated furnace designs.

An aluminium and carbon soot containing 10 to 12 % aluminium was believed to form at low temperatures, which would account for material loss during experiments. Mabery [12] reported this in 1887 during experiments conducted to perfect the Cowles process.

The production of Al_2O has been proposed by various researches to account for product loss. [10-14] The phenomenon was confirmed by researchers at the Farben Works [13] during experiments on distillation of aluminium in alumina containers under vacuum.

$$Al_2O_3(s) + 2Si(l) \Leftrightarrow 2SiO(l,g) + Al_2O(g) \qquad (2.3\ n)$$

Hoch and Johnson [14] reported that Al_2O was formed between 1100 °C and 1500 °C while AlO was produced between 1500 °C and 1600 °C. Conclusive proof of the two products not was proven, but experiments carried out at Alcoa with the use of an arc furnace produced the Al_2O spectra. [8] This could have been from

reactions taking place between the aluminium and oxygen in the atmosphere at the exhaust from the furnace.

The following table gives a summary of the free energies of formation of the compounds that have been discussed. The temperature range for the reactions is 1500 - 2500 K [15 - 22]. All values and subsequent Gibbs free energies of formation are given in joules per mol.

Table 2.3 **Standard Free Energies of Formation of Important Species in the Al-C-O System**

Compound	Standard Free Energy of Formation (J/mol)
Al(g)	303,102 - 108.965 T
AlO(g)	40,764 - 58.200 T
AlO_2(g)	- 106,164 + 1.784 T
Al_2O(g)	- 196,839 - 39.042 T
Al_2O_2(g)	- 441,553 + 29.298 T
Al_2O_3(s)	- 1,680,432 + 322.786 T
Al_4O_4C(s)	- 2,340,048 + 464.894 T
Al_4C_3(s)	- 278,262 +103.361 T
CO(g)	- 118,673 - 83.495 T
CO_2(g)	- 396,721 +0.214 T

2.3.2 The Ternary Al-C-O System

2.3.2.1 Introduction

The ternary diagram is shown in Figure 2.3. The diagram depicting the reactions that take place and the compounds that are found in the areas labelled I, II, III and IV, are taken primarily from work by Motzfeldt [8,24] who has had most of his conclusions confirmed by later works as previously discussed. The work that has been done recently on low temperature reduction (1700 to 1800 °C) has concentrated on the condensed phases rather than any gaseous intermediate products. The gaseous products have been included but the concentrations of these products are believed to be very small in comparison with carbon monoxide and metallic gases produced. [5,8,16,23 - 25]

2.3.2.2 Gaseous Products

Gaseous products of carbothermic reduction are believed to comprise primarily the following species: Al, Al_2O, AlO and CO. The amount of carbon dioxide present can be assumed to be negligible and have for the purpose of this investigation been ignored. The carbide $Al_2C_2(g)$ has been reported by Chupka et al [26] to have a vapour pressure about 1000 times lower than Al(g) at the temperatures for these experiments, and have again been assumed to be insignificant as a gaseous product.

Investigations carried out to prove the existence of Al_2O and AlO and gain thermodynamic data have done little to show that these compounds have a substantantial concentration at lower temperatures. [8,13,14,26] These compounds are possibly however important steps in the reaction processes that take place.

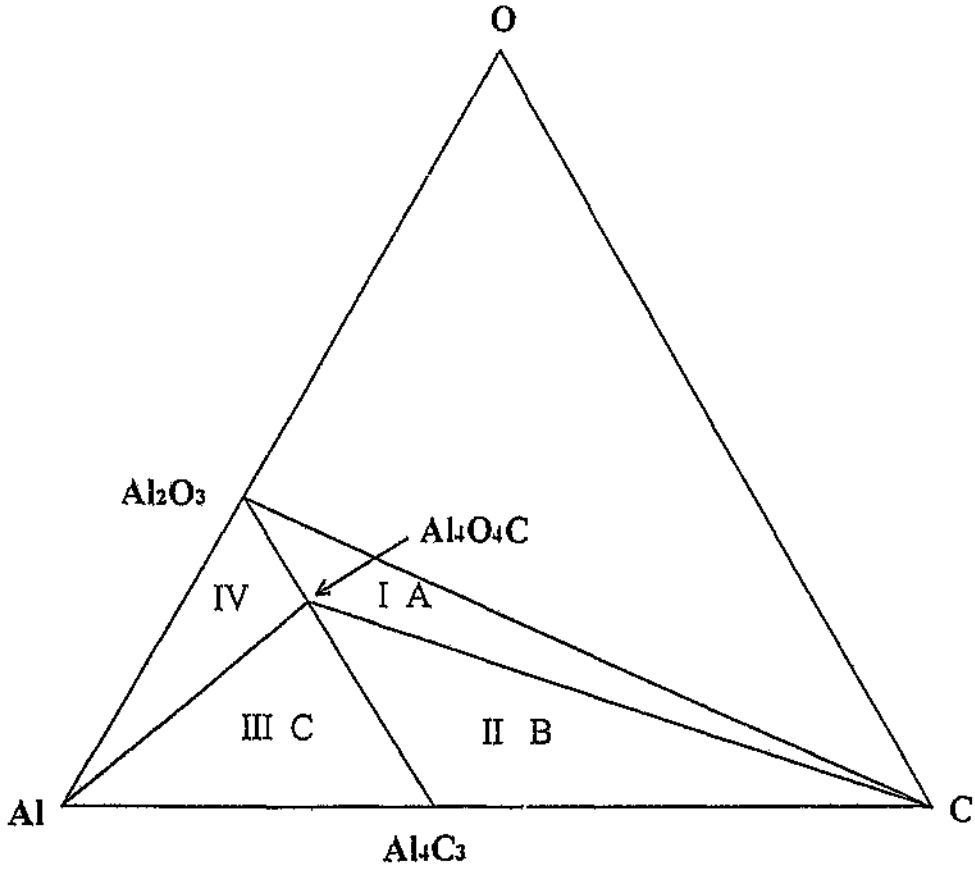


Figure 2.3 The Al-O-C Ternary Illustrating the Binary and Ternary Compounds in the Condensed Phase Regions at Temperatures Up to Approximately 1800 ^{0}C

2.3.2.3 Condensed Phases

Oxides, carbides and oxy-carbides that have been identified in the system are Al_4C_3, Al_4O_4C, Al_2O_3 and Al_2OC (believed to be a metastable compound brought about by nitrogen contamination). [8] Intermediate reactions that take place during the carbothermic reduction result in the production of these oxycarbides.

It is believed that the compound Al_2OC is formed in small amounts by the following reaction.

$$Al_4O_4C(s) + Al_4C_3(s) \Leftrightarrow 4Al_2OC(s) \qquad (2.3\ o)$$

As previously stated Motzfeldt [8] has concluded that the solid state precipitate is an unstable compound formed during rapid cooling of the compound and not an equilibrium situation. Herstad [11] has reported a solid solution of Al_2OC and AlN by mixing nitrogen in with the CO gas, but not by the pure reaction above.

2.3.2.4 Reactions in the Al-O-C Ternary

Motzfeldt [8,24] has extensively analysed the Al-O-C ternary presented above and the results are summarised below.

The system can be effectively divided into various triangles of which the corners are the various compounds that are formed. The equilibrium lines

between the compounds define certain equilibria that are found. The 3 main equilibrium areas of concern are shown in the diagram and explained below.

Small amounts of alumina can be directly reduced to carbon monoxide and aluminium, but most of the reduction takes place by the following

$$2Al_2O_3(s) + 3C(s) \Leftrightarrow Al_4O_4C(s) + 2CO(g) \qquad (2.3\ p)$$

$$\Delta G^\circ = 783{,}470 - 347.668T\ (J/mol)$$

In area A, the above reaction is predominant, and all gas phase compositions are set depending on the temperature of the system. Thus the partial pressures of CO, Al and Al_2O are fixed.

The following reaction takes place to a limited extent:

$$Al_4O_4C(s) + C(s) \Leftrightarrow 2Al_2O(g) + 2CO(g) \qquad (2.3\ q)$$

$$\Delta G^\circ = 1{,}709{,}024 - 709.968T$$

In area B, the following reactions can take place:

$$Al_4O_4C(s) + 6C(s) \Leftrightarrow Al_4C_3(s) + 4CO(g) \qquad (2.3\ r)$$

$$\Delta G^\circ = 1{,}587{,}094 - 695.513T$$

and to a much lesser extent the following 2 reactions:

$$Al_4O_4C(s) + C(s) \Leftrightarrow 2Al_2O(g) + 2CO(g) \qquad \textbf{(2.3 s)}$$

$$\Delta G^o = 1{,}709{,}024 - 709.968T$$

$$Al_4O_4C(s) + 3C(s) \Leftrightarrow 4Al(l) + 4CO(g) \qquad \textbf{(2.3 t)}$$

$$\Delta G^o = 3{,}184{,}156 - 1{,}456.634T$$

Again the phase rule dictates that the gas phase composition is set according to the system temperature.

In area C, the following reactions may take place:

$$Al_4O_4C(s) + Al_4C_3(s) \Leftrightarrow 8Al(l) + 4CO(g) \qquad \textbf{(2.3 u)}$$

$$\Delta G^o = 2{,}209{,}482 - 1{,}180.116T$$

$$Al_4O_4C(s) + 2Al(l) \Leftrightarrow 3Al_2O(g) + CO(g) \qquad \textbf{(2.3 v)}$$

$$\Delta G^o = 1{,}344{,}577 - 630.780T$$

$$Al(l) = Al(g) \qquad \textbf{(2.3 w)}$$

$$\Delta G^o = 303{,}102 - 108.965T$$

For triangles A and B, the primary component is CO, with the other two gaseous compounds Al(g) and $Al_2O(g)$ contributing less than 2%.

In area C the partial pressures of aluminium and Al_2O are approximately the same as that of CO. At temperatures below 1900°C where Al_4O_4C and Al_4C_3 are solid, the equilibrium pressure of Al(g) is considerable, which will result in some evaporation.

The compound $Al_2O(g)$ exists in area C, but does not occur in areas A or B.

There are thus two mechanisms of producing metallic aluminium from the alumina reactant employing carbon as reductant:

1) A reaction of the oxycarbide, Al_4O_4C, with aluminium carbide to form Al and CO, probably by the mechanism outlined below.

$$4Al_2O_3(s) + 6C(s) \Leftrightarrow 2Al_4O_4C(s) + 4CO(g) \qquad (2.3\ p)$$

$$Al_4O_4C(s) + 6C(s) \Leftrightarrow Al_4C_3(s) + 4CO(g) \qquad (2.3\ r)$$

$$Al_4O_4C(s) + Al_4C_3(s) \Leftrightarrow 8Al(l) + 4CO(g) \qquad (2.3\ u)$$

$$\mathbf{4Al_2O_3(s) + 12C(s) \Leftrightarrow 8Al(l) + 12CO(g)} \qquad (2.3\ d)$$

2) The aluminium carbide can also react with the alumina to form the aluminium and carbon monoxide.

Combining reactions ↄ u and 2.3 f the following occurs

$$3Al_4O_4C(s) + 3Al_4C_3(s) \Leftrightarrow 24Al(l) + 12CO(g) \qquad (2.3\ u)$$

$$4Al_2O_3(s) + Al_4C_3(s) \Leftrightarrow 3Al_4O_4C \qquad (2.3\ f)$$

$$4Al_2C_3(s) + 4Al_4C_3(s) = 24Al(l) + 12CO(g) \qquad (2.3\ v)$$

It should be noted that three times as much CO gas is produced per mol Al(l) by reaction sequence 1 as opposed to reaction sequence 2. Excess production of aluminium carbide or oxy-carbide will influence the CO production during the reaction sequence affecting ratios of products and pressure.

2.4 Carbothermic Reduction of Alumina in the Presence of a Metallic ⌣ lvent

2.4.1 Introduction

The pyrometallurgical carbothermic reduction of the alumina side-steps the need for a large amount of electrical energy by using carbon to reduce the oxide to its metallic form. The overall reaction for the carbothermic reduction of alumina is as follows:

$$Al_2O_3(s) + 3C(s) \Leftrightarrow 2Al(l) + 3CO(g) \qquad (2.4\ a)$$

There are various problems associated with this process, some of which are as follows:

Temperatures of 2200 °C are required to effect reduction, which results in various problems. The high temperatures that need to be reached cause multiple problems with respect to the choice of reactor and reactor lining used. The high temperatures also promote vaporisation of the aluminium and its compounds. The carbon content of the product is also very high due to the high solubility of the carbon in the metal at this temperature. Many oxycarbides and carbide phases containing aluminium will also form in competition with the aluminium formation. [5,23] Attaining and maintaining temperatures in excess of 2000 °C is also problematic.

At these high temperatures there are obvious problems associated with analysis of the resultant vapour and condensed products at room temperature, as they may only be thermodynamically stable at these temperatures. In the condensed phase system there is a lack of suboxides of alumina, but formation of carbides and oxycarbides does occur readily. Al_4C_3 is present but decompose at higher temperatures to graphite and a carbon saturated metal phase.

The Oxy-carbides that are predicted are Al_4O_4C and Al_2OC, although the presence (in a stable form) of the second oxy-carbide Al_2OC has not been proven conclusively. Aluminium tetraoxy-carbide (Al_4O_4C) has been widely reported and its thermochemical data is being acquired. [8,11,15-21] It should be noted that within the gas system, Al(g) is abundant, as is the vapour oxide Al_2O.

2.4.2 Use of Solvents

In order to reduce the high temperatures required, manipulation of thermodynamics is necessary. It is possible, by reducing the overall pressure of the reaction system, to force the equilibrium to the right and hence employ lower temperatures for similar yields. The use of a metallic solvent phase will reduce the concentration, or more accurately, the activity of the aluminium produced, assisting in the reduction process by again shifting the equilibrium to the right. The choice of solvent must incorporate various advantageous properties, some of which are:

Low vapour pressure at reaction temperature
High boiling point
High solubility of aluminium in liquid phase
Low propensity for aluminium to form compounds with the solvent
Environmentally friendly, and non toxic (or at least controllable)
Preferably cheap

The overall reaction will now be as follows:

$$Al_2O_3(s) + 3C(s) \Leftrightarrow 2\underline{Al} + 3CO(g) \qquad (2.4\ b)$$

The bar under the aluminium component ($\underline{Al}$) indicates that the aluminium metal is dissolved in a solvent.

2.4.3 Effect of Pressure

If the pressure is lowered to a value that will affect the formation and hence release of CO gas, the reaction will be forced to proceed to the right. System pressures in the region of 10 kPa will be sufficient to remove the carbon monoxide from the vicinity of the reaction rapidly [16], and shift the equilibrium position. The temperature range that the process and experimentation will be carried out under can now effectively be lowered to a value of approximately 1700 °C.

Tests carried out using silicon, iron, nickel, copper and tin[27-33] have given results indicating that interactions between the first four solvents and aluminium occur. This makes separation of aluminium from the solvent metal difficult. There is very little interaction between tin and aluminium so separation has been made possible by liquid-liquid gravity separation or fractional distillation. [28]

The use of silicon [27-30] and iron [29-32] as solvents for aluminium has been tested widely. There were and are still quite a few problems associated with the carbide formation from these two solvents. SiC and Fe_3C are formed quite readily with the excess carbon in the system. Even if there is no excess of carbon in the charge, the free portions of the iron and silicon solvents react with the carbon in the charge. This results in a reduction of the amount of carbon available to react with the alumina charge. The use of SiC [37] as a reductant is possible, but the temperature required to effect the decomposition of the silicon carbide is around 2830 K. This temperature is beyond the scope of this investigation, and has not been considered.

The reactions predicted for SiC and Al_4C_3 are shown below. It was assumed here that there was sufficient excess carbon in the system to produce Al_4C_3 and only the two reactants were considered.

$$Al_4C_3 + SiC \Leftrightarrow Al_4SiC_4 \qquad (2.4\ c)$$

or

$$Al_4C_3 + 2SiC \Leftrightarrow Al_4Si_2C_5 \qquad (2.4\ d)$$

$2Al_4C_3.SiC$ has also been identified as an intermediate phase [28] by reacting the following

$$2Al_4C_3 + SiC = 2Al_4C_3.SiC \qquad (2.4\ e)$$

The intermediate alloys are not final products in the processing of the alumina but stepping stones to a final product. Research is being carried out to try and find ways to process raw materials with impurities that will minimise wastage of valuable material. Silicon is an impurity that is always present in the ore deposits with alumina, and is very difficult to separate from alumina. Economical processing of the contaminated ore will increase the viable deposits of alumina substantially. Therefore attempts to try and find new recovery methods to process ore deposits with higher than normal silicon contents, should be pursued.

The effect and form of the products in the iron rich region of the Fe-Al-C is generally unknown. Large discrepancies in the solidus and liquidus curves have been noted, and work is still being carried out to try and identify the regions accurately. [32]

2.4.4 Related Studies

Much of the theory for the current project was taken from work by Frank, Finn and Elliot. [16] A summary of their conclusions makes up the rest of the section.

Composition ratios of the reactants were tested, the results indicating that the rate of reduction of alumina is not affected by the ratio of alumina to carbon. The type of alumina used, i.e. porous or fused, made no apparent difference to the rate of reduction of the alumina either. The particle porosity had no discernible affect on the rate of the reaction, neither did the size of the alumina particles. The time constant τ, is not affected by the carbon to oxygen ratio in the charge.

Further, the driving force behind the reaction is the activity of the aluminium in the solvent metal bath, and the carbon monoxide partial pressure. The use of copper as a solvent rather than tin results in the rate being about 70 % faster. The cause of this phenomenon is unknown and further research is to be performed by the authors.

The rate of the reaction is heavily dependent on the temperature of the system, as can be seen in Figure 2.4. The pressure of the reaction system also has a substantial affect on the reaction rate. From Figure 2.5 it can be shown that as the pressure is reduced from 0.20 atm. to 0.08 atm, the pseudo first order time constant drops from 158 minutes to 23.

The researchers also made the observation that the pronounced negative deviation from ideality in the Al-Cu system, resulted in the initial reaction rate being far faster than that for the Al-Sn system. When the initial concentration

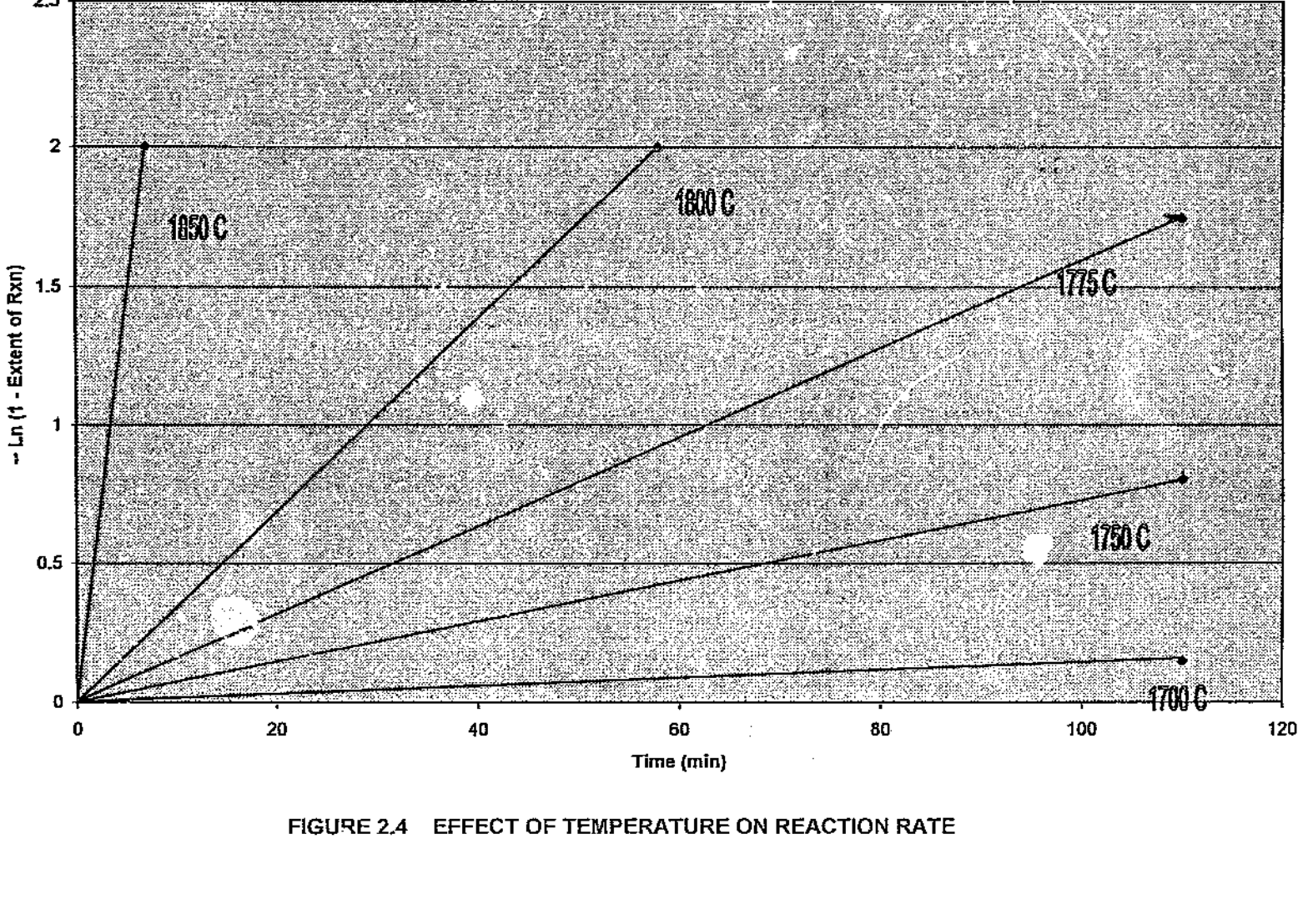


FIGURE 2.4 EFFECT OF TEMPERATURE ON REACTION RATE

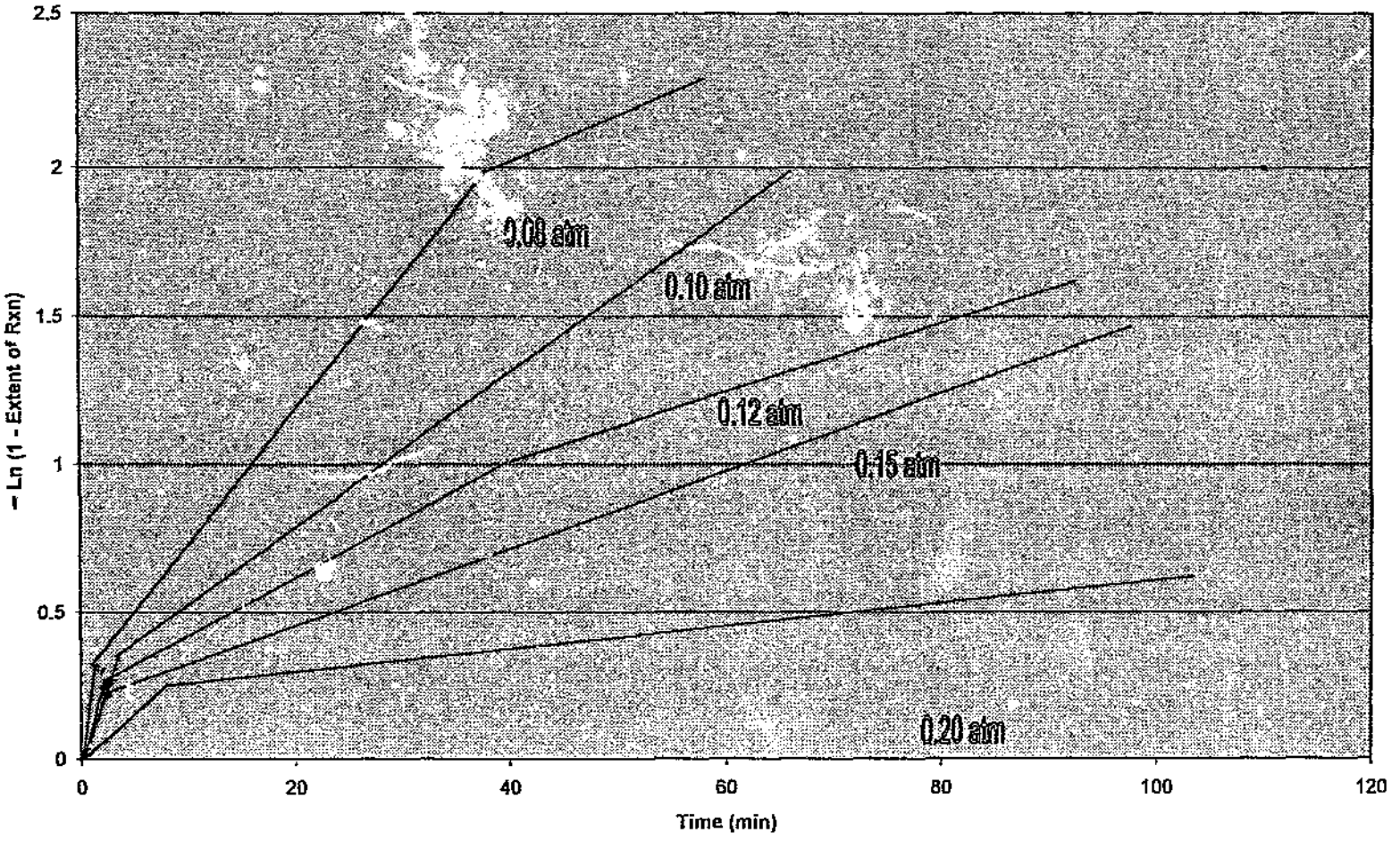


Figure 2.5 EFFECT OF PRESSURE ON REACTION RATE

of aluminium in the solvent bath was set at 1 wt%, the activity of the aluminium was approximately 150 times larger in the tin bath than in the copper bath. The time constants however only differed by a factor of 3. The suggested explanation for this difference could be that the initial rate in the experiment with copper as the solvent is much higher.

In systems where there is a significant amount of aluminium in the initial charge, various reactions may take place before any reduction of alumina is possible. The product that is most likely is Al_4C_3, which will in turn react with alumina and carbon. The reaction that will then take place is as follows.

$$2Al_2O_3(s) + 9\,C(s) \Leftrightarrow Al_4C_3(s) + 6CO(g) \qquad (2.4\ f)$$

The production of Al_4O_4C will in turn take place when temperatures and equilibrium conditions permit.

The observation has been made that the volume of carbon monoxide released during the production of Al_4C_3 per mole of Al_2O_3, is the same as for reaction

$$Al_2O_3(s) + 3C(s) \Leftrightarrow 2\underline{Al} + 3CO(g) \qquad (2.4\ g)$$

The rate of reduction of alumina by (2.4 f) would be faster due to the lower activation energy required for the reaction producing Al_4C_3. They have claimed that this alternate reaction would account for the higher rate of evolution of carbon monoxide in their experiments with an initial aluminium concentration of 10 to 12 wt%.

The terminal carbon solubility in aluminium has been determined to be 1.96% and the terminal carbon solubility in iron is 22.5%. The formation of aluminium carbide is strong in the system under analysis, but at temperatures

above 2156°C it decomposes peritectically to yield solid carbon and aluminium saturated with about 20 % carbon.

2.5 Effect of Highly Solvating Metallic Compounds

From the paper "Thermodynamic Activity of Magnesium in Several Highly-Solvating Liquid Alloys" by Eckert, Erwin and Smith [34], various conclusions have been drawn with respect to solvating metals. Although this has no direct bearing on the project, various parallels can be drawn between the compounds in the above paper, and possible effects of aluminium on solvents used.

During carbothermic reduction of MgO in the presence of lead as a solvent, it is found that there is a large negative deviation from Raoult's law due to the extreme solvation caused by the formation of intermetallic compounds in solution. This can be represented mathematically by what is called a "chemical" or "Dolezalek" theory. This is when a binary mixture is regarded as a multicomponent mixture of both metal atoms plus one or more compounds. For example in the Mg-Pb system there exist four species: Mg, Pb, MgPb and Mg_2Pb. The activity values measured are those of the monomeric species only, i.e. the overall or measured chemical potential μ_{Mg} is equal to that for monomeric magnesium, μ_{Mgl}.

$$\mu_{Mgl} = \mu_{Mg} \qquad (2.5\ a)$$

or in terms of the apparent mole fraction χ_{Mg}

$$z_{Mg}\, a_{Mg} = \chi_{Mg}\, \gamma_{Mg} \qquad (2.5\ b)$$

μ_{Mg} = measure chemical potential

μ_{Mg1} = chemical potential of monomeric magnesium

χ_{Mg} = apparent mole fraction

γ_{Mg} = usual apparent activity coefficient of magnesium

z_{Mg} = true mole fraction of monomeric Mg

α_{Mg} = true activity coefficient of Mg

From the following equations:

$$Mg + Pb \overset{K1}{\Leftrightarrow} MgPb \qquad (2.5\ c)$$

$$2Mg + Pb \overset{K2}{\Leftrightarrow} Mg_2Pb \qquad (2.5\ d)$$

two equilibria can be formed:

$$K_1 = \frac{z_{MgPb}\ \alpha_{MgPb}}{z_{Mg}\, z_{Pb}\, \alpha_{Mg}\, \alpha_{Pb}} \qquad (2.5\ e)$$

$$K_2 = \frac{z_{Mg_2Pb}}{z^2_{Mg}\ z_{Pb}} \frac{\alpha_{Mg_2Pb}}{\alpha^2_{Mg}\ \alpha_{Pb}} \qquad (2.5\ f)$$

The following independent stoichiometric relationships exist:

$$z_{Mg} + z_{Pb} + z_{MgPb} + z_{Mg2Pb} = 1 \qquad (2.5\ g)$$

$$x_{Mg} = \frac{z_{Mg} + z_{MgPb} + 2\,z_{Mg_2Pb}}{z_{Mg} + z_{Pb} + 2\,Z_{MgPb} + 3\,z_{Mg_2Pb}} \qquad (2.5\ h)$$

The limiting assumption is made that all true activity coefficients are unity. The assumption is made that the chemical forces are much stronger than the physical forces. This assumption is valid for this case. For the case of aluminium, no strong reactions take place between any of the alloys that have been used.

The four equations above may then be solved to give resulting expressions in terms of activity or activity coefficients of both components, without any separate Gibbs-Duhem integration.

The effect of different solvents can be shown, by plotting the activity coefficients of the metals, against their mole fractions. Figure 2.6 gives a comparative analysis of the experimental activity coefficients for magnesium in various solvent metals at 850 °C.[34]

Tables 2.4 to 2.6 below detail some information at various temperatures of activity coefficients of aluminium in various solvents.[17,18] The temperatures of the different solvents differ by substantial amounts, but even with the temperature difference, it can be seen that the behaviour of the solvents is heavily influenced by their deviations from ideality. The solvents in decreasing order are nickel having the greatest negative deviation followed by iron and copper. Tin has a positive deviation from ideality and has not been included.

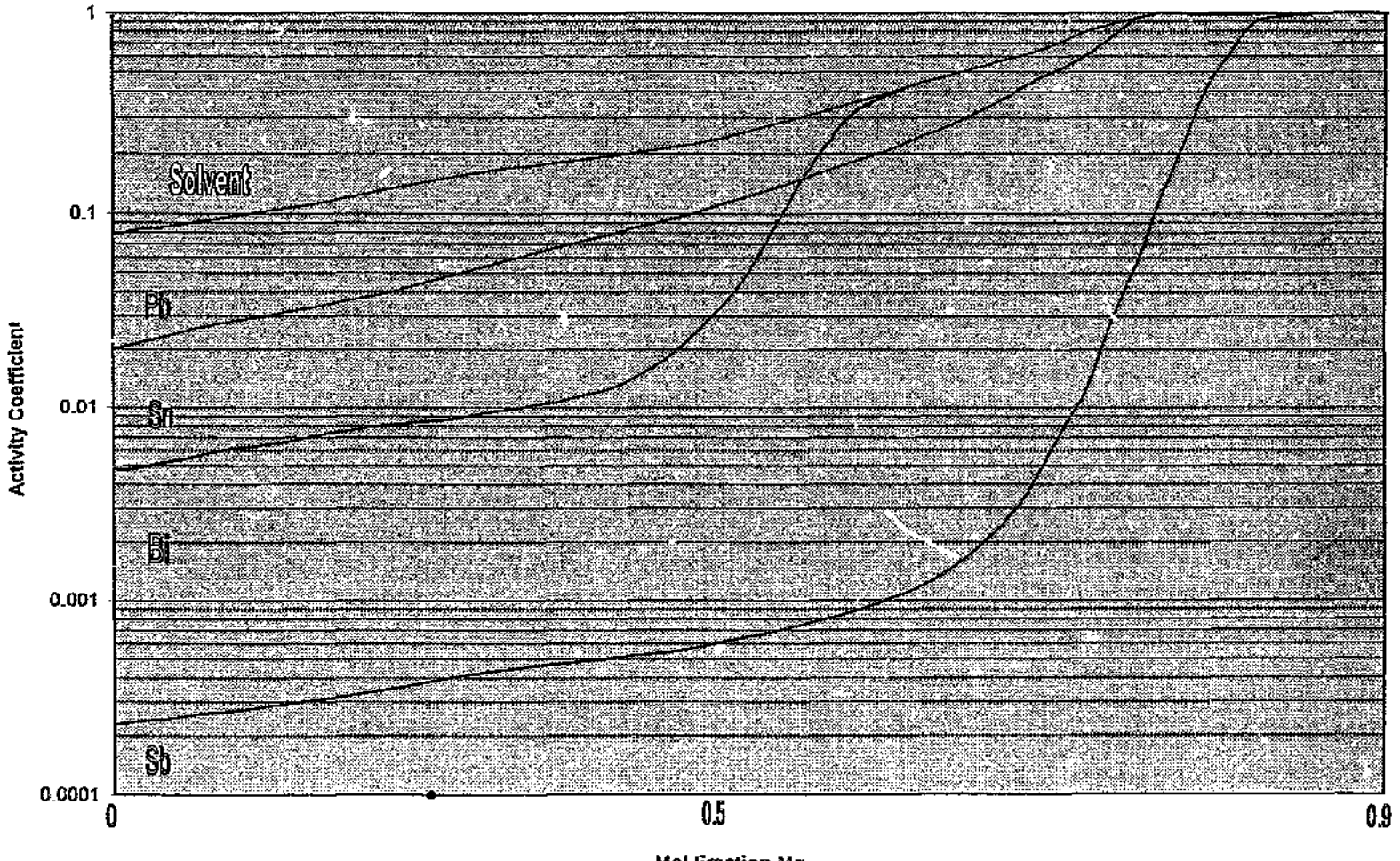


Figure 2.6 ACTIVITY COEFFICIENTS OF Mg IN VARIOUS SOLVENTS

Table 2.4 Activity Coefficient of Aluminium in Copper-Aluminium System At 1373K

x_{Al}	γ_{Al}
0.3	0.095
0.2	0.029
0.1	0.008
0.0	0.002

Table 2.5 Activity Coefficient of Aluminium in Iron-Aluminium System At 1873K

x_{Al}	γ_{Al}
0.3	0.021
0.2	0.007
0.1	0.002
0.0	0.00001

Table 2.6 Activity Coefficient of Aluminium in Nickel-Aluminium System At 1273K

x_{Al}	γ_{Al}
0.275	0.000158
0.143	0.000124
0.100	0.0000314
0.050	0.0000061
0.000	0.0000011

In a dilute solution, Henrys law i. obeyed. which is limiting under certain conditions. For the system we are considering, it is reasonable to assume that aluminium will obey Henrys law. However there is no data on Henrian activity coefficients (constant) of aluminium in the solvent metals discussed except in the Al-Fe-C. The data for this system is illustrated in **Figure 2.7** in terms of Henrian constant of aluminium as a function of temperature. [15,17,18,31,35]

This data is only however valid for the Al-C-Fe system, no accurate data at appropriate temperatures could be found for any of the other solvents. The lowering of the Henrian constant as the temperature decreases is notable.

2.6 The Toth Thermal Reduction Process

The process is named after its inventor Charles Toth and is a process for producing aluminium from clay. The basic material is not a very expensive material, such as clay, which is dried and then transformed in the presence of carbon and chlorine, into aluminium chloride. This is then purified and reduced to aluminium by metallic manganese. The drop in electrical energy consumption of the Toth process is however countered by an increase in carbon use

The steps involved are as follows:

$$Al_2O_3(\text{in clay}) + 3C + 3Cl_2 \Leftrightarrow 2AlCl_3 + 3CO \quad (925^{\circ}C) \qquad (2.6\ a)$$

$$\Delta G^{\circ} = 140{,}058 - 310.989T$$

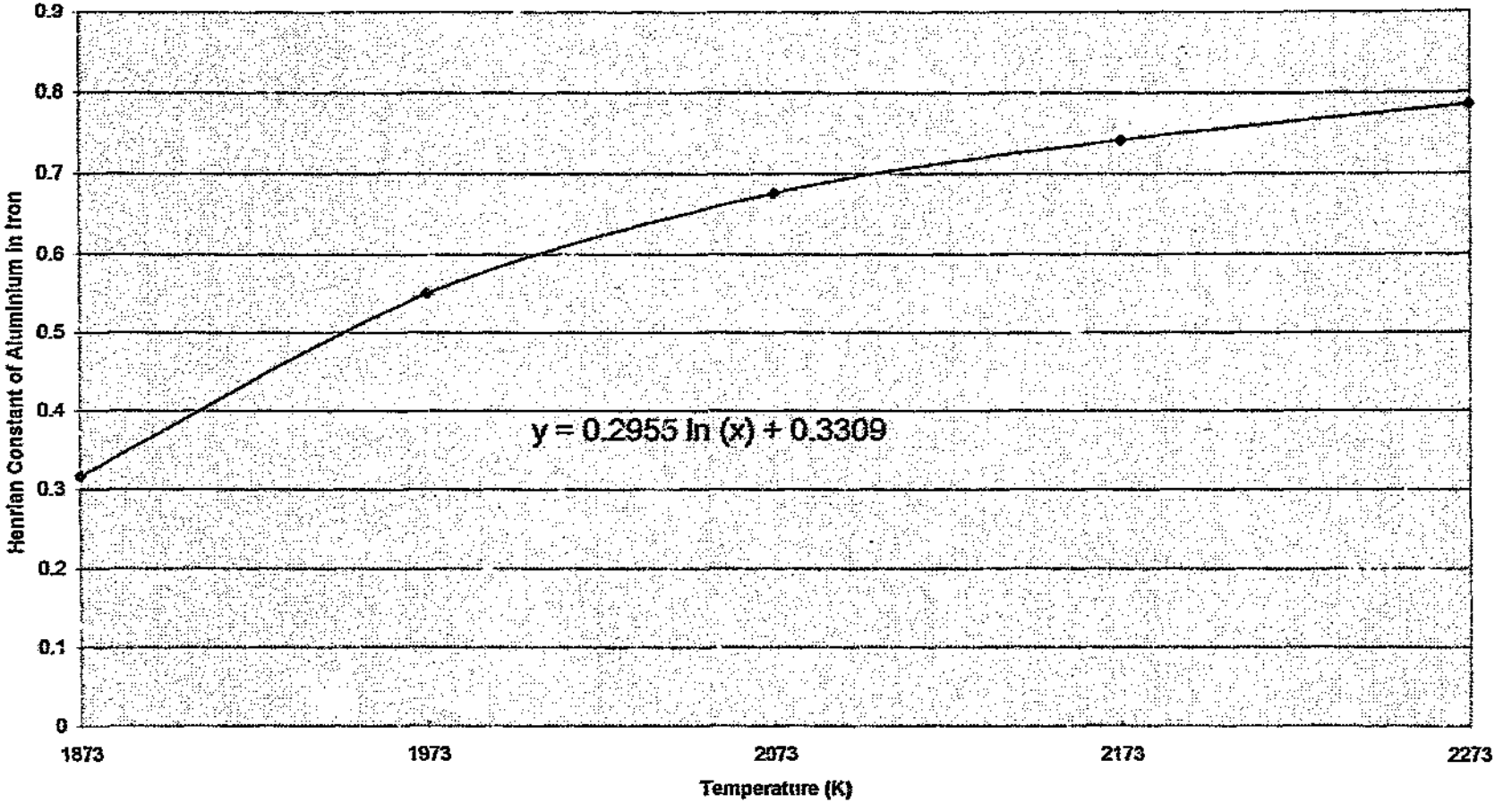


Figure 2.7 HENRIAN CONSTANT OF ALUMINIUM IN Fe-C-Al SYSTEM

$$2AlCl_3 + 3Mn \Leftrightarrow 2Al + 3MnCl_2 \quad (230°C, 4\ torr) \qquad (2.6\ b)$$

$$\Delta G^o = -230{,}455 + 247.192T$$

$$2MnCl_2 + O_2 \Leftrightarrow 2MnO + 2Cl_2 \quad (600°C) \qquad (2.6\ c)$$

$$\Delta G^o = 178{,}741 - 102.760T$$

$$MnO + C \Leftrightarrow Mn + CO \qquad (2.6\ d)$$

$$\Delta G^o = 275{,}984 - 162.830T$$

The overall reaction being

$$2Al_2O_3(\text{in clay}) + 3O_2 + 12C \Leftrightarrow 4Al + 12CO \qquad (2.6\ e)$$

This is therefor· in indirect carbothermal reduction process. In order to get the required products, the reaction would have to take place at a relatively low temperature, which would slow down the rate of the reaction quite extensively.

Toth's original thoughts were that a high temperature process was required in the region of 1300°C. [36] Later, this temperature was lowered to 230 to 300 degrees centigrade to maximise yield values.

Levels of manganese in the product must also be controlled which may be difficult as solid reactants are to be used in the reaction. This may not be a major hindrance as manganese contents of one percent or less can be sold as a manganese-aluminium alloy. [3,37] Higher purity aluminium would have to be sent through a purification process to remove the manganese.

The purification processes involved present a range of problems that require attention. The recovery of the manganese may however be costly. When cheaper raw materials are used, various impurities are removed by the chlorination process. Silica and Na_2O do not present a serious problem, but impurities such as Fe_2O_3 and TiO_2, comprising about 8 % of the feed material metal content, consume large amounts of chlorine. Moisture is another impurity that must be removed, as it had negative effects on the rate of the reaction. [37]

2.7 The Mitsui Alumina Blast Furnace Process

In Japan, high electricity costs have forced aluminium production to be reduced. Dr Kuwahara [38] developed a process that would need little or no electricity to keep the process continuing independently.

The process has the following basic steps.

1 To mix alumina and silica containing ores in powder form with coal powder, press the mixture into briquettes and coke them in a non oxidising atmosphere. Low grade ores such as clays and shale rock with as little as 35% aluminium content can be used.

2 By heating to 2000°C or more, the ore is reduced and an Al-Si alloy forms in the sump of the blast furnace. [29] This temperature is believed to be too high to occur in a standard blast furnace, unfortunately the authors do not expand on this particular issue. The composition of the alloy is: 50-60% aluminium, 20-25% iron and 10-15% silicon.

3 Injection of liquid lead into the alloy to "absorb" the aluminium. Subsequent cooling in a holding furnace separates the melt into a lead and an aluminium layer, the latter containing about 1% lead.

4 Further refining of the product takes place by fractional evaporation of lead. An aluminium purity of 99.5 - 99.7% is easily obtained and may reach 99.9%. Residual lead in the aluminium is 0.001%.

Expensive cell linings are required as the temperatures reached are very high and the conditions harsh.

The quantities of carbon monoxide produced could be burned and used to produce any electricity that is needed by the process. The conversion of bauxite ores into alumina is not required for this process to run either.

3 EXPERIMENTAL DESIGN AND PROCEDURE

3.1 Experimental Set-up

The furnace used for the experiments was a Carbolite PVT18/60 with a vertical work tube. The maximum temperature of the furnace is limited to 1750°C, 1700°C is the recommended maximum continuous running temperature. Temperature measurement control was effected by a pair of type "B" thermocouples inserted near the centre of the work tube.

The temperature was controlled by a "Eurotherm Microprocessor Based 818 PID 3 Term Programme / Controller" with a digital readout and set-point. The power control was through a solid state relay with a nominal power output of 6 kW.

The work tube dimensions are 55mm ID, 65 mm OD and 1200m long. The work tube was made from recrystalised alumina and all seals were gas tight around the work tube. The work chamber (hot zone) is approximately 200 mm long and is situated in the middle of the insulating case. The work chamber is situated approximately two fifths from the bottom of the full length of the work tube. The additional length that sticks out the top of the insulation casing is used to house a heat shield, which hangs from the top of the work tube.

The temperature indicated by the furnace control system, was externally checked and found to be within 2 degrees centigrade of the external control thermocouple.

The pedestal used to insert the crucible into the work chamber comprised a motor driven platform attached to a set of Teflon knife bellows, manufactured

by Fabflex (Pty) Ltd. The bellows used showed no physical deterioration over time after exposure to high temperatures and aggressive environmental conditions. The bellows were however physically very strong, and did not compress or expand very easily and were therefore contained in a slid , cage. The seals used to ensure the vacuum, were manufactured from viton, as the rubber seals initially used tended to perish very quickly.

A vacuum pump was connected to the furnace with glass taps used to seal the system from the environment. The internal system pressure was measured by a Druck pressure transducer, type PTX 600. The output from the transducer was a 4 to 20 mA output, related directly to the pressure of the system, i.e. a 4mA output would represent a system pressure of 0 kPa, up to a 20m ut for a system pressure of 100kPa. The mA output from the transducer onverted via an A/D converter card in a PC, to a digita ignal. This digital signal (or system pressure) was recorded on a dedicated PC approximately once every second.

3.2 The Gas Train

The system atmosphere was regulated through a flow meter. It was further purified by passing the gas through a desiccator and a deoxidation chamber where necessary to remove any contaminants that would adversely affect the experiment. The purging gas volume flow rate was set at approximately 5 litres a minute. The specific gases used were ultra high purity argon and a high purity carbon monoxide.

The system integrity was checked before every experiment was carried out, by sealing the system and evacuating. The pressure change of the system was

recorded and any pressure rise indicated an unsound system, which would be checked again until a stable vacuum was achieved.

3.3 Charge Preparation

The charge mixture was prepared using stoichiometric amounts of alumina and graphite, according to Reaction 2.3 d. The reaction charge was prepared in batches of approximately 100 grams, and each constituent weighed to an accuracy of 1 milligram. A 1% initial weight percent of aluminium was added to the mixture to assist in reduction.

No screening of the charge was carried out, but the carbon and alumina mixture was always -50μ after mixing. The aluminium metal particles were larger and slightly elongated in their supplied state, and were not subjected to any size reduction or size classification. All produced batches were stored in a desiccator until required. The purity of each of the components is given in **Table 3.1.**

3.4 The Crucible

The crucible in which the charge was contained, was manufactured from ECS grade graphite rods supplied by EMSA (Pty) Ltd. The purity of the graphite was quoted at greater than 99.0% carbon. The graphite rod supplied was machined to 40mm OD, 36mm ID and an internal depth of 55mm. The base thickness was 8 mm.

The empty crucible was weighed to the nearest milligram before any additions were made to the crucible. The solvent and reactants were then added in separate steps to the crucible and weighed after each addition.

3.5 Experimental Procedure

After initial weighing of the crucible, the solvent was added, and the crucible was again weighed to the nearest milligram. The carbon, alumina and aluminium mixture added, and the crucible was weighed for a final time.

Approximately 1 mol of solvent was used in each of the experiments. The charge was either mixed with the solid solvent inside the crucible, or allowed to rest on top of the solvent. The mass of charge varied from 2 grams to 5 grams, with the bulk of the experiments having approximately 3 grams of charge mixture.

The crucible was placed onto the alumina tube support, which was attached to the platform. The platform was slowly raised up towards the work tube enough to allow for the seal to be clamped in place. The system was subsequently evacuated and refilled with argon. When pressure reached atmospheric, the system was purged with argon for 30 minutes. The system was then again evacuated and carbon monoxide was allowed into the system.

The sample was then slowly raised into the hot zone of the furnace while continually purging the system with carbon monoxide. The system was allowed to purge for at least 30 minutes during the final stage. The crucible was raised very slowly towards the hot zone as the crucible and its contents acted as a very effective heat sink. By raising the crucible into the hot zone too quickly, the

resultant thermal shock to the alumina work tube would have been, and unfortunately proved to be, more than sufficient to crack the tube.

When the crucible reached the bottom of the hot zone, it was raised in one step completely into the centre of the work tube hot zone or work chamber. When this was completed, the system pressure was lowered to a pressure of about 9 kPa and then isolated from the vacuum pump. The pressure of the system was recorded on the PC for the duration of the experiment.

The mass of the crucible and the resultant solvent pellet were measured after the experiment. Any residual charge mixture was collected and sent for chemical analysis and ash analysis. The metal solvent pellet that was formed from the reactants and solvent charge was analysed for carbon, the respective solvent metal used, aluminium, various impurities, and in several cases, for oxygen as well.

3.6 Chemical Analysis

Sample preparation of the pellet for analysis, was performed by taking drillings from the pellet produced from the experiment. It was assumed that the aluminium was distributed evenly through out the solvent matrix and that no areas of high aluminium concentration existed. Despite this assumption multiple holes were drilled from different areas of the solvent pellet to try and get a representative sample.

To avoid contamination, the drillings were taken without the use of drilling lubrication. In addition the drill bit was not allowed to overheat which could also result in contamination of the sample. The drill bits were cleaned after

each sample was taken, in addition each solvent type had its own drill bit to prevent sample contamination.

Analysis of the results was conducted using various methods. Analysis of the products was performed by Mintek's Analytical Department, using wet chemistry methods. The results were presented as a mass percentage of the total sample presented to them. EDX analysis was performed at Wits University with School of Process and Materials Engineering's equipment. SEM/EDX analysis was carried out in the Biology Department at Wits University and the School of Process Engineering. Ash analysis was performed at Wits Campus according to British Standards Institution Format 1016 Part 3 (1957).

Table 3.1 Details of the Impurity Levels of the Materials Used in the Experiments

Sample	Impurity
Alumina Assay 98.5%	Chloride 0.02% Sulphate 0.05% Iron 0.03% Arsenic 0.001%
Aluminium Metal Powder Assay 95%	Acid-Insoluble matter and greasing substances 5% Alkalis 0.5%
Copper Metal Powder	Lead 0.005% Iron 0.005% Arsenic 0.001%
Iron Fine Powder Assay 99%	Carbon 0.01% Phosphorus and Sulphur 0.015%

Nickel Metal Pellets Assay 99.9%	Cobalt 0.005% Iron 0.1%
Graphite Powder Assay 99%	
Tin Fine Powder Assay 99.5%	
Vacuum Grease	Unknown composition
Carbon Monoxide Gas Assay >99.0%	$O_2 \leq 900$ vpm $N_2 \leq 4{,}000$ vpm $H_2 \leq 3{,}000$ vpm HC ≤ 100 vpm
Argon Gas UHP > 99.999 %	$O_2 \leq 2$ ppm $H_2O \leq 3$ ppm $N_2 \leq 5$ ppm $CO_2 + CO \leq 1$ ppm $CH_4 \leq 1$ ppm
Graphite Crucibles Grade ECS	> 99.0 % Purity
Alumina Work Tube Al_2O_3 > 99.8%	SiO_2 0.080% MgO 0.035% Na_2O 0.008% CaO 0.040% Fe_2O_3 0.025% Cr_2O_3 < 0.003% TiO_2 0.004% B_2O_3 < 0.001% K_2O < 0.001%

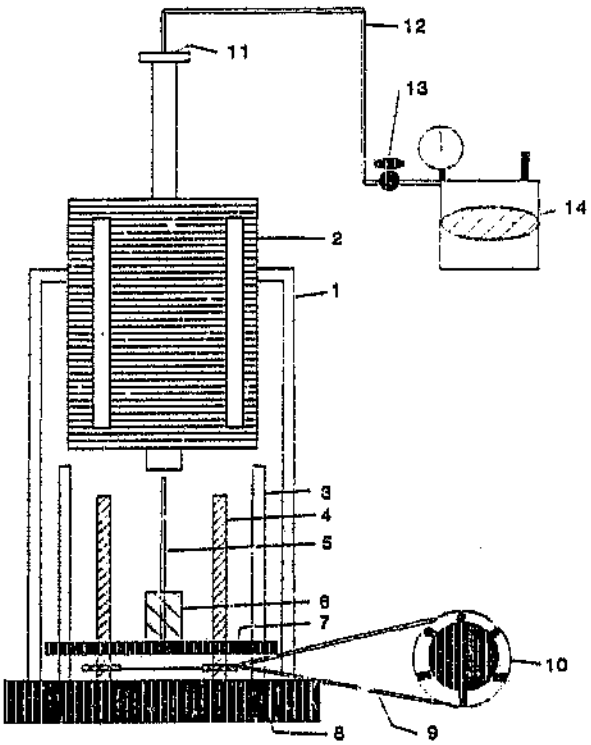


Figure 3.1 Furnace Set-up

Index

1 Furnace Support

2 Furnace Case and Insulating Material Containing the Heating Elements

3 Pedestal Alignment Support Rods	4 Screwed Rod
5 Alumina Rod (Crucible support)	6 Bellows + Gas Train Inlet Coupling
7 Pedestal	8 Furnace Foundation
9 Drive Train and Gears	10 Pedestal Motor
11 Work Tube	12 Gas Train and Copper Pipe
13 Pressure Transducer	14 Vacuum Pump

4 RESULTS AND DISCUSSION

4.1 Results

Detailed below are results from the experimental runs performed. Failed experiments due to worktube breakages or sudden vacuum losses were not included in the table and were not used in data evaluations.

Table 4.1 Experimental Results on Aluminium Recoveries After a Reaction Period of 100 Minutes

No.	Mass of Al Recovered / gram of Al Charged (g)	Percentage Al Recovered (%)	Vacuum	Temperature (K)	Solvent
1	0.202	51.66	Yes	1973	Cu
2	0.343	87.72	Yes	1983	Cu
3	0.350	89.51	Yes	1973	Cu
4	0.032	8.13	Yes	1953	Cu
5	0.038	9.67	Yes	1973	Sn
6	0.047	11.92	Yes	1978	Sn
7	0.029	7.42	Yes	1983	Sn
8	0.011	2.74	Yes	1963	Sn
9	0.028	7.24	Yes	1978	Sn
10	0.008	1.99	Yes	1923	Sn
11	0.172	43.99	Yes	1978	Fe
12	0.116	29.62	Yes	1973	Fe
13	0.365	93.35	Yes	1973	Fe
14	0.048	12.28	Yes	1973	Fe

15	0.044	11.25	Yes	1943	Fe
16	0.081	6.14	Yes	1953	Fe
17	0.245	62.66	Yes	1973	Fe
18	0.200	51.15	Yes	1973	Fe
19	0.024	38.62	Yes	1973	Fe
20	0.151	20.72	No	1973	Fe
21	0.097	24.81	No	1973	Fe
22	0.156	39.90	Yes	1973	Fe
23	0.175	44.76	Yes	1973	Fe
24	0.156	39.90	Yes	1973	Fe
25	0.119	30.43	Yes	1973	Fe
26	0.162	41.48	Yes	1943	Fe/Ni
27	0.444	113.55	Yes	1973	Ni
28	0.031	8.03	Yes	1973	Ni
29	0.213	54.48	Yes	1973	Ni
30	0.211	53.96	Yes	1943	Ni
31	0.153	39.13	Yes	1973	Ni
32	0.325	83.12	Yes	1973	Ni
33	0.264	67.52	Yes	1973	Ni
34	0.157	40.15	Yes	1973	Ni
35	0.296	75.70	Yes	1973	Ni
36	0.200	51.15	Yes	1973	Ni
37	0.199	50.90	Yes	1953	Ni
38	0.174	44.50	Yes	1953	Ni
39	0.166	42.46	Yes	1953	Ni
40	0.161	41.18	Yes	1943	Ni
41	0.082	24.60	No	1963	Ni
42	0.039	11.31	No	1973	Ni

4.2 Copper Solvent

Copper has been used before as a solvent [16], in an attempt to produce a viable operation. The results have indicated a definite tendency for copper to be a good solvent for aluminium. It is believed that small amounts of Al_4O_4C are produced at the temperatures tested, the low percentages (<120 ppm) of oxygen found in the alloy sample after the experiments seem to validate this. No copper oxide compounds could be identified from EDX analysis. The low oxygen content recorded can possibly be attributed to small amounts of Al_4O_4C present, or contamination of the solvent with unreacted alumina, however microscope work performed showed no inclusions of solid particles of alumina.

The copper-aluminium system does not have an exceptionally large negative deviation from ideality, but a significant number of intermediate phases form as a function of composition and temperature as indicated by the binary diagram.

Oxy-carbides were found to be negligible, but the carbide Al_4C_3 was identified in the system at approximately 0.2 wt% of the alloy weight. The small amount of carbide formed was believed to originate from the reaction of the graphite and the aluminium initially charged. This was the conclusion reached as the mass loss of carbon from the crucible was found to be less than 0.01% after the test runs. The mass loss was attributed to volatilisation of impurities within the graphite in the crucible.

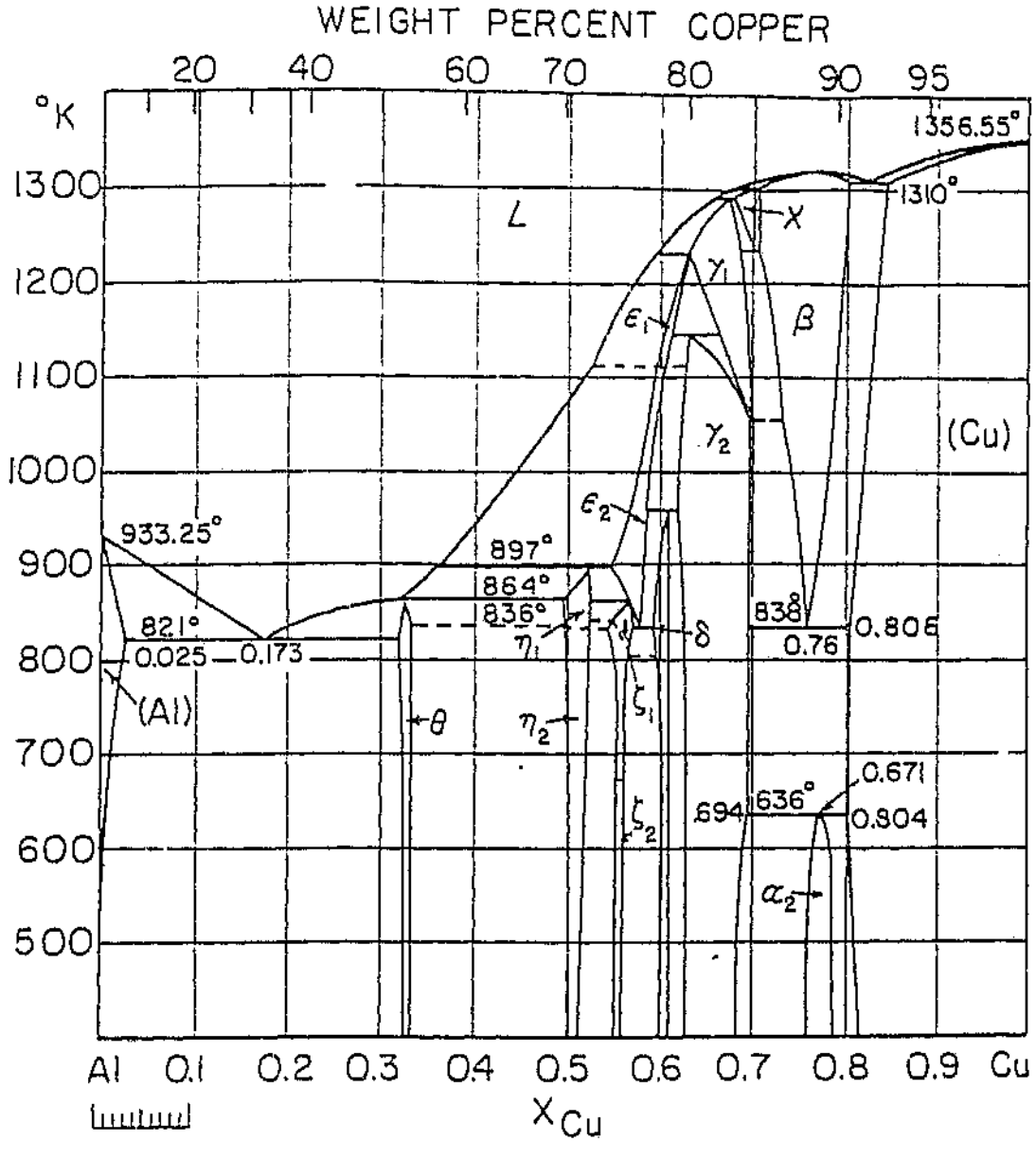


Figure 4.1 Al - Cu Binary System

4.3 Tin Solvent

The tin solvent did not produce very good results. The recovery was very low, but reduction of alumina did however take place in small amounts. The rate of Al formation in the test was slow, with a large percentage of the charge remaining unreacted. Generally 60 to 70 % of the charged Al_2O_3 remained unreacted and was recovered after the experiment.

It is believed that the residual charge left did not undergo any reactions, nor form substantial amounts of gaseous products. There is a positive deviation from ideality in the Al-Sn system, resulting in low percentages of aluminium dissolving in the tin for a given activity value. The amount of aluminium initially charged to the crucible, could set the initial activity of the aluminium in the solvent to prohibitive level, which could start to limit any further reactions of alumina and carbon. This was discussed in section 2.4.4.

Thermodynamics of the system predicts small amounts of gaseous aluminium and Al_2O, but analysis of the residual charge showed that total loss of material (from the reactants and crucible) was a less than 10% during the test runs.

The amount of oxygen reported in the final product was less than about 400 ppm. The oxygen content is slightly higher than reported for copper. A weak tin oxide formation may be present, but the stability of alumina negates this option. The more likely reason for the higher oxygen content, is a residual percentage of unreacted alumina in the product, in the form of solid particulate inclusions in the solvent.

No noticeable amounts of aluminium carbide or Al_4O_4C were reported during any analysis of the tin pellet.

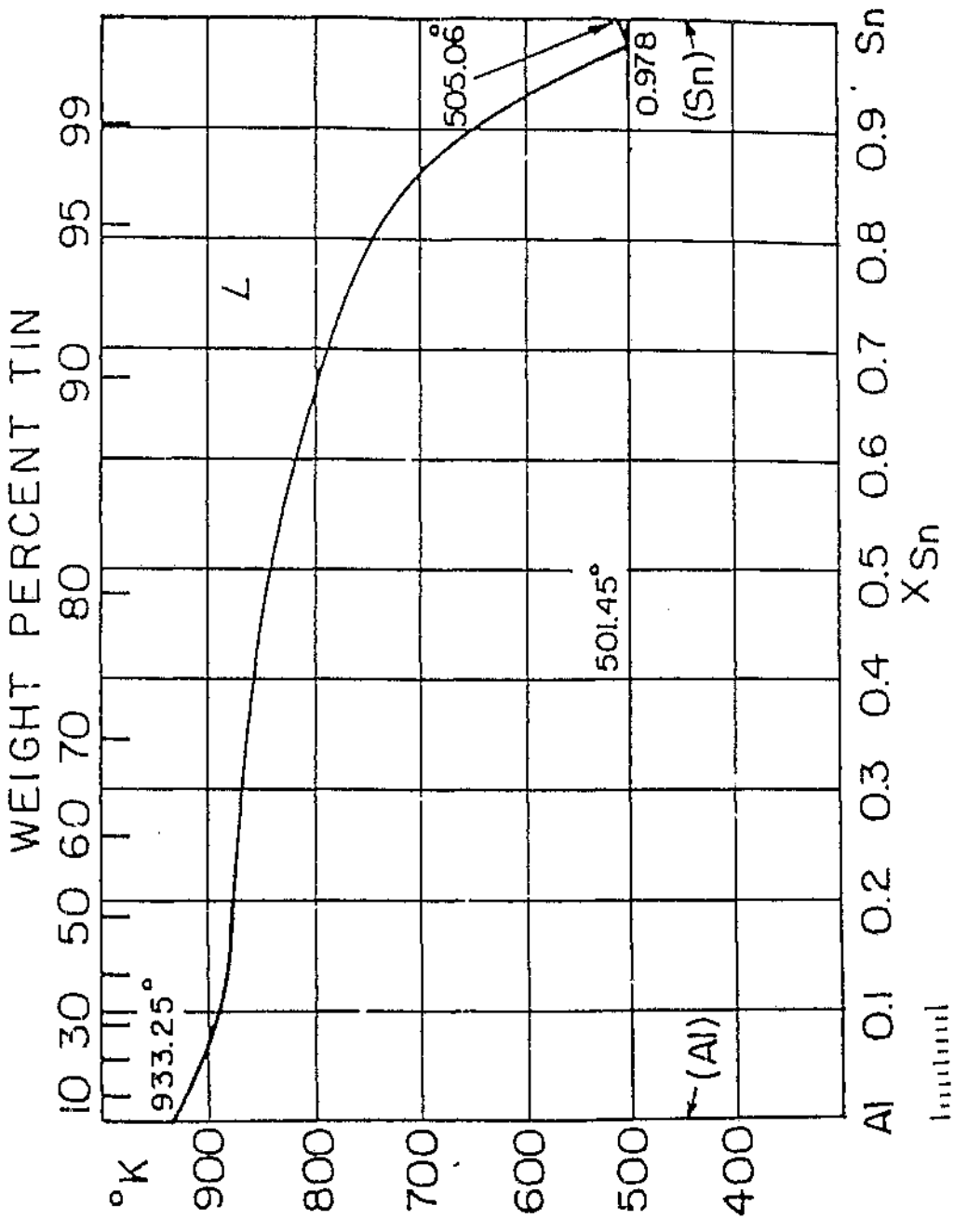


Figure 4.2 Al - Sn Binary System

4.4 Iron Solvent

The recovery of aluminium into the iron solvent was higher than the previous two solvents used. Thermodynamics predicts that there would be a higher recovery of aluminium to this solvent in contrast to the other two solvents discussed. This is true assuming that there was a minimal amount of loss to the system as gaseous products of the aluminium metal produced.

During the running of experiments using this particular solvent, there was a substantially higher reaction rate, indicated by a faster initial pressure change in the system. The faster reaction rate should have been accompanied by a higher recovery of aluminium. This was not found, in fact the total amount of aluminium recovered (reacted and unreacted) was approximately 15 to 20 % less than that of the total aluminium charged.

Vaporisation of the aluminium was believed to be the primary reason for the loss of the metal as Al(g) or $Al_2O(g)$. The product lost was believed to precipitate in cooler parts of the furnace as various different compounds as discussed in section 4.9. The form of the vaporised product was not accurately identified, as recovery of the product in the cooler parts of the furnace proved impractical. This was due to the design of the furnace, specifically heat shields directly above the hot zone.

Oxygen contents were significantly higher than any values for the previous solvents. Oxygen contents ranged from 800 ppm to 1300 ppm. The formation of iron oxides was ruled out as a product on simple thermodynamic principles. The amount of alumina present as solid inclusions was not enough to produce the higher oxygen contents found. The last alternative was that there was a significant amount of Al_4O_4C present in the iron solvent. Though various

methods were tried, X-Ray, EDX and electron microscopy, no positive identification was made of this compound.

There was substantial formation of iron carbide from the carbon in the charge and from the graphite crucible. A separate experiment to investigate the extent of the reaction between the crucible and iron solvent was conducted. The iron solvent reacted with the crucible wall to such an extent that the iron was almost able to break through the crucible side wall. During standard test runs, the iron did react with the side wall, but to a much lesser extent. The diminished corrosion can be attributed to the carbon in the charge being preferentially used as a reactant with the iron. The subsequent reaction of iron carbide with alumina was believed to be the primary reduction process.

EDX and X-Ray analysis performed on the samples showed the obvious products very well. The products identified were the iron solvent, iron carbide, small residual amounts of alumina, aluminium and various contaminants. Identification of the minor peaks was however very difficult, thus the intermediate products were not easily identified.

Graphite inclusions were more numerous near the edges of the metal pellet in contact with the wall as shown in **Figure 4.3**, but smaller sized inclusions were spread throughout the product. Iron carbide can be seen surrounding the graphite grains in the iron solvent matrix. This is not very clear in **Figure 4.3**, although electron microscopy identified the 3 distinct layers. **Figure 4.4** shows a much clearer picture of the case in point, taken from reference 32. The darkest areas are solid graphite grains, surrounded by a lighter grey, which is the iron carbide. The white matrix is the iron solvent.





Figure 4.3 Graphite Flakes in Iron

(x 400) (x 400)



Figure 4.4 Flakes of Graphite in Iron (Fr... ...ef. 32 (x 376))

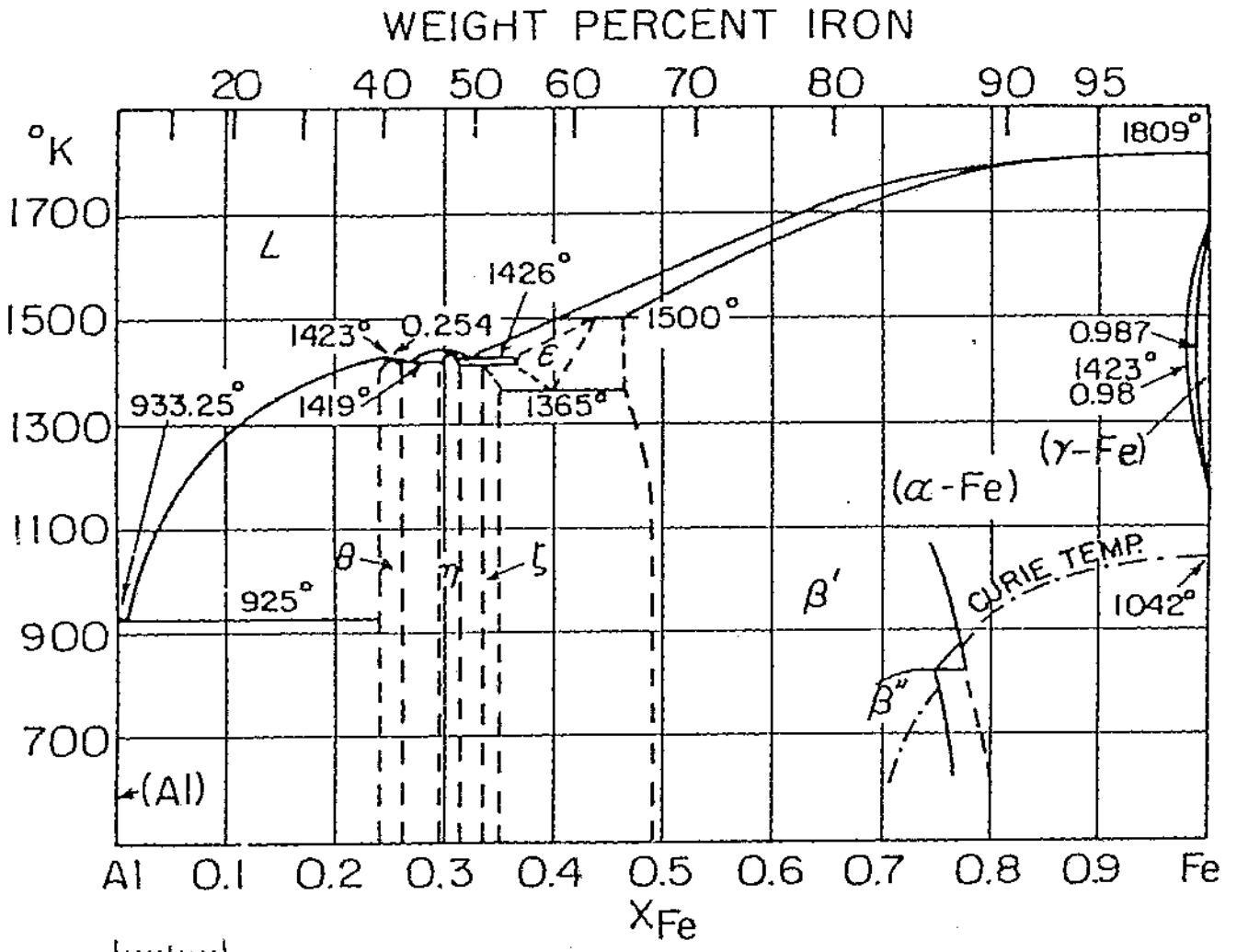


Figure 4.5 Al – Fe Binary System

4.5 Nickel Solvent

The recovery of aluminium to the nickel solvent was on average very good. The amount of unreacted material found after the experiments were run was minimal. It was again believed that the lost aluminium evaporated as gaseous Al(g) or $Al_2O(s)$. Precipitation of the aluminium metal was found in the lower cooler regions of the furnace, or at the base of the bellows. This was not however the case with iron, as very little precipitate was found in the lower half of the furnace. Accurate mass balances and analysis of material lost to the system, was not possible. Approximate aluminium metal loss was 10 to 15 %, while solvent loss was approximately 5%.

Products within the nickel solvent appeared to be again primarily Al_4C_3 and minor amounts of aluminium metal in solution. The pure graphite inclusions in the nickel varied between 3% and 5%. The lower amounts of carbon can be attributed to the lower tendency of nickel to form carbides.

The oxygen content of the product was less than 200 ppm for all tests carried out. The lack of oxygen in the solution again tends to indicate a low amount of unreacted alumina inclusions in the product. Inclusions of alumina can be seen under the electron microscope, and identified during the chemical analysis. The negative deviation of nickel from an ideal solution, make nickel a favourable solvent for the production of aluminium. The initial amount of aluminium charged to the reactants did not appear to have any negative influence on the rest of the reaction by raising the activity of aluminium in solution.

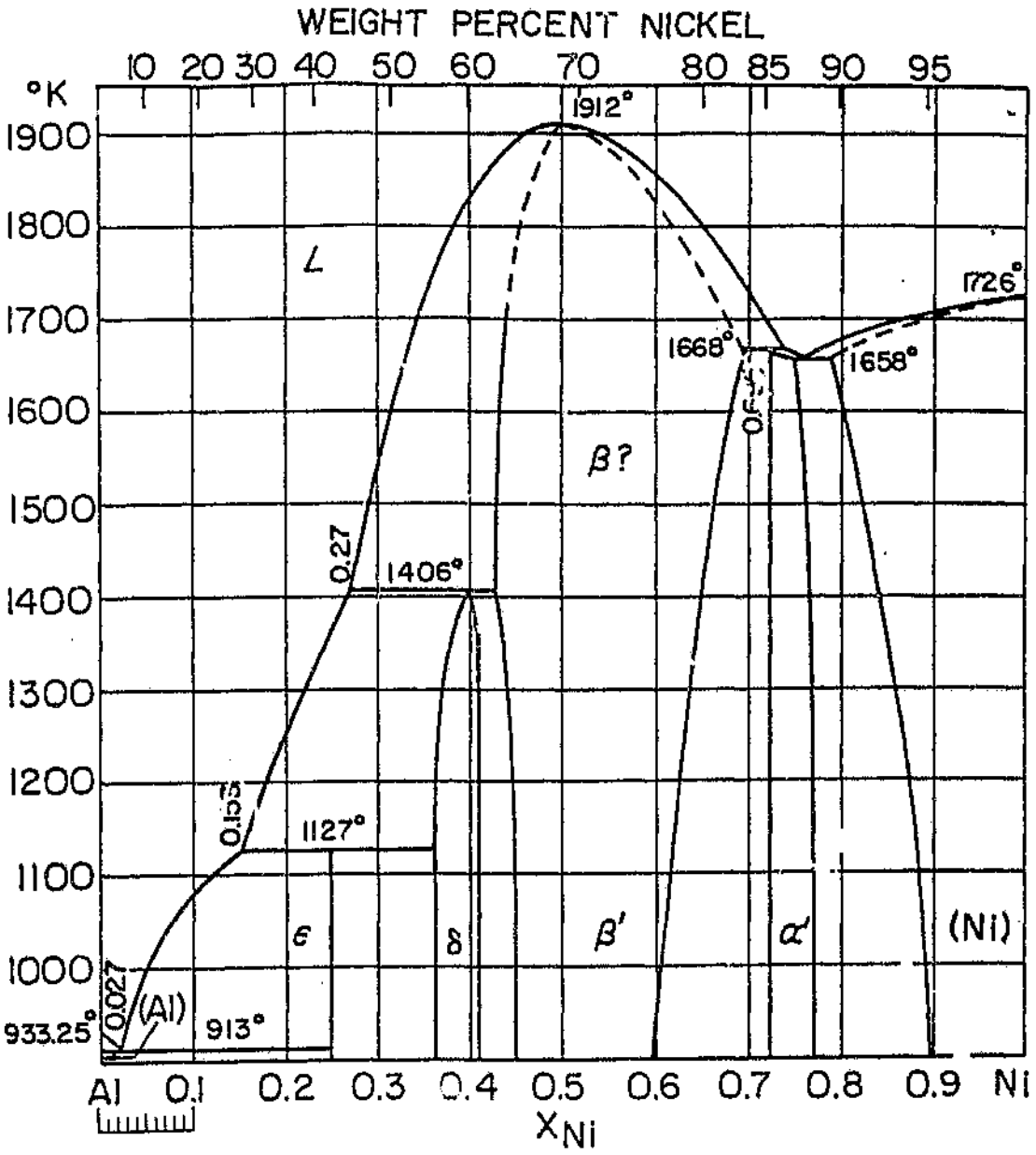


Figure 4.6 Al – Ni Binary System

4.6 Comparison of Results

4.6.1 Comparison of Solvents

The more negative the deviation in a system from ideality, the greater will be the solubility of a solute in the solvent. It is apparent from the results and the theory, that copper has the lowest affinity for aluminium, while nickel and iron are far better solvents for aluminium. The transport of aluminium into the copper solvent appeared to be much slower, and this may have added to the effect of slow $Al_2O(g)$ formation.

As discussed above, the effect of the solvent appeared to produce a distinct difference in the reaction rate. The greater the negative deviation from an ideal solution, the higher the average recovery of the aluminium to the solvent will be. Nickel having the greatest deviation from ideality produced the greatest recoveries according to the presented set of experimental conditions.

The positive deviation from ideality in the tin aluminium system means that the initial activity of the aluminium in the solvent would be far greater than that in any of the other solvents mentioned above. The 1 weight % initial charge of aluminium to the reactants meant that the aluminium in the copper solvent had an activity approximately 150 times smaller than that it would have tin. Iron aluminium and nickel aluminium systems having an even greater negative deviation from ideality, would therefore result in an activity of aluminium that would be even smaller for a given composition and temperature. This would in principle result in more aluminium recoveries as substantiated by present experiments.

4.6.2 Analysis of Other Recovered Products

The recovery of soot from the various cooler regions of the furnace was difficult, as the furnace was held at temperatures over 1500° C thus cleaning out the system was not possible. There was substantial soot build up in the evacuation section of the system as the air was removed from the system via a small diameter copper tube. Valves were often blocked, and the vacuum pump was cleaned regularly to remove dirty oil.

Analysis of the soot and other precipitates that were recovered from the evacuation system, showed that ± 70% of the soot was carbon. The aluminium content of the soot averaged 12%, with the rest of the composition comprising the different solvent metals.

The lower section of the furnace where the bellows were located, also contained soot and solid beads of solvent metal. The percentages of solvent metal varied according to the particular solvent being used at the time. The residue was solvent metal (Fe, Cu, Ni and Sn) based and about 15% aluminium with carbon contents in the region of 12 to 20%, as summarised in Table 4.2.

Table 4.2 Chemical Analysis of Residue

Soot Component	Carbon	Aluminium	Solvent Metals
Percentage	12 - 20 %	12-15 %	60-80 %

A dust or soot was also found in the bottom of the bellows as well as various precipitated compounds within the work tube. The soot had a silver-grey colour, its analysis showed a high aluminium cont ', approx. 5 to 8%. The bulk of the dust was carbon (60 to 70%), silicon oxide (10%), and solvent dusts

(15 to 25%). The solvent having the highest concentration found in the dust was on average copper, with concentrations of the solvent last used being greater than the others.

Precipitated compounds from the work tube wall showed 50% aluminium, with carbon being less than 5%. The solvents used made up the rest of the analysis, with the most recent solvent used having the greater percentage.

4.7 Reaction Rates

4.7.1 Reaction Order

The rate of change of pressure within the system can be used as an indicator of the kinetics of the reaction between carbon and alumina. After each experiment was concluded a pressure time plot was produced from the stored data. Examples are shown in Appendix 1. The chemical analysis of the alloy produced would show the amount of aluminium in solution, and thus the amount of alumina that had reacted from the initial charge amount.

In order to plot the extent of reaction vs. time for each experiment, the final amount of aluminium in the metal aluminium alloy pellet was needed as a suitable frame of reference. Chemical analysis allowed the total mass of aluminium in solution to be calculated. This showed the actual total extent to which the alumina had reacted with the carbon, i.e. the mass of aluminium dissolved in the aluminium metal alloy. Knowing the initial and final concentration of aluminium, a simple line could be drawn between the two values with the values between these points linked to some relevant variable.

For this case the relevant variable would be the system pressure. The system pressure change would indicate that the reaction was taking place as carbon monoxide gas was produced. Thus as the reaction takes place the system pressure would change from pressure "A" at the start of the experiment to pressure "B" when the experiment was terminated. By the same token the extent of reaction would proceed from 0% at the start of the experiment (pressure "A") to 100% at the end of the experiment (pressure "B"). The pressure values could then be superimposed between the initial and final aluminium concentrations with a resultant plot indicating the extent of reaction.

From the analytical chemical analysis, the mass of alumina that had reacted to form aluminium was added to the aluminium component of the unreacted alumina, this was cross-referenced with the initial charge mass. When the two masses were compared with each other, any discrepancies could easily be seen and noted. The amount of alumina that had reacted and formed aluminium represented the full extent of the reaction. However, the volatilisation and subsequent precipitation of material within the system did complicate the situation substantially by distorting and exaggerating the discrepancies in the mass balance calculations.

The reaction order was calculated by plotting ***-ln(1-extent of reaction)*** against ***time***. The graphs are shown in **Figures 4.7 to 4.10.** The plots were found to be virtually straight in all cases, thus fitting the pseudo first order reaction rate well. In various tests there were slight deviations in the slope of the plot. It is believed that the deviation was due to a possible alternate reaction. This may be a direct influence of pressure on the system changing between the reaction mechanism:

$$2Al_2O_3(s) + 3C(s) \Leftrightarrow Al_4O_4C(s) + 2CO(g) \qquad \textbf{(2.3 p)}$$

$$Al_4O_4C(s) + 6C(s) \Leftrightarrow Al_4C_3(s) + 4CO(g) \qquad \textbf{(2.3 r)}$$

$$Al_4O_4C(s) + Al_4C_3(s) \Leftrightarrow 8Al(l) + 4CO(g) \qquad (2.3\ u)$$

$$4Al_2O_3(s) + 12C(s) \Leftrightarrow 8Al(l) + 12CO(g) \qquad (2.3\ d)$$

and the alternate reaction mechanism:

$$3Al_4O_4C(s) + 3Al_4C_3(s) \Leftrightarrow 24Al(l) + 12CO(g) \qquad (2.3\ u)$$

$$4Al_2O_3(s) + Al_4C_3(s) \Leftrightarrow 3Al_4O_4C \qquad (2.3\ f)$$

combining **2.3 f** and **2.3 u** the reactions simplify to

$$Al_2O_3(s) + Al_4C_3(s) \Leftrightarrow 6Al(l) + 3CO(g) \qquad (2.3\ x)$$

This sequence produces 3 times less carbon monoxide gas per mol of aluminium. The excess of carbide and oxycarbide that are formed, may have an influence on the rates and extents of reaction. These alternate reactions have been discussed in the literature survey.

From the plots, the reaction rate constant k can be calculated very easily as the slopes of the graphs. Alternatively we can look at the reaction time constant τ, which is the inverse of the reaction rate constant and has units of minutes. It is unclear what the reasons are for the curved region of the plot at the beginning of many of the experiments. The rapid rate of reduction of the alumina in the initial stages of the test added to the instability of the system and recording of the data. The effect disappeared within a few minutes of the test being initiated.

4.7.2 Effect of Temperature

The effect of the temperature on the reaction rate appeared to differ according to the solvent. However even small increases in general, increased both the reaction rates and the extent of reaction considerably. This showed the fact that carbothermic reduction of alumina is very temperature sensitive. This temperature effect also implies the possibility that the rate control is dominated by chemical reaction rates and not by transport.

From the results presented, it is believed that as the temperature is increased further, the rate at which the reaction takes place will increase exponentially and not linearly.

The use of nickel as a solvent is shown in **Figure 4.7** and shows a clear change according to the reaction temperature. The higher the temperature the greater the reaction rate and extent. The temperature ranges used were fairly narrow and the lower temperature reactions produced gradients with very little difference. In the case of the iron solvent, the initial rate of the reaction had significant deviations from the first order reaction rate, but after ±5 minutes the rate stabilised. There was however very little difference in the slope of the graphs, the reaction rates were not significantly different.

When studying the copper solvent results, **Figure 4.8**, it can be seen that there is an anomaly where the slope of the graph at 1973 K is greater than the slope at 1983K. The reason for this result is not clearly known. The slope of all 3 graphs is very similar and it may thus be the small deviation from ideality, which allows for small changes in reaction rates. The extent of reaction at any particular time is still higher at greater temperatures, which confirms the effect of temperature on extent of reaction. At the higher temperatures there appears to be a decrease in the rate of reaction shortly after the start of the experiment.

Figure 4.7 Extent of Reaction vs. Time in Nickel Solvent

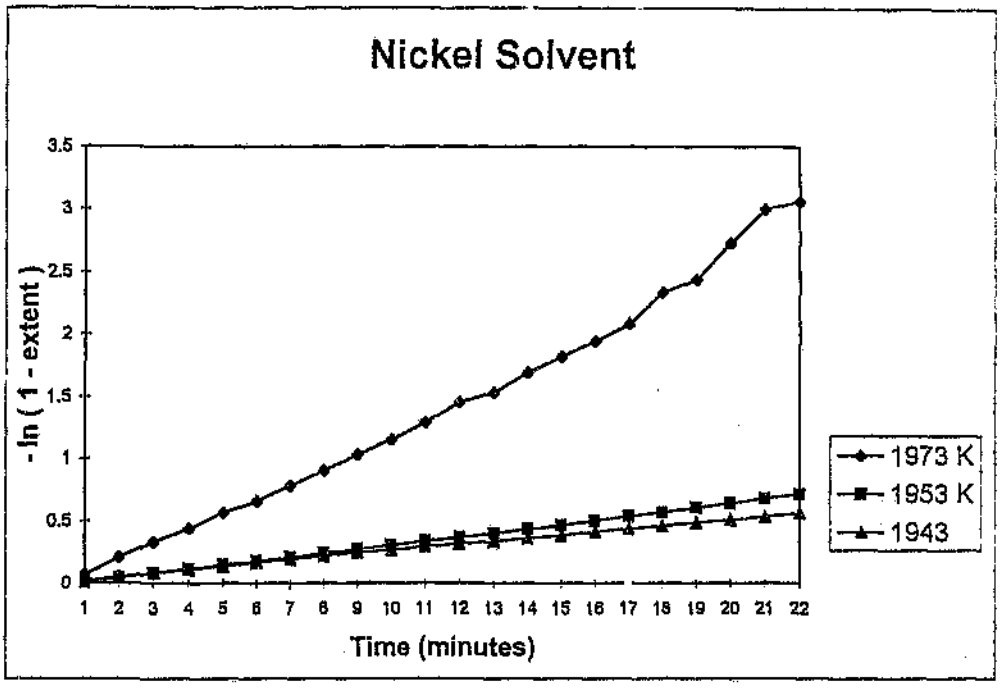


Table 4.3 Rate and Time Constants in Nickel Solvent at Different Temperatures

Experiment	Temperature (K)	k (min^{-1})	τ (min)
32	1973 K	0.125	8
38	1953 K	0.029	34
40	1943 K	0.023	44

Figure 4.8 Extent of Reaction vs. Time in Copper Solvent

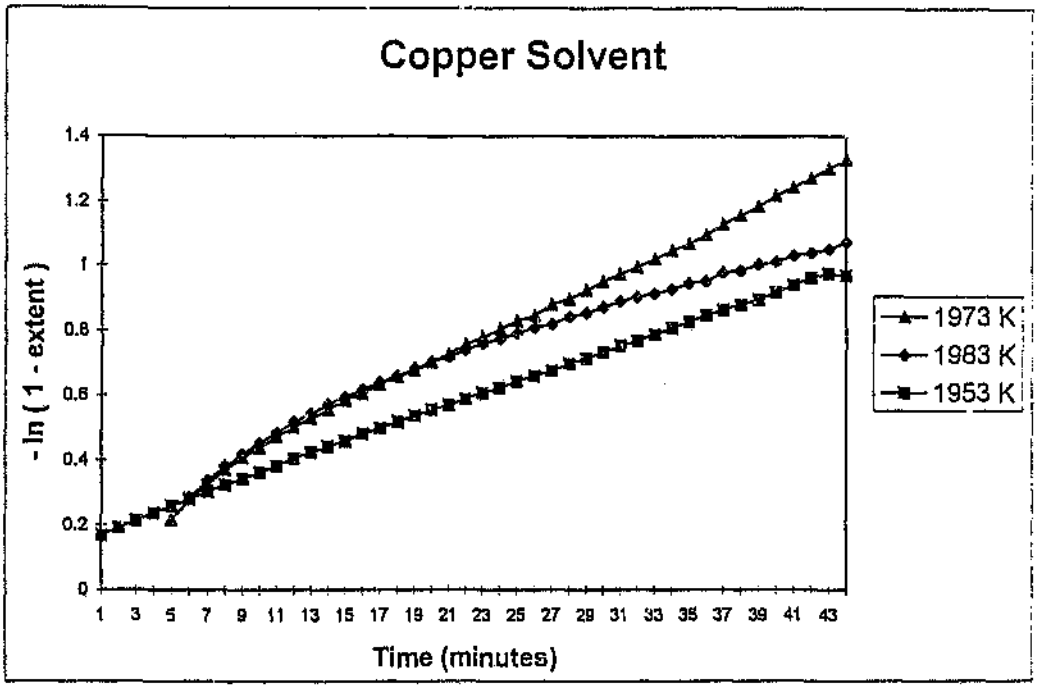


Table 4.4 Rate and Time Constants in Copper Solvent at Different Temperatures

Experiment	Temperature (K)	k (min^{-1})	τ (min)
3	1973 K	0.023	45
2	1983 K	0.022	43
4	1953 K	0.017	59

Figure 4.9 Extent of Reaction vs. Time in Iron Solvent

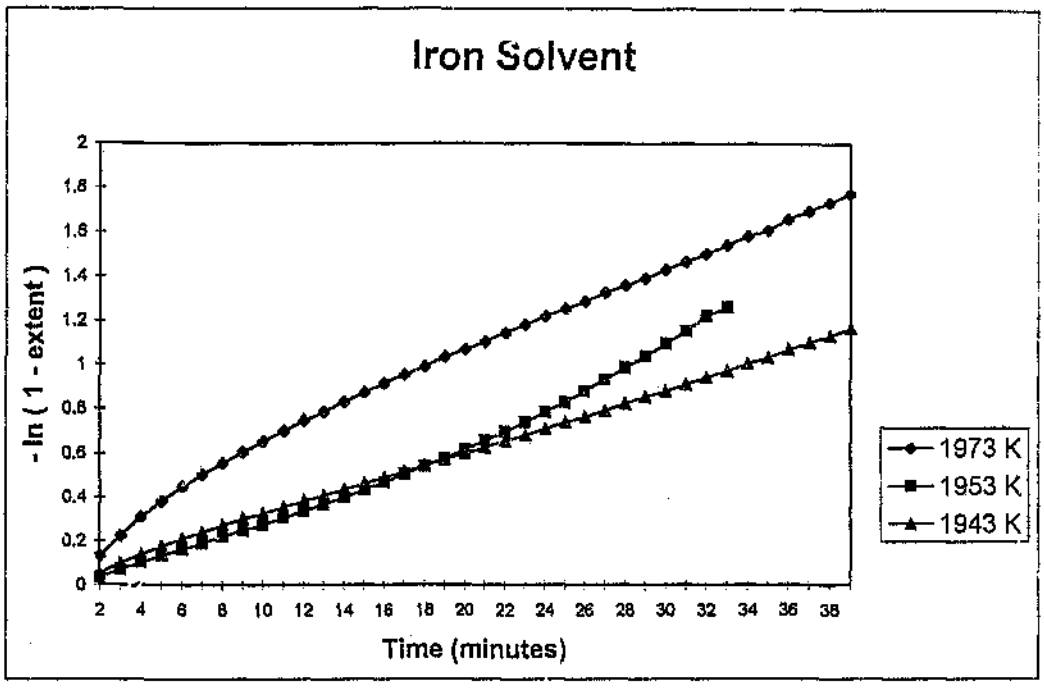


Table 4.5 Rate and Time Constants in Iron Solvent at Different Temperatures

Experiment	Temperature (K)	k (min^{-1})	τ (min)
13	1973 K	0.047	21
16	1953 K	0.036	28
15	1943 K	0.029	34

Figure 4.10 Extent of Reaction vs. Time in Tin Solvent

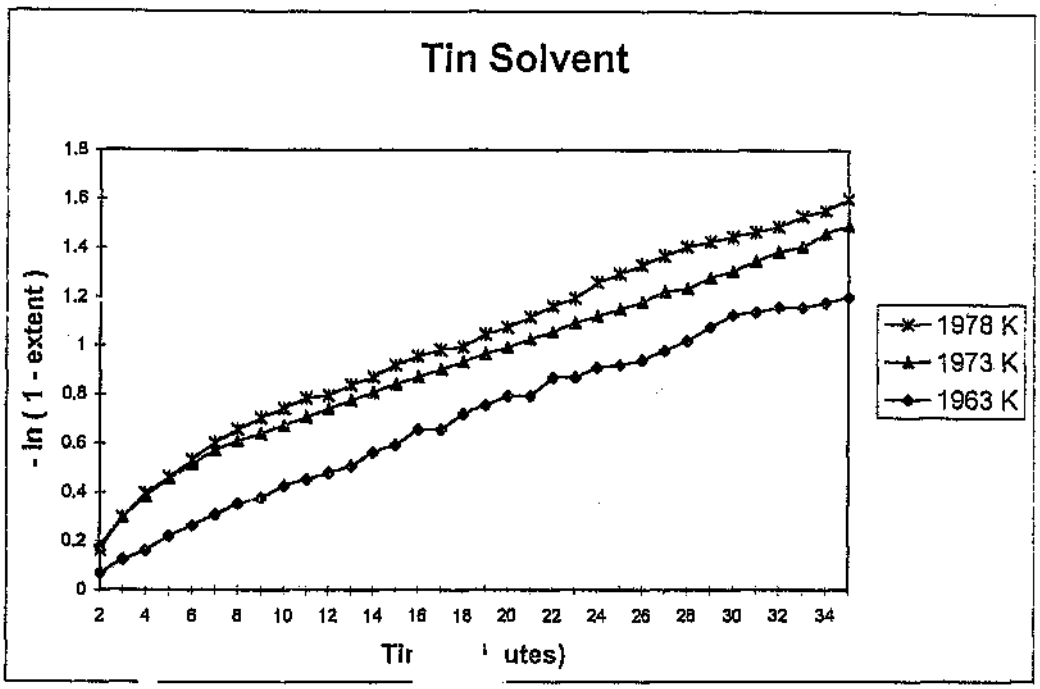


Table 4.6 Rate and Time Constants in Tin Solvent at Different Temperatures

Experiment	Temperature	k (min^{-1})	τ (min)
6	1978 K	0.057	18
5	1973 K	0.050	20
8	1963 K	0.037	27

This may again be the change from one alternate reaction mechanism to an alternate depending on the system pressure.

The iron solvent plot, **Figure 4.9**, shows a fairly similar plot to the copper solvent. There is a distinct difference in the extents of the reaction, but the slopes of the plots are all fairly similar with comparable rate constants. It can be seen that the slope of the graph at 1953K tends to increase as time increases. This runs against most thermodynamic principles and can probably be attributed to a small leak in the system. The extent difference is still visible indicating the temperature effect on extent of reaction. The plot at 1963K again shows the double slope phenomenon discussed previously.

The reaction rates in the tin solvent shown in **Figure 4.10**, showed very little difference with an increase in temperature. However there were again significant increases in extent of reaction. The low solubility of aluminium in the tin would cause this effect, the formation of alternate aluminium compounds, vapours of aluminium or precipitates would have a similar effect

When a plot is produced showing the 4 different solvents used in **Figure 4.11**, the results again show the effect of the deviation from ideality. The massive slope difference between nickel and the other solvents should not be taken to indicate the actual effect of the solvents, as other influences may also have had an impact on the extent of reaction for the nickel solvent result used in the plot.

Although the difference between time constant values between copper and the two solvents tin and iron, is substantial, the amount of aluminium recovered in the copper and iron solvents was approximately the same (87 – 93% respectively), while the tin solvent had a very low total aluminium metal

Figure 4.11 Extent of Reaction vs. Solvent Type at 1973K

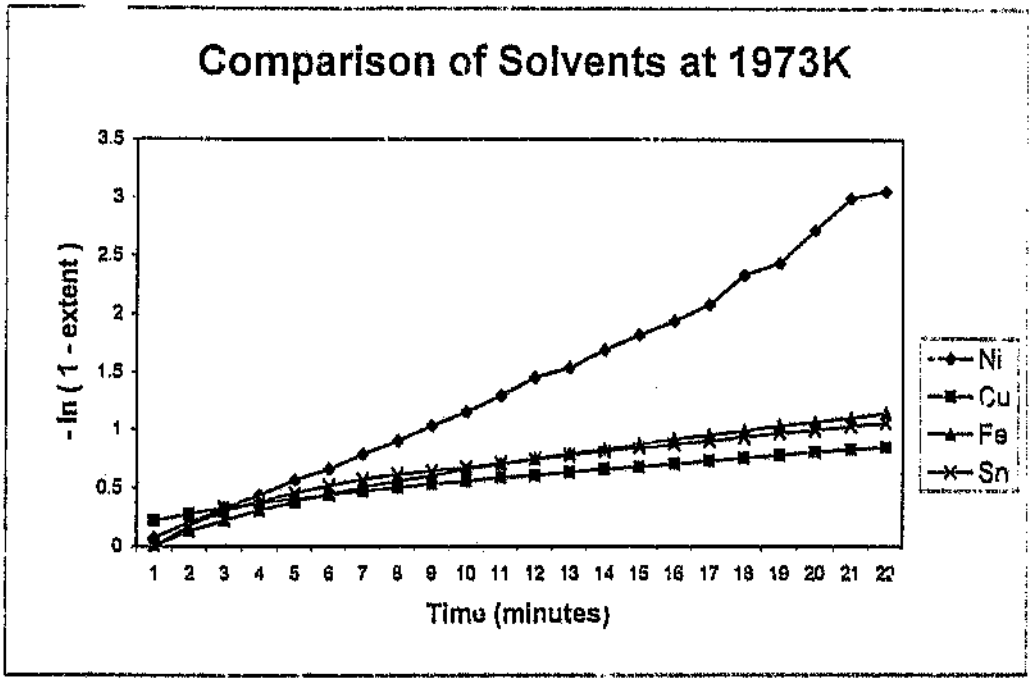


Table 4.7 Rate and Time Constants for Various Solvents at 1973K

Solvent	Temperature	k (min^{-1})	τ (min)
Ni	1973 K	0.125	8
Cu	1973 K	0.023	45
Fe	1973 K	0.047	21
Sn	1973 K	0.050	20

recovery (10 %). It should therefore be noted that direct comparison of various solvents is difficult and could lead to erroneous conclusions.

In general the initial reaction rates were different for the different solvents, but after 7 minutes or so the difference becomes slight. This is significant when selection of an appropriate solvent is made. Extent and rate of reaction will be important, and accurate results of both will be required.

4.7.3 Effect of Pressure

The effect of pressure on the rate of reaction is quite drastic. It can be seen from the overall reaction

$$Al_2O_3\,(s) + 3\,C(s) = 2\,\underline{Al} + 3\,CO\,(g) \qquad (4.7\,c)$$

that the reaction depends on pressure strongly in reaching equilibrium. It has been reported [16] that the reaction only starts to have a significant rate when the pressure drops below about 40 kPa. This results in a couple of practical problems. The rate is most rapid in the initial stages, and if the pump is unable to remove the gas, the initial rate becomes difficult to record.

Depending on the experimental set-up, there is a significant problem associated with the evaporation of sample from the crucible. Both aluminium and the solvent are susceptible to this evaporation.

Although it has been reported[16] that the reduction of alumina begins to have a significant rate when the total pressure in the system is less than 40 kPa, test work was carried out to establish if any significant amount of reduction takes place at atmospheric pressure. The experiments conducted at atmospheric

pressure were runs 20, 21, 41 and 42, the rate of the reaction produced results that indicate that the reaction does definitely take place, but at significantly lower rates. Depending on the solvent, the reaction can therefore proceed to a certain extent. Results showed that the final concentration of aluminium dissolved in the solvent was greater than the initial amount of metallic aluminium in the initial charge, as was expected. The time period for these experiments was significantly higher than for the normal experiments. Tests lasted for 9 to 12 hours as opposed to 1 to 2 hours for the standard test runs.

Results from analysis after these atmospheric pressure experiments have indicated that less than 450 - 500 ppm oxygen was present in the solvent. The formation of aluminium oxycarbide as well as a minor amount of unreacted alumina trapped in the solvent produced the small amounts of oxygen detected. However the amount of aluminium recovered indicates that there is a significant amount of reduction taking place.

The origin and movement of all the aluminium within the system can not be pin pointed accurately. The apparent loss of aluminium to the system during the standard tests may not be permanent. The precipitation of various aluminium compounds in the cooler parts of the furnace may not represent the final state for these compounds. The transport of part of the aluminium and various solvent compounds was believed to be an ongoing event within the furnace depending on the conditions within the furnace. The lowering of the pressure before and during experiments, or using different temperature are believed to result in movement of product within the furnace on a level that can not be ignored. As previously mentioned all attempts to recover these compounds were unsuccessful.

4.8 Effect of Impurities

Table 4.8 Product Impurity Percentages

Impurity	Concentration
Lanthanum	0.3 %
Chromium	0.28 %
Manganese	0.86 %
Silicon	2.39 %

The amount of impurities found in various parts of the system was greater than expected. Impurities such as silicon and silicon based compounds were a product primarily of the vacuum grease. The vacuum grease was needed to ensure an adequate seal between the bellows and the work tube. The heat in the vicinity of the work tube was approximately 250 degrees centigrade. The temperature and low pressure were enough to result in vaporisation of components within the grease resulting in contamination of the product. The grease was also believed to vaporise and move into various regions of the furnace where it would reprecipitate as a different compound.

One form of precipitated material was a "fluffy cotton wool like" disk that formed during two experiments in a region of the work tube just outside the hot zone. The disk was found just outside the hot zone attached the pedestal used to insert the crucible into the hot zone. Analysis revealed that there was a significant amount of silicon, with the bulk of its analysis being carbon and oxygen. Previous researchers [8,11] have claimed that a similar precipitate is the nitrogen stabilised Al_2OC compound. During the first occurrence, there was a leak in the furnace and after the experiment was abandoned, the precipitate was found. The second occurrence was not associated with an obvious leak in the system.

It was believed that most of the carbon found in the condensate was from the reactants as a soot form, rather than as a part of a compound. Identification of the compounds was not possible from X-ray diffraction and EDX, as various contaminants clouded the analysis of a pure product. Al_2OC was not identified during any analysis performed. Some typical EDX results have been included in Appendix 2.

Other impurities included lanthanum, chromium, manganese and trace amounts of the other elements. The lanthanum and chromium constituents are believed to originate from the heating elements. The elements are manufactured from a mixture of lanthanum oxide and chromite and were very fragile and breakages were regular. The elements appeared to sublime at working temperatures and slowly degrade as time passed. The contaminant elements were believed to have diffused through the work tube at operational temperatures. This was because detectable amounts of these compounds were identified in virtually all solvent pellets produced. The amounts were very small, less than 0.05%, but there was a reading of these materials from all tests carried out. Example is shown in Appendix 3.

The origin of the manganese found in the solvent pellets produced is unknown. It may have been associated with one of the many reactants or furnace components used in the experiments.

4.9 Vapour Pressure Effects

With the total pressure of the system being relatively low, there is a heightened effect on the vapour pressures of the components in the system. The vapour pressures of the liquid components at 1973 K are given below in Table 4.9 [15,40]

Table 4.9 Vapour Pressure of Solvents

Reactant	Vapour Pressure (Pa)
Aluminium	704
Iron	16
Nickel	12
Copper	293
Tin	315

It is clear that the vapour pressure of aluminium is substantially higher than any of the other components, but it is still low enough not to evaporate completely. The problem is compounded by the fact that there is also an alternative product in the production of aluminium, which is the gas Al_2O. The production of the gas Al_2O and the high vapour pressure of liquid aluminium can greatly affect the resultant recovery of aluminium to the solvent.

To test this effect, various runs were conducted using nickel as the solvent at 1973 K. The system pressure was held between 15 and 20 kPa for different lengths of time to determine the effect on recovery. Figure 4.12 shows the results.

The time constants for the experiments varied from 8 to 20 minutes. There is a definite negative trend in the recovery of the aluminium to the solvent, as the time is increased. The effective test runs were conducted for time spans from 30 to 120 minutes. The straight line trend can be changed to a log type curve. This gives a slightly closer fit but the variance of the results was still too great to show any effective improvement

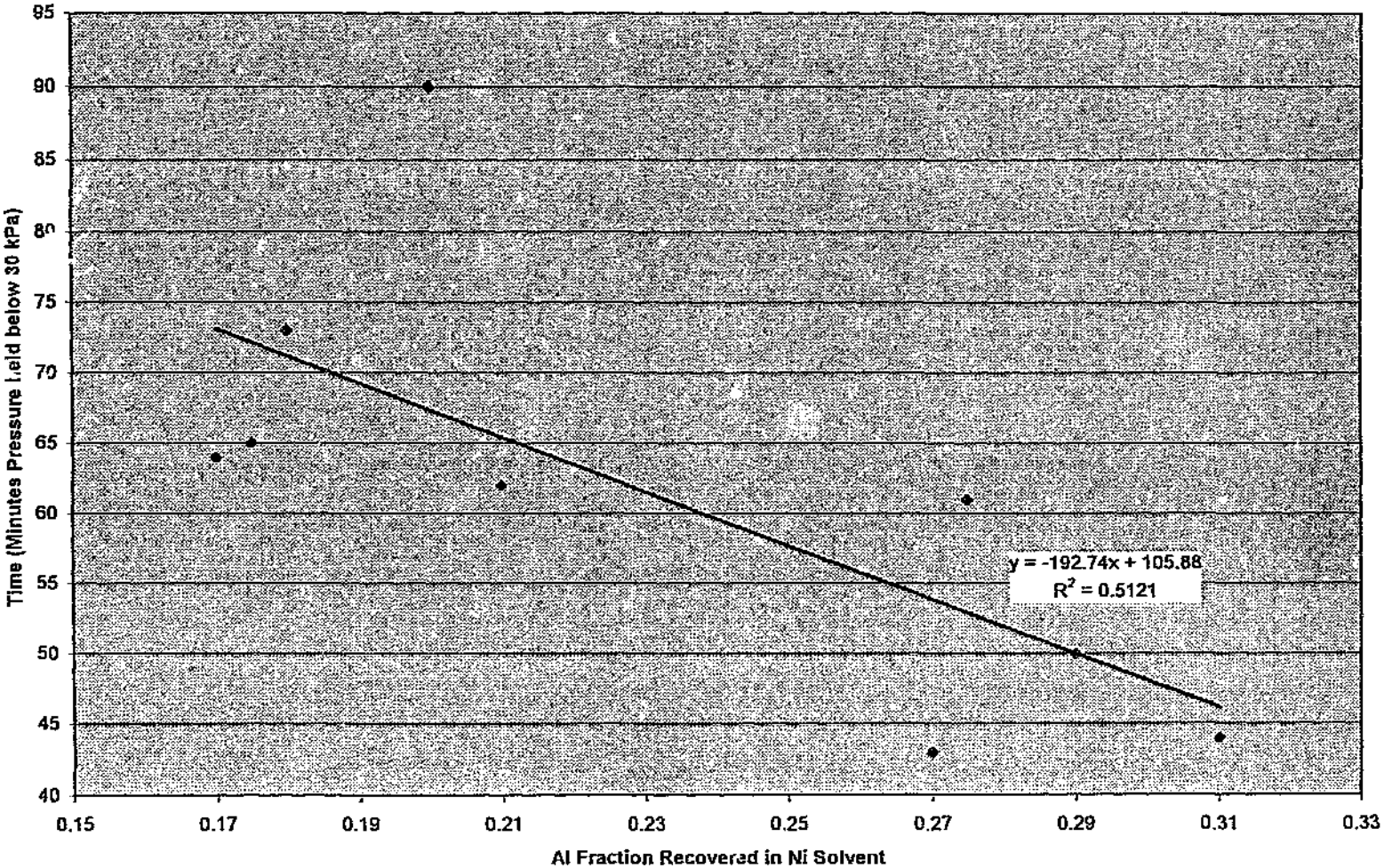


Figure 4.12 EFFECT OF PRESSURE ON VAPORISATION OF Al

The set-up used for the experiments was believed to aggravate the possible vaporisation of the products. The fact that the hot zone is very small in comparison to the rest of the system would assist the loss of material. The aluminium and Al_2O vapours are free to move around in the work tube, and the physical distance to move to a cooler zone is short.

4.10 Mass Balance

Analysis of the material losses from the system, show that the set-up is susceptible to vaporisation of reactants. The loss of reactants was primarily from the solvent, with a substantial amount of aluminium also being lost to the system. Average mass loss of material from the reactants and solvent during the running of the experiment was 2.51 grams, with a standard deviation of 1.5 grams. The loss of material is greater than the mass of oxygen in the alumina, which would have reacted with carbon to form carbon monoxide gas. Assuming a 100 % completion of the reaction, the mass of oxygen lost should have been in the region of 1.8 grams. This is clearly not the case when compared to the actual results.

Table 4.10 Average Mass Loss

Average Mass Loss (Total)	Standard Deviation
2.51 g	1.5

As tin appeared to have a slow reaction rate with low aluminium recoveries, there would be a residual amount of unreacted charge recovered at the end of the experiment. This was in the form of a white chalk like pellet lying on the

top of the solvent bath. The unreacted charge had silicon contents that were about 1.5 percent. Carbon in the pellet comprised about 20 percent of its mass as compared to the 26% in the initial charge. The unreacted alumina in the pellet made up the bulk of material. Total mass of the pellet was between 1.5 and 2.0 grams for tin, while the iron solvent had a standard mass of unreacted charge weighing approximately 0.5 grams.

Recovery of all the material and a comprehensive mass balance to determine the movement of all materials was not possible. There was a significant loss of reactant, with an average loss of aluminium of 25 to 50% depending on temperature and the time the system pressure was held below 50 kPa. This part of the project has thus been deemed to be inconclusive given the variance of the results.

5 SUMMARY AND CONCLUSIONS

5.1 Summary and Conclusions

The results have shown that reduction of alumina into a solvent phase is possible at temperatures in the region of 1700°C. The rate and extent of the reaction is highly dependent on the pressure and temperature. In addition the type of solvent used is very important. Although the number of solvents tested was not large, many possible solvents could n ed because of their vapour pressure and various other physical properties. The propensity of the aluminium to form compounds with the solvent can be advantageous, if applications for these compounds or alloys can be found, or if aluminium can be separated cost effectively since the separation can be a chemical step.

Getting accurate and repeatable results is dependent on the physical integrity of the furnace and ancillary equipment, which in this case was not entirely satisfactory. However it must be borne in mind that operating under a vacuum is arguably the most difficult task a metallurgist will encounter. The frequent leaks prevented accurate analysis of the rate of the reactions and many tests had to be abandoned, but sufficient data was acquired to show that the nickel solvent had the highest solubility for aluminium. Additionally the rate calculations showed reaction rates and extents tended to increase at higher temperatures. The tin solvent did not show much solubility for aluminium, but production of alternative products may have occurred.

The pseudo first order reaction rate is the primary reaction order for reduction of alumina in all the solvents used. The time constants calculated behaved according to thermodynamic and metallurgical principles. The problems

involved in the atmosphere control contributed to the repeatability problems encountered in the experiments. In all but one case, the time constant behaved according to thermodynamic principl 'y becoming smaller as the temperature increased.

The dual gradients noticed in various experiments was attributed to an alternate reaction sequence taking place, probably due to pressure changes affecting the reaction kinetics and products as discussed earlier.[8] In almost all cases the reduction rate was very dependant on temperature, indicating that the chemical reaction rate was the dominant factor in rate control.

The loss of product to the system may have serious influences on larger scale tests conducted under similar conditions. The loss of product encountered in the trial experimental stage was high, but controlling of the physical set-up, and each of its short comings may be possible.

Production of aluminium gas was not identified as a major reaction, although it may account for various losses of product in the system. The identification of the various aluminium gases that are thermodynamically possible requires the implementation of an on-line sampling and analytical system during the experiment.

5.2 Suggestions for Future Work

The crucibles used in all experimentation were manufactured from high purity graphite. There was substantial degradation of the crucible by the iron solvent, resulting in carbon compounds in the alloy. Possible breakouts could cause damage to the vacuum system. Breakage of the crucible also occurred in

various tests. It is possible to use alumina crucibles, although they are more susceptible to thermal shock, and may well be reduced by the graphite charge in the reactants.

There was a distinct reaction between the 10 mm diameter alumina tube, used to raise the crucible into the hot zone, and the graphite crucibles used to contain the charge. Although complete reduction of the alumina tube by the graphite crucible was never achieved, there was a 15% reduction in the diameter of the tube where it made contact with the crucible. Checking the effect of using different crucibles on reproducible results would be advised. Part of the excess aluminium found in the system may have come from the reaction of the alumina tube with graphite. This excess material could then also have reacted further to form oxides and some of the other complex compounds found elsewhere in the work tube.

Within the furnace used in these experiments, the effect of volatilisation should be checked. There was a problem associated with the recovery of the material lost, resulting in incomplete analysis. Materials lost to the system included alumina, carbon and depending on the vapour pressure of the solvent metals, varying amounts of solvent. Therefore the use of a furnace with a different physical set-up is advised. i.e. A furnace with massive temperature gradients over short physical distances must be avoided, although from a practical point of view, this may be impossible to achieve.

Reducing the size of the system surrounding the crucible is advised. This would also assist in the recovery of the particles that move out of the crucible as a vapour, solid or liquid. Furnaces that can be heated and cooled at rapid rates without damage to the work tube would be advantageous.

Using a different furnace, it may be possible to check the effect of volatilisation on the recovery of aluminium to the solvent. The effect of the atmosphere on the system may also be checked. The difference between argon and carbon monoxide gas may have a substantial influence on the rate and extent of the reaction. The partial pressure of carbon monoxide gas has been shown to be a major force in the reduction of the aluminium. Reducing the partial pressure of the carbon monoxide gas further by using argon may assist reduction.

Further test work is advised to see if a slow reaction does occur with highly solvating alloys. Previous work has indicated that at high pressures the reaction rate is very slow if not zero.[16] The use of a highly solvating material may increase the reaction rate above that of copper or tin.

The use of on-line thermo-gravimetric analysis (TGA) as well as a check on the pressure of the system is suggested. This will assist in the analysis and plotting of reaction and or vaporisation of reactants in the system. The TGA analysis would assist in the tracking of vaporisation where the use of a pressure transducer is not possible. The comparison of the weight loss to pressure gain should give similar slopes while the reaction is taking place. Any further differences would be attributed to unwanted evaporation and precipitation of product in other regions of the furnace.

Within all systems, a full range of tests should be conducted across the range of mole fractions of aluminium from 0.00 to 1.00. This may give a better picture of the solubility of aluminium and aluminium compounds within a solvent at elevated temperatures. The furnace-vacuum system must be designed in such a way that it would have far fewer leaks, which would also make the evaluation of the results much simpler. The accurate measurement of the activity of aluminium in solvents is also required to make sound calculations.

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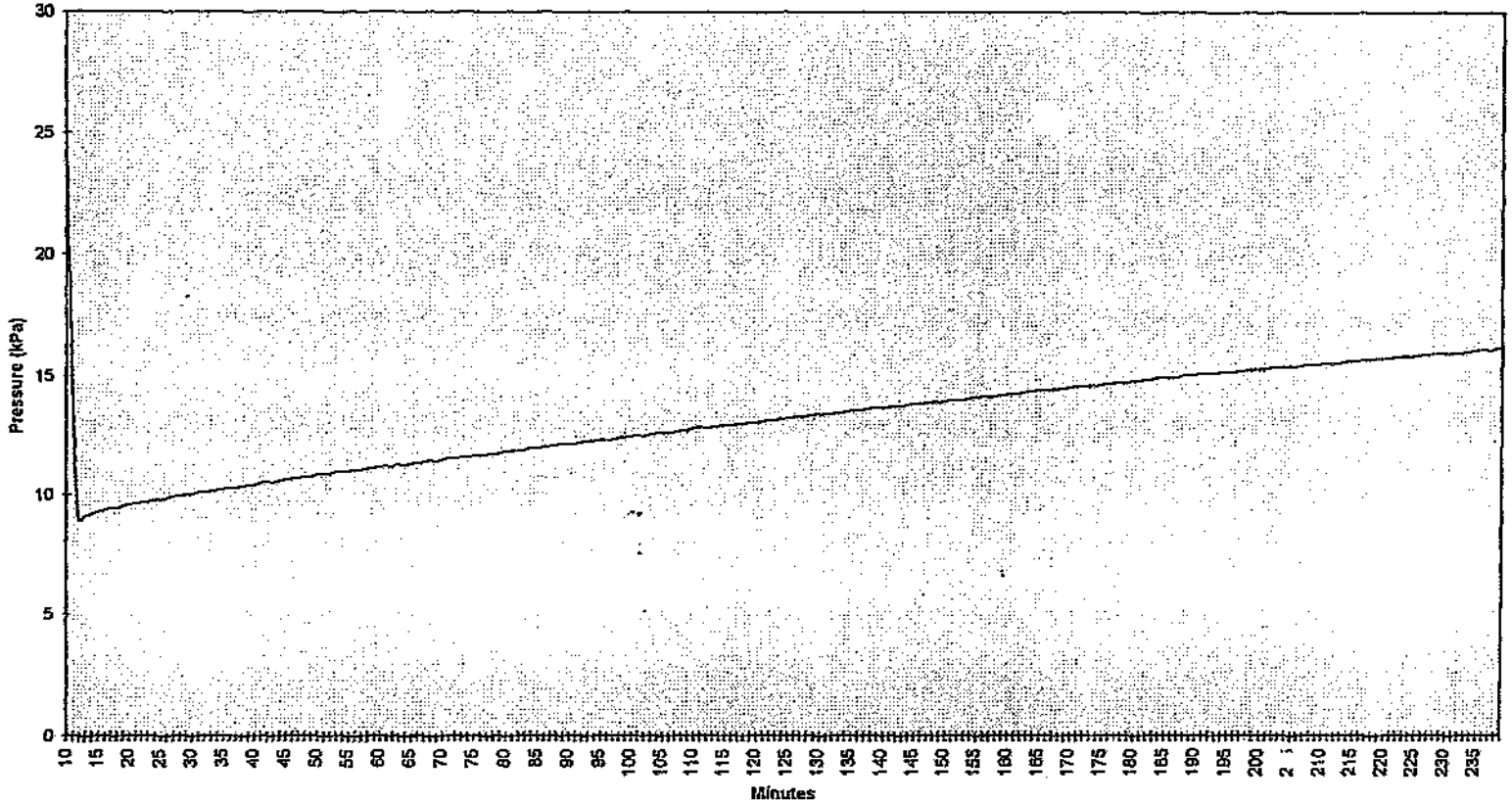
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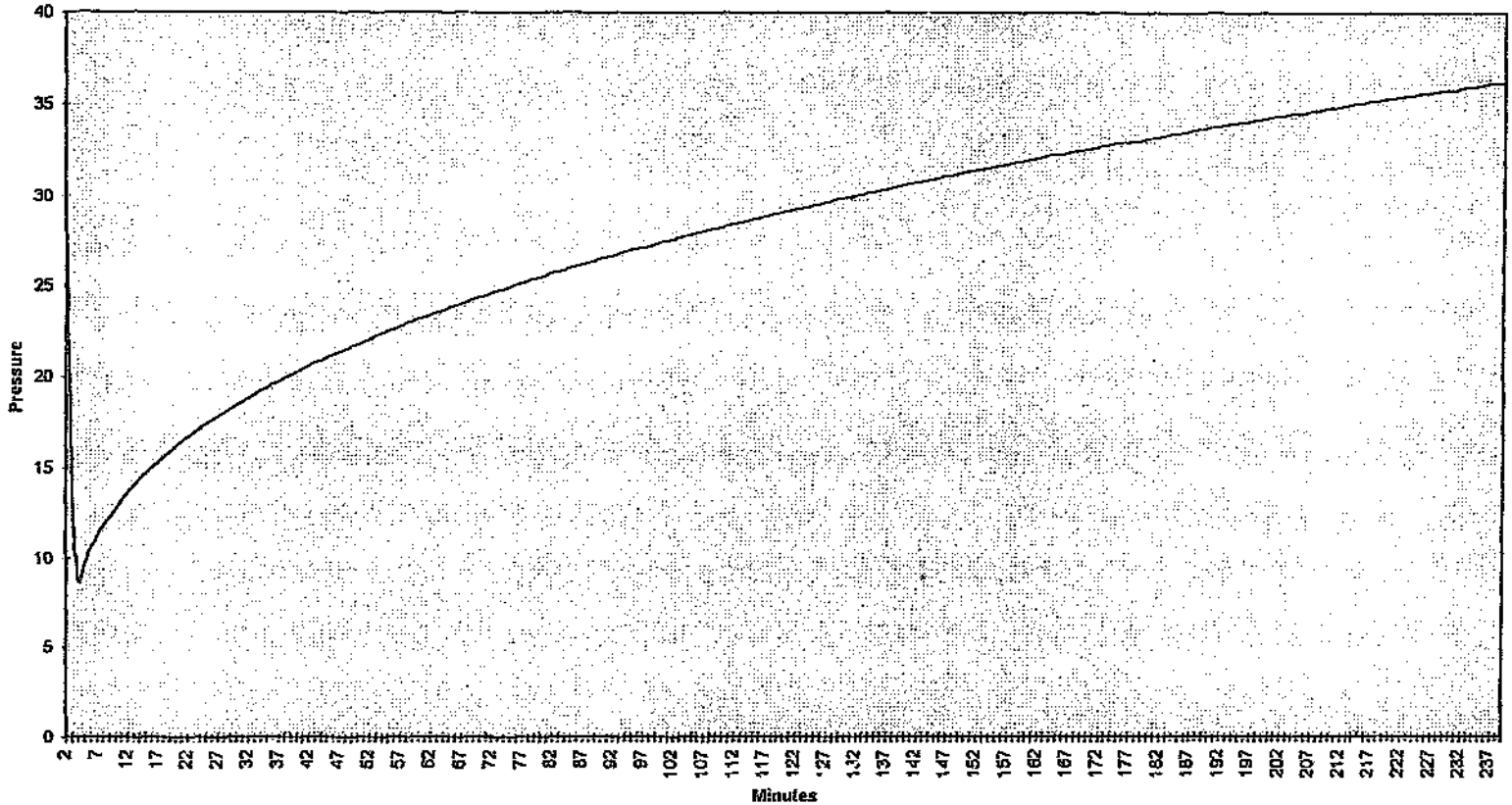
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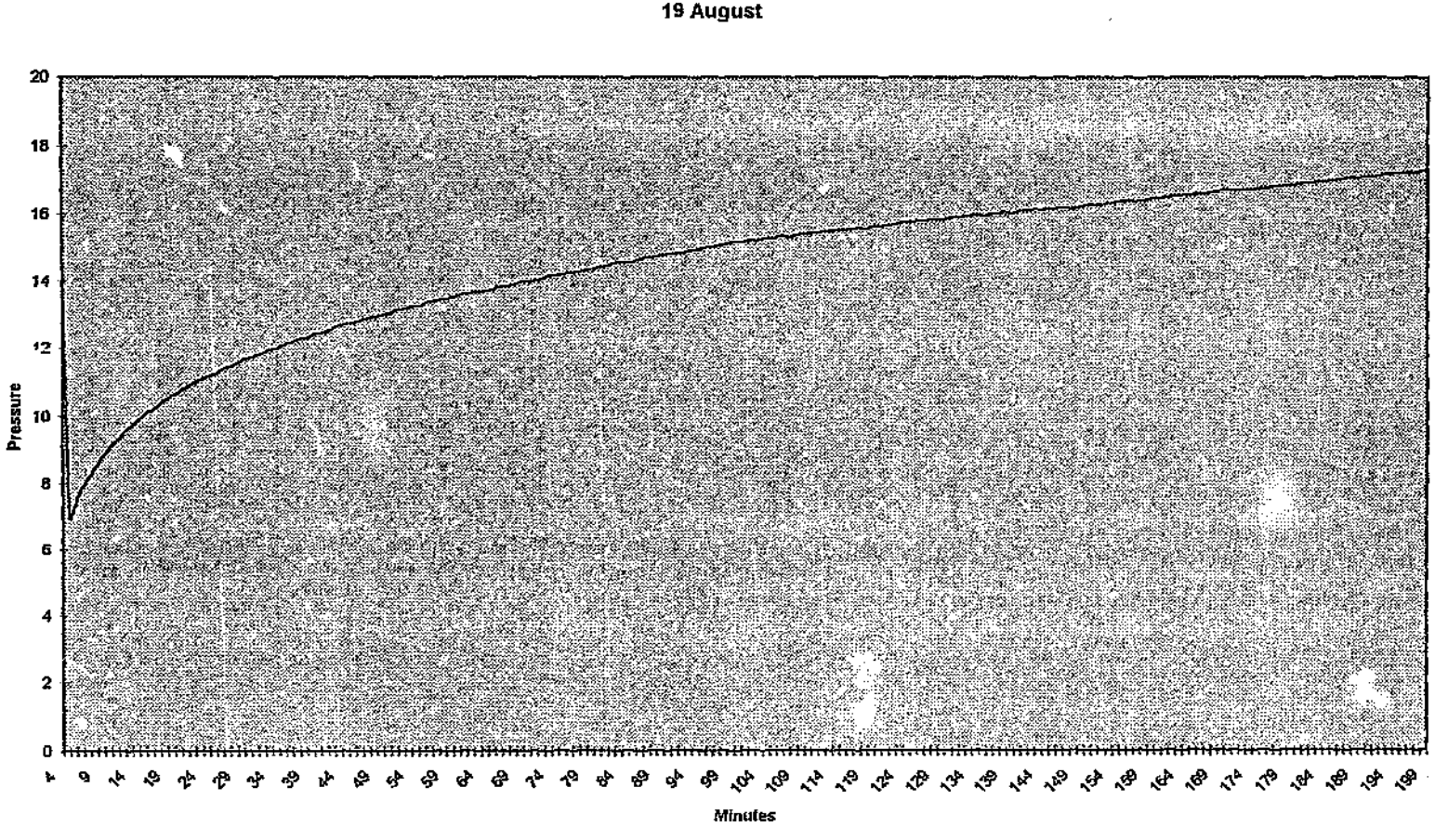
APPENDIX A Selected Pressure-Time Plots

Number	Graph Date	Test Number (Refer Table 4.1)
1	20 July	8
2	22 July	1
3	19 August	32
4	16 November	13
5	17 November	15
6	21 November	11

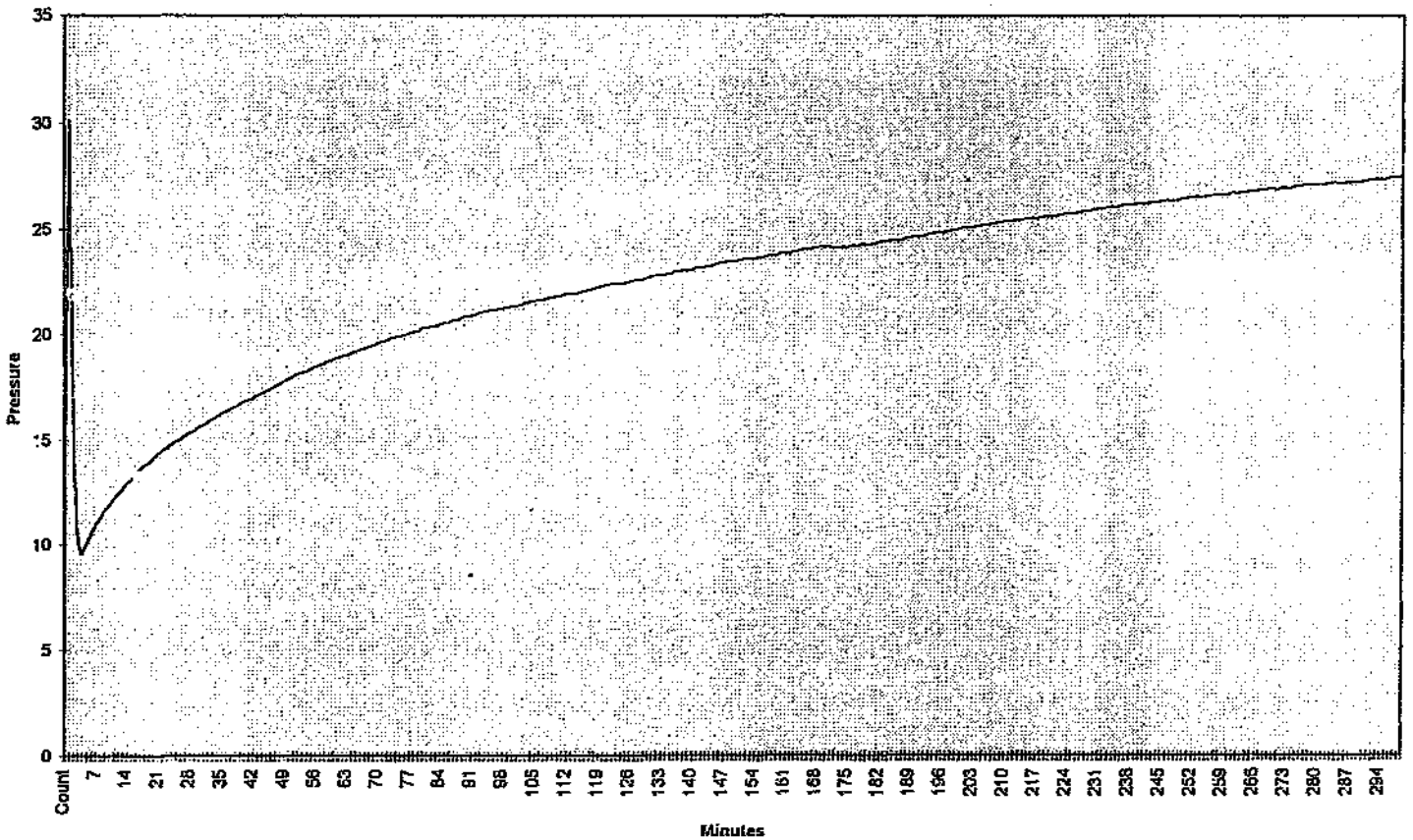

20 July
Pressure (kPa)
Minutes

22 July

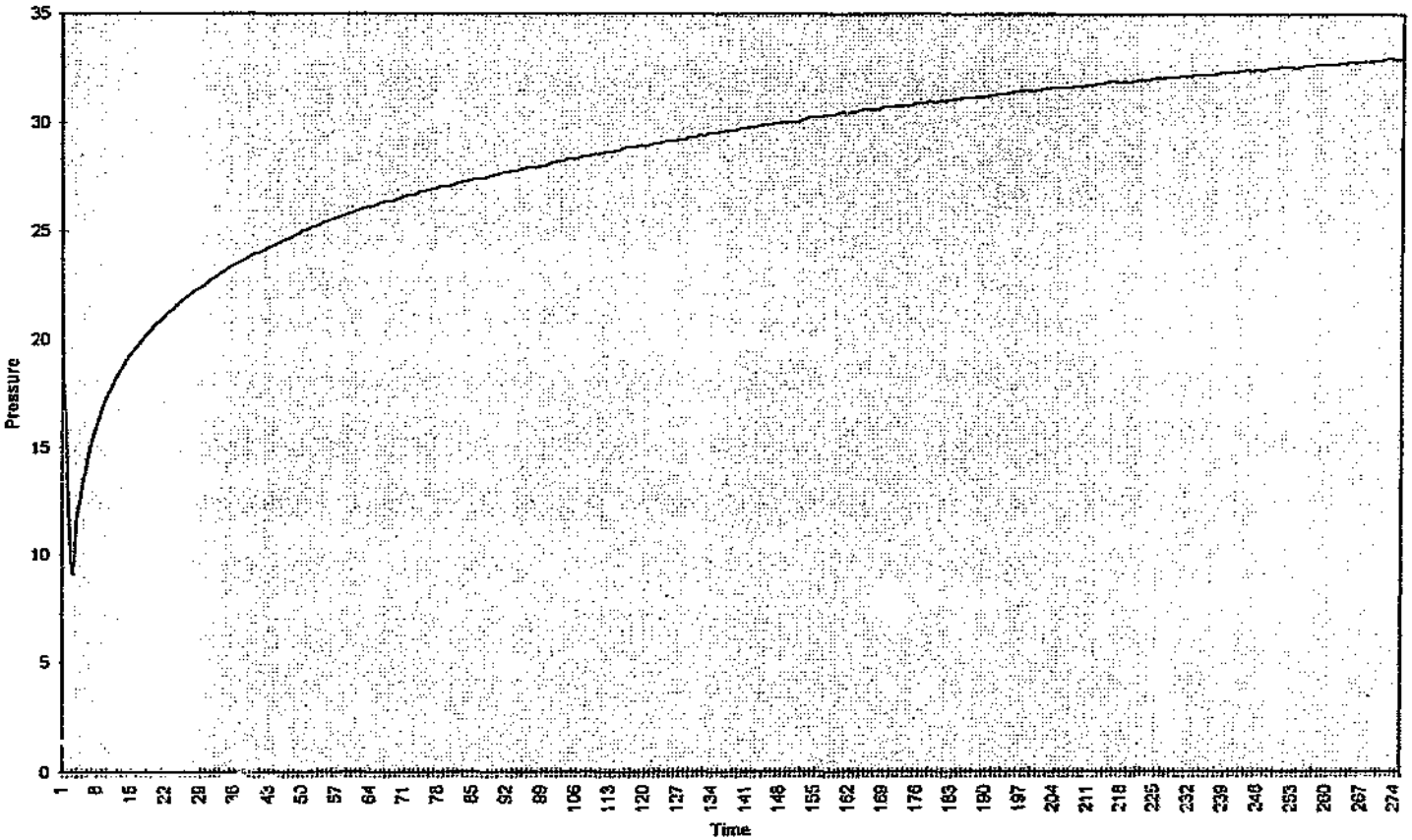

Pressure
Minutes
0
5
10
15
20
25
30
35
40
2
7
12
17
22
27
32
37
42
47
52
57
62
67
72
77
82
87
92
97
102
107
112
117
122
127
132
137
142
147
152
157
162
167
172
177
182
187
192
197
202
207
212
217
222
227
232
237


19 August
Pressure
Minutes
0
2
4
6
8
10
12
14
16
18
20
4
9
14
19
24
29
34
39
44
49
54
59
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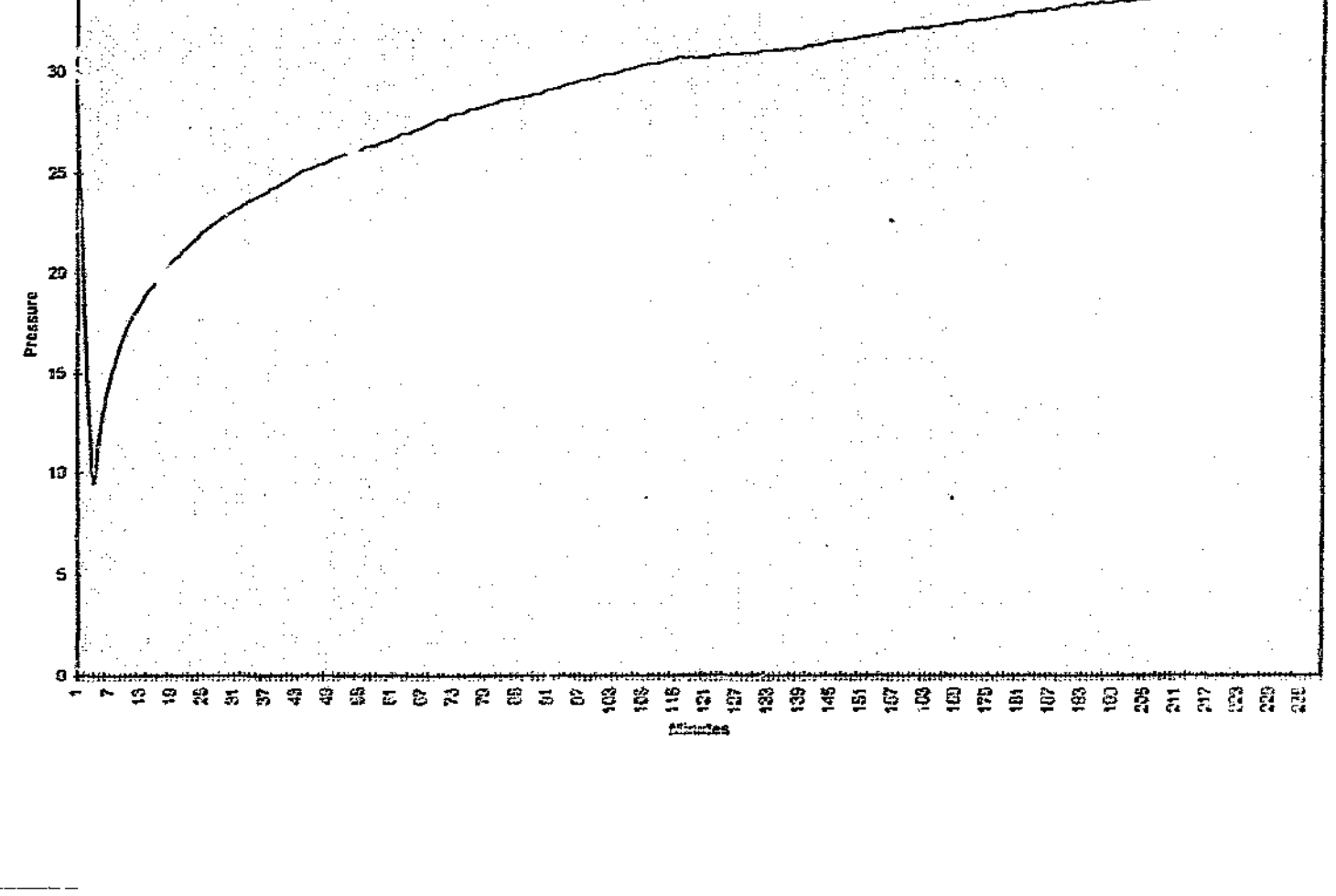
16 November


35
30
25
20
15
10
5
0
Pressure
Count
7
14
21
28
35
42
49
56
63
70
77
84
91
98
105
112
119
126
133
140
147
154
161
168
175
182
189
196
203
210
217
224
231
238
245
252
259
265
273
280
287
294
Minutes

17November


Pressure
Time
0
5
10
15
20
25
30
35
1
8
15
22
29
36
43
50
57
64
71
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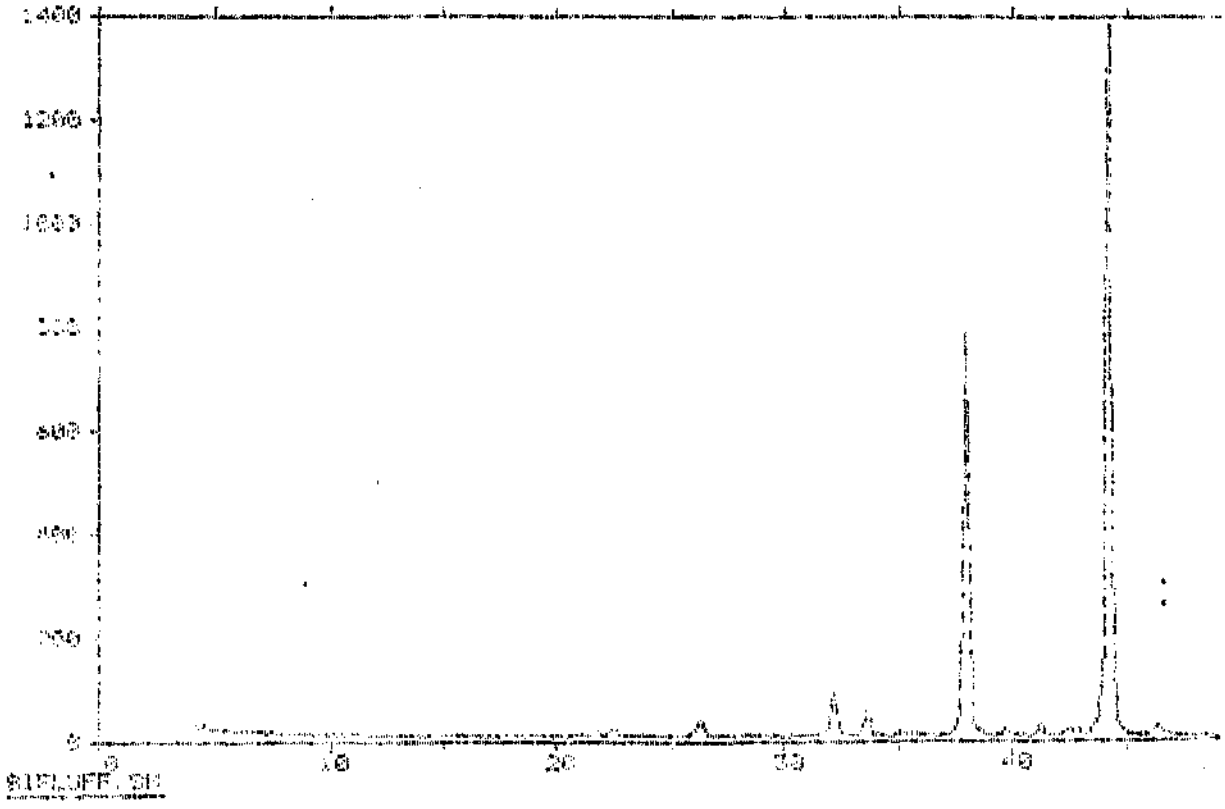
21 November

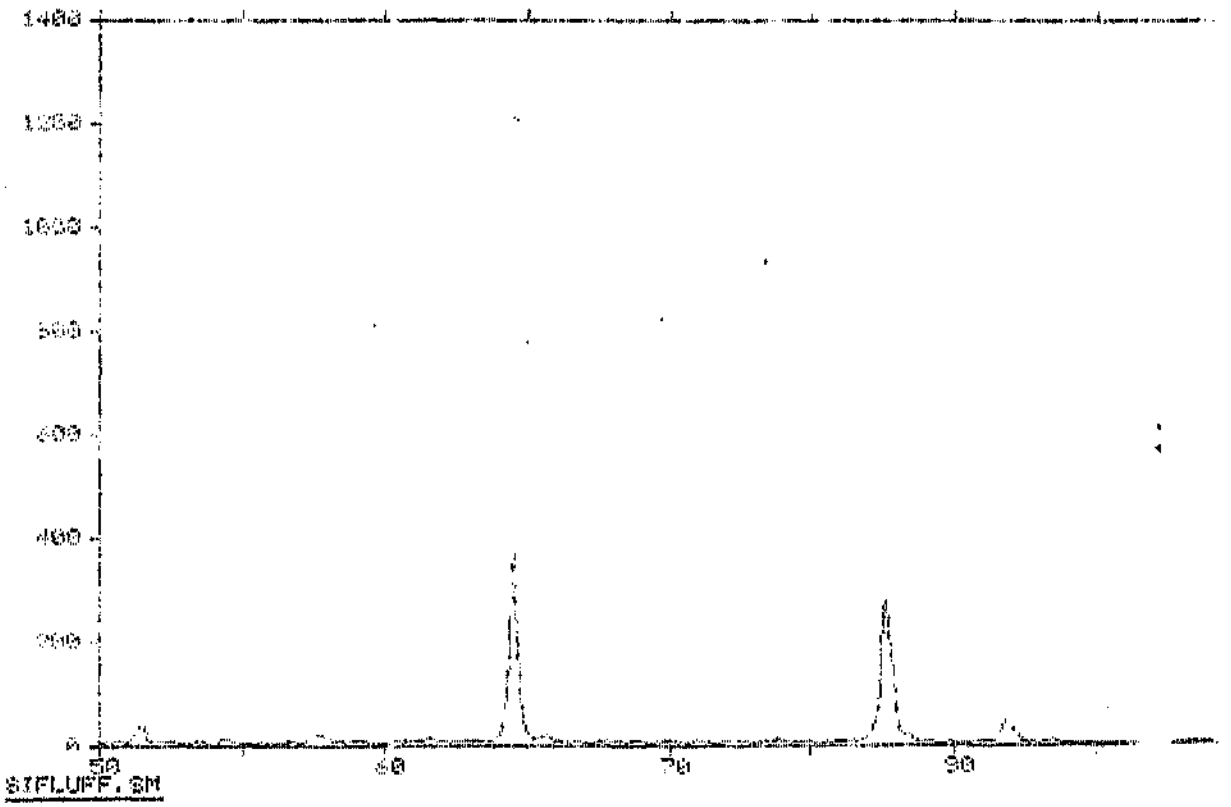


APPENDIX B X-Ray Diffraction Analysis on Condensate

HIGH METALLOMY DSET.

peak	ht	area	width	area	peak	filter	signal/noise
no.	(mm)	(mm)	(min)	counts	(min)	(%)	
1	[illegible]	22.363	0.213	14	1	1.32	.43
2	[illegible]	34.413	0.655	37	1	2.47	0.78
3	[illegible]	37.439	0.200	13	1	2.73	0.76
4	[illegible]	39.279	0.553	37	1	5.52	1.53
5	[illegible]	40.[illegible]	[illegible]	[illegible]	1	3.35	1.01
6	[illegible]	41.[illegible]	[illegible]	[illegible]	1	2.17	0.83
7	[illegible]	42.[illegible]	[illegible]	[illegible]	1	11.47	1.92
8	[illegible]	43.[illegible]	[illegible]	[illegible]	1	1.34	0.70
9	[illegible]	44.[illegible]	[illegible]	[illegible]	1	0.32	1.00
10	[illegible]	45.[illegible]	0.200	[illegible]	1	3.53	0.41
11	[illegible]	46.[illegible]	0.320	[illegible]	1	0.90	0.71
12	[illegible]	47.[illegible]	0.353	[illegible]	1	1.77	1.75
13	[illegible]	48.[illegible]	[illegible]	[illegible]	1	0.70	0.53
14	[illegible]	49.[illegible]	0.453	[illegible]	1	0.95	1.36
15	[illegible]	[illegible]	0.850	[illegible]	1	87.45	0.78
16	2.0539	44.125	0.050	1142	3	100.00	0.90
17	1.9610	48.259	0.200	[illegible]	2	1.69	1.53
18	1.8112	50.340	0.130	[illegible]	0	0.90	0.91
19	1.7731	51.500	0.143	[illegible]	1	2.75	1.73
20	1.6851	54.423	0.240	[illegible]	0	0.90	1.01
21	1.6427	55.930	0.120	[illegible]	0	0.90	0.75
22	1.6000	57.560	0.400	[illegible]	1	1.20	1.47
23	1.5217	60.525	0.160	[illegible]	1	0.90	0.85
24	1.5054	61.555	0.240	[illegible]	1	0.90	1.83
25	1.4936	62.463	0.160	[illegible]	1	0.90	1.31
26	1.4425	64.593	0.060	[illegible]	2	24.71	0.86
27	1.4344	64.960	[illegible]	[illegible]	1	1.69	0.84
28	1.4211	65.565	[illegible]	[illegible]	1	1.21	1.33
29	1.3993	66.605	[illegible]	[illegible]	1	0.90	2.39
30	1.3823	67.735	[illegible]	[illegible]	0	0.90	0.79
31	1.3437	69.840	0.120	[illegible]	0	0.90	0.75
32	1.3270	70.940	0.320	[illegible]	0	0.90	0.99
33	1.2946	72.698	0.160	[illegible]	0	0.90	0.93
34	1.2547	75.219	0.120	[illegible]	1	0.90	0.90
35	1.2326	76.338	0.242	[illegible]	1	0.94	1.01
36	1.2291	77.620	0.140	[illegible]	1	25.15	3.54
37	1.1689	80.770	0.320	[illegible]	1	0.90	0.82
38	1.1754	81.810	0.140	[illegible]	0	4.05	1.22
39	1.1593	83.285	0.240	[illegible]	0	0.90	1.39
40	1.1202	86.885	0.120	[illegible]	0	0.90	0.88
41	1.1055	88.340	0.060	[illegible]	0	0.90	1.34
42	1.1023	88.660	0.240	[illegible]	0	0.90	1.09
43	1.0948	89.435	0.240	[illegible]	0	0.90	0.79


1400
1200
1000
800
600
400
200
0
0
10
20
30
40
SILICONE OIL


50
60
70
80
SIFLUFF.SM

APPENDIX C EDX Impurity Analysis Results

Spectrum file : DJCBUB02 Spectrum :
LIVETIME = 100 I/P = 3688 cps

ENERGY	FWHM	AREA
1.8	88.89	54884
7066.6	121.74	11591

TOTAL AREA = 366600 GF = 1.037

CURRENT ELEMENT LIST :- 1 : 32 p.a. on 11 /Aug / 1990

CURRENT ELEMENT REFERENCE FILE : I:\ASHSTD.DT

EL	L	R	KV	TILT	ELEV	AZIM	PROFILE	VAL	CST%	FST	CONDITION
La	L	0	20.0	.00	40.00	.00	LAL$	3	88.15	.9230	
P	K	0	20.0	.00	40.00	.00	PSK$	5	30.79	.7420	
Al	K	1	20.0	.00	40.00	.00	ALK1	3	100.00	1.0000	
Si	K	1	20.0	.00	40.00	.00	SIK1	4	100.00	1.0000	
Cr	K	1	20.0	.00	40.00	.00	CRK1	3	100.00	1.0000	
Mn	K	1	20.0	.00	40.00	.00	MNK1	2	100.00	1.0000	
Fe	K	1	20.0	.00	40.00	.00	FEK1	3	100.00	1.0000	

Spectrum file : DJCBUB02

LIVETIME(spec.) = 100

ENERGY	RES	AREA
1.8	86.8?	54884

TOTAL AREA = 348606

Peak at .68 keV omitted ?

FIT INDEX = 5.47

ELMT	APP.CONC	ERROR(1 SIGMA)
LaL : 0	.043	.116 = 1 Sigma =
P K : 0	-.063	.038 = Between 1 and 2 Sigma =
AlK : 1	.298	.052
SiK : 1	.431	.032
CrK : 1	.202	.270 = Between 2 and 3 Sigma =
MnK : 1	.099	.065
FeK : 1	56.701	.2-8

ZAF CALCULATIONS

..5 2 iterations3

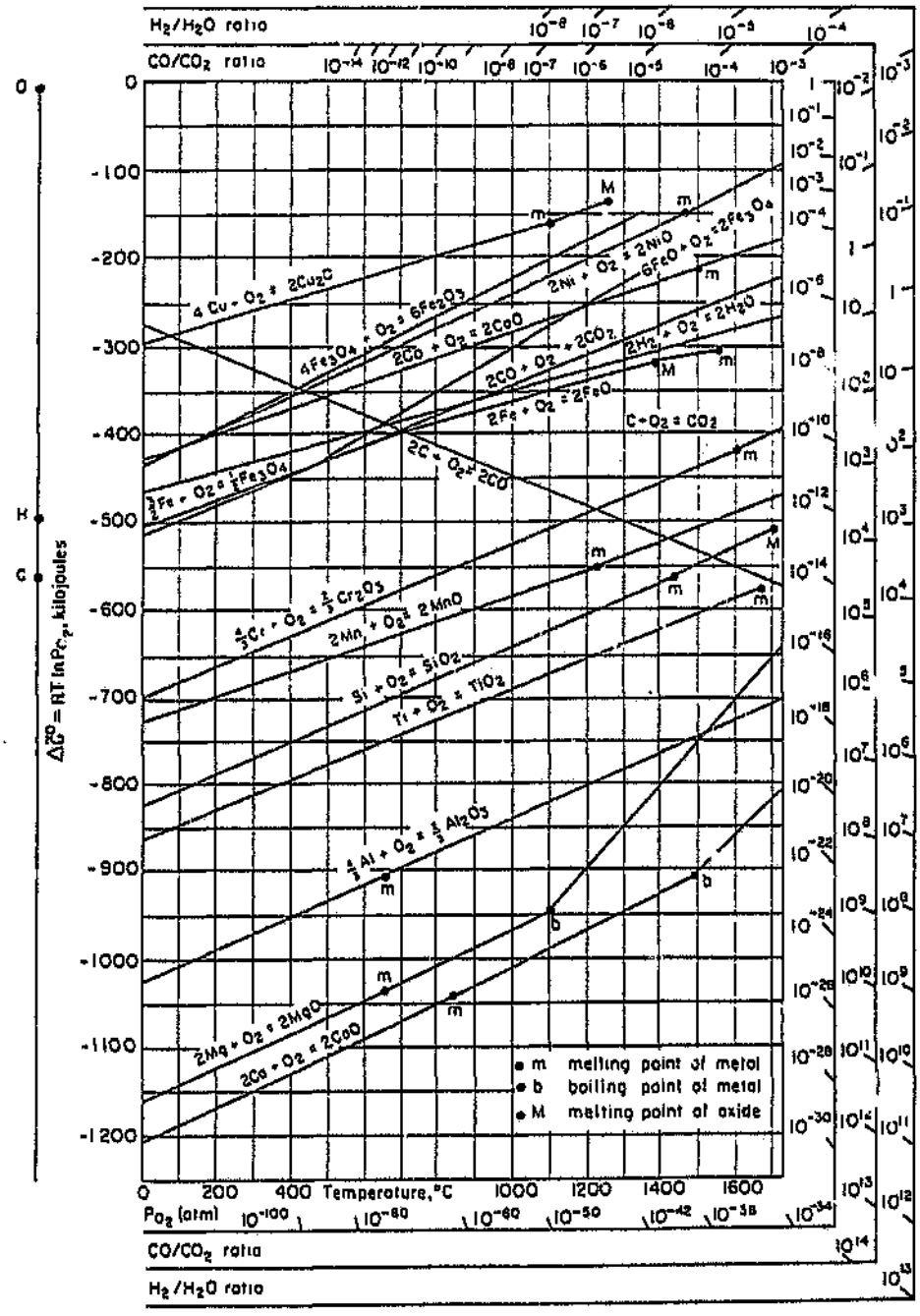
30.00 kV TILT = .00 T.O. = 40.00 AZIM = .00 COSINE = 1.000

Spectrums DJCSUS

All elmts anal/sed

ELMT	ZAF	Ratio	%E_MT		Error		ATOM.%
LaL : 0	1.052		.041	+-	.120	<1 sd	below confidence limit
P K : 0	.916		-.069	+-	.061	<2 sd	warning -ve conc. not in totals
AlK : 1	.451		.660	+-	.070		2.369
SiK : 1	.591		.728	+-	.054		2.394
CrK : 1	1.273		.158	+-	.055	<3 sd	.281
MnK : 1	.973		.513	+-	.098		.861
FeK : 1	.995		57.004	+-	.249		94.205
TOTAL			59.063				100.000

APPENDIX D Ellingham Diagram for Some Oxides (From Ref. 15)



Ellingham diagram for some oxides; Richardson nomographic scales are included. (Adapted from D. R. Gaskell, *Introduction to Metallurgical Thermodynamics*, 2nd ed., Hemisphere Publishing, New York, 1981.)

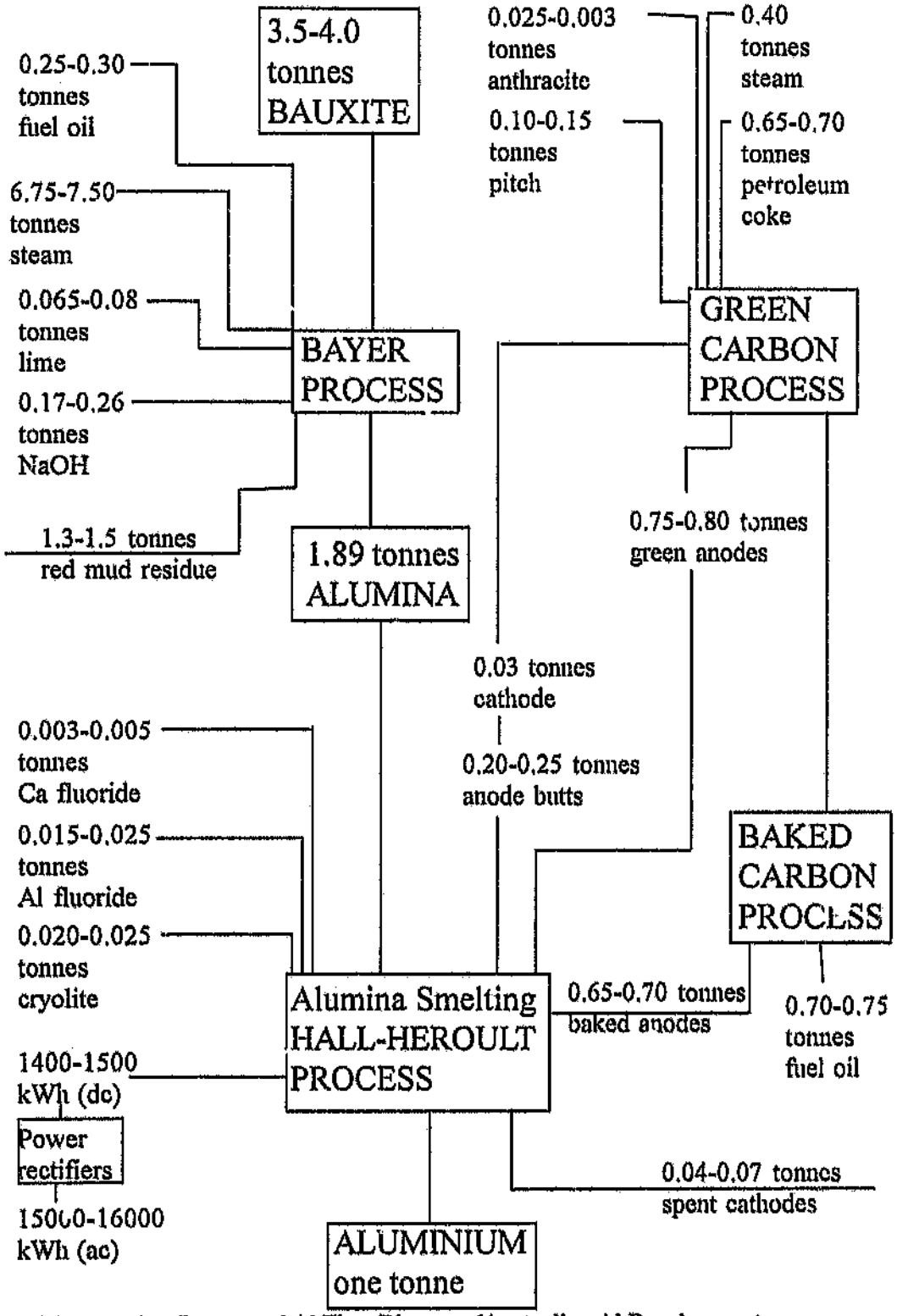


Figure 2.2 Integrated Al Flow Diagram (Australian Al Development Council)

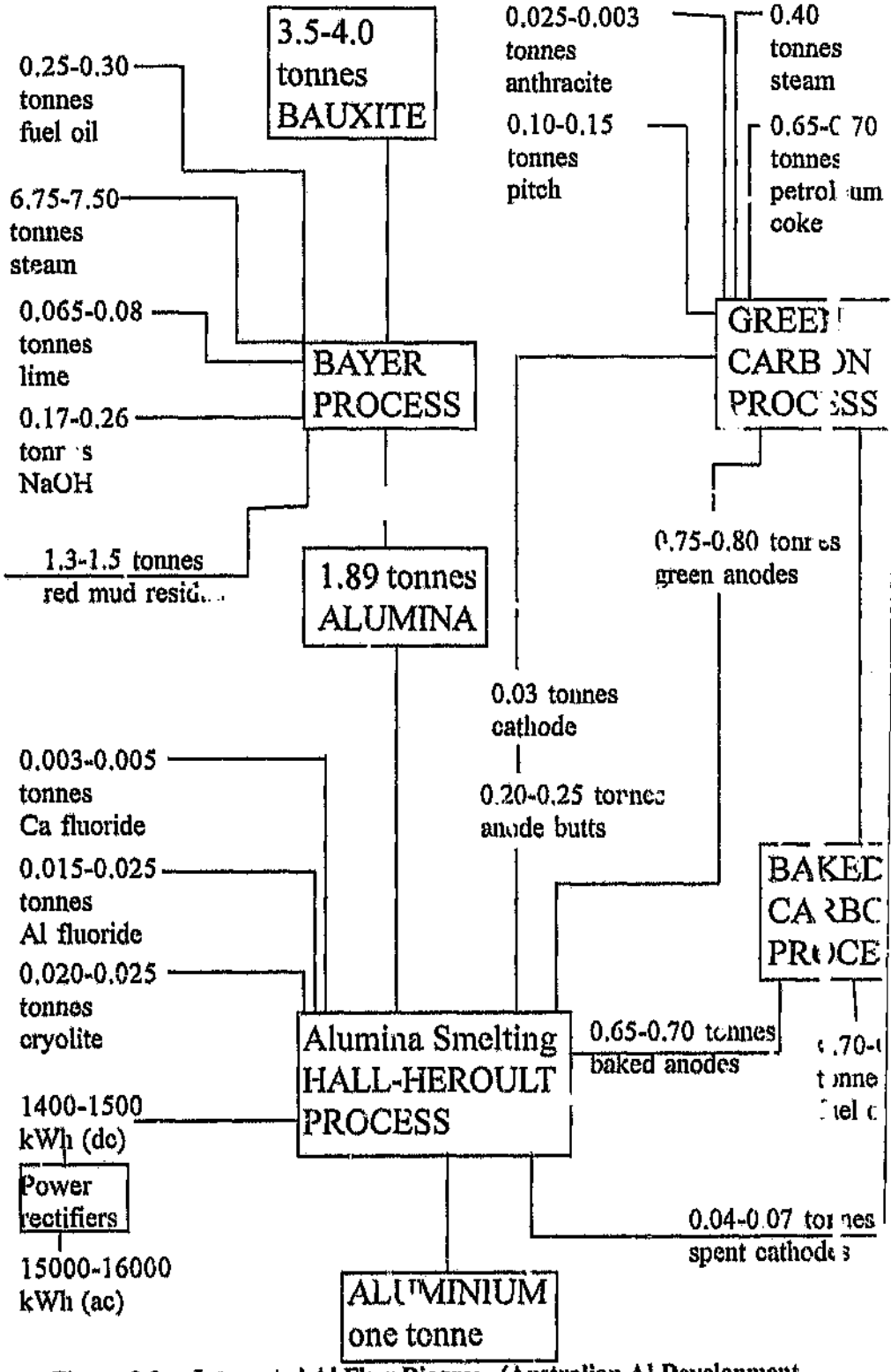


Figure 2.2 Integrated Al Flow Diagram (Australian Al Development Council)

Author: Caizergues, Derek.
Name of thesis: Carbothermic reduction of alumina into a metallic solvent phase.

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