PRODUCTION AND APPLICATION OF AlCl₃ AS A REDUCTANT FOR SOLAR GRADE SILICON MANUFACTURE

by

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Abstract

Solar grade silicon is currently produced mainly through blending semiconductor grade silicon waste with metallurgical grade silicon. As the demand for solar cells continues to increase rapidly, soon demand will outstrip supply of semiconductor grade silicon waste. A process for producing solar grade silicon efficiently and without relying on other industries is needed. It is proposed to produce solar grade silicon of 6N purity (99.9999%) by reacting silicon tetrachloride with aluminum monochloride via the following reaction:

\[ 2 \text{AlCl}_3(g) + \text{SiCl}_4(g) \rightarrow \text{Si}(s) + 2 \text{AlCl}_3(g) \]

Aluminum monochloride is proposed as the reductant for silicon tetrachloride because it is an extremely strong reducing agent and the reaction will produce all gaseous by-products. Additionally, the aluminum trichloride produced can be recycled to form more aluminum monochloride, which is produced by reacting aluminum metal with aluminum trichloride in the following reaction:

\[ \text{AlCl}_3(g) + 2 \text{Al}(l) \rightarrow 3 \text{AlCl}_3(g) \]

High yields of AlCl have only been found above 1200°C, with very little AlCl present in equilibrium with Al and AlCl\textsubscript{3} at lower temperatures. The high temperatures under which AlCl can be found in larger quantities makes it difficult to determine if the AlCl\textsubscript{3} reacting with Al is actually producing AlCl as opposed to another subhalide such as AlCl\textsubscript{2}. Numerous IR spectroscopy studies have been undertaken to confirm that the reaction of aluminum trichloride gas with molten aluminum does produce aluminum monochloride, with all such studies confirming that this theoretical path is correct. Unlike previous studies, which pass the AlCl\textsubscript{3} gas over molten aluminum, it is proposed to bubble the AlCl\textsubscript{3} gas into the molten aluminum. This should increase yield of aluminum monochloride, which was not a priority in previous studies.
In order to achieve the project objectives a literature review of silicon manufacturing techniques as well as aluminum monochloride production was completed. Experiments to determine the rate of sublimation of aluminum trichloride were to be done in order to determine what temperature at which to sublime the aluminum trichloride. Aluminum trichloride was bubbled into aluminum metal to form aluminum monochloride with experimental conditions being varied to increase yield. Yield was determined through analysis of the reaction products, which was difficult due to the instability of aluminum monochloride, which dissociates at room temperature back into aluminum trichloride and aluminum metal. After the yield of aluminum monochloride was maximized, silicon tetrachloride was introduced into the reactor to react with the aluminum monochloride to form silicon metal.
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Chapter 1

Introduction

The purpose of this work is to investigate the potential of using aluminum monochloride (AlCl) as a reductant in chemical reactions and more specifically in the production of silicon from silicon tetrachloride (SiCl$_4$) via reaction 1:

$$2\text{AlCl}_3(g) + \text{SiCl}_4(g) \rightarrow \text{Si(s)} + 2\text{AlCl}_3(g) \quad [1]$$

There has been some research into the conditions necessary to form AlCl, however very few papers cover the rates of formation and do not address issues around commercial (tonnage) production. This thesis will focus on the most likely commercial method to produce AlCl, the injection of gaseous aluminum trichloride (AlCl$_3$) into molten aluminum; however, there are other possible approaches to producing AlCl and these will be briefly covered. None of the papers reviewed has shown any work on AlCl reacting directly with aluminum metal through injection in molten aluminum. Since the long term goal of the thesis is to research silicon production through gaseous reaction of AlCl and SiCl$_4$, it would be useful to begin with an outline of current and proposed methods of silicon production.

1.1 Silicon Production

Pure silicon is derived from silica or silicate-containing compounds, normally quartz, via carbothermic reduction. The carbothermic reduction process consists of three steps$^1$: First, the silica is reduced by carbon via reaction 2:

$$\text{SiO}_2(l) + C(s) \rightarrow \text{SiO}(g) + \text{CO}(g) \quad [2]$$

Next, the silicon monoxide is reduced via reaction 3:
\[
\text{SiO}_2(g) + 2\text{C}(s) \rightarrow \text{SiC}(s) + \text{CO}(g) \quad [3]
\]

Finally the silicon carbide is reduced to silicon metal via reaction 4:

\[
\text{SiC}(s) + \text{SiO}_2(l) \rightarrow \text{Si}(l) + \text{SiO}(g) + \text{CO}(g) \quad [4]
\]

The silicon produced after carbothermic reduction is metallurgical grade silicon (MGS), which has a purity of approximately 98.0% - 99.0% and can be used directly as an alloying agent or further refined to make ultra high purity polysilicon for electronic applications. Currently, 90% of the production of polysilicon is accomplished through the Siemens process, while the rest is manufactured using the Union Carbide or Ethyl Corporation processes, see Figure 1.¹

![Figure 1: Relative Share of Production for Solar Grade Silicon (2006)](image)

As can be seen in Figure 1, the Siemens process accounts for the majority of the solar grade silicon produced. FBR are Fluidized Bed Reactor based processes that use silane (SiH₄), which includes both the Union Carbide and Ethyl Corporation processes, while UMGSI stands for Upgraded Metallurgical Grade Silicon.

The majority of polysilicon produced is for the semiconductor industry and is of a purity of 9N or 99.9999999% silicon. Solar grade silicon only requires a purity of 6N, 99.9999%, and contain less than 0.00001% each of boron and phosphorus (the major impurities), and can be produced using waste semiconductor silicon blended with metallurgical grade silicon.
1.1.1 Siemens Process

The Siemens process upgrades the metallurgical grade silicon produced by carbothermic reduction by first reacting it with anhydrous hydrochloric gas at 350°C in a fluid bed to produce trichlorosilane, as shown by reaction 5:

$$\text{Si}(l) + 3\text{HCl}_(g) \rightarrow \text{HSiCl}_3(g) + \text{H}_2(g)$$  \[5\]

Trichlorosilane has a low boiling point and high volatility, which makes it easy to separate from impurities found in metallurgical grade silicon such as phosphorus and boron. The reaction of silicon with anhydrous hydrochloric acid produces other undesired silanes which are removed through a fractional distillation step. The resulting trichlorosilane is of 8N purity. The trichlorosilane is decomposed by mixing with a stream of high purity hydrogen in a deposition reactor where the silicon is deposited onto heated silicon seed rods, as shown by reaction 6:

$$\text{SiHCl}_3(g) + \text{H}_2(g) \rightarrow \text{Si}(s) + 3\text{HCl}(g)$$  \[6\]

The silicon seed rods are heated to 1100°C electrically and the deposition chambers are steel bell jars that contain 30 inverted U-rods. This is because it is necessary that the silicon deposits only on the seed rods and not on the chamber walls, which are water cooled to ensure this. Once the rods reach a desired thickness, they are removed and the batch process begins again with new seed rods. Electrical heating of the seed rods along with multiple distillation steps and batch processing makes this process highly energy intensive and therefore very expensive ($25-$30/kg).³

1.1.2 Union Carbide Process

The Union Carbide process similarly starts off by producing a trichlorosilane stream, but then this is fed into a packed bed reactor with an ammonium ion exchange resin to produce gaseous silane, which is then deposited on seed rods similar to those used in the Siemens process.
1.1.3 Ethyl Corporation Process

The Ethyl Corporation process uses a completely different approach, using silicon fluoride instead of metallurgical grade silicon as the feed material. The silicon fluoride is hydrogenated in the presence of a metal aluminum hydride to produce silane, as shown in reaction 7:

\[
\text{SiF}_4(g) + \text{AlMH}_4(g) \rightarrow \text{SiH}_4(g) + \text{AlMF}_4(g)
\]  

[7]

The silane is distilled to purify it and then deposited on silicon seed spheres in a fluid bed reactor. This results in silicon spheres of 9N purity, 1mm in diameter. This presents many advantages over the bell reactor including continuous operation, lower operating temperature, a reduced cooling requirement, lower production costs and higher throughput.

1.2 Impurities

Impurities in solar grade silicon are important because of allowable doping levels in semiconductors. Boron and phosphorous are both used as dopants in silicon crystals replacing a silicon atom and thereby enhancing conductivity. The doping of too much boron and phosphorous results in the silicon matrix moving into the conductive range and no longer functioning as a semiconductor, and the semiconductor is then considered degenerate. This prohibits use as a solar cell by making it impossible for the silicon to retain the solar energy. The silicon will absorb the energy, but act as a conductor and merely act as a medium for the energy to pass through as opposed to converting the energy. Limits on the amount of doping are in the parts per million range, with significant decrease in silicon semiconductor behaviour above 0.2 ppm phosphorus and 1 ppm boron.⁴
1.3 Current Market

The use of the Siemens process to produce 90% of the polysilicon thus means 90% of the solar grade silicon in the world relies on the Siemens process, which is highly energy intensive and requires extensive by-product recycling. The demand for solar cells has been compounding at an annual rate of 20%. The demand for solar grade silicon will soon outweigh the supply available from scrap from the semiconductor industry. Figure 2 shows the rapid growth of photovoltaic cell production over the last couple of years (in GW per year, GW being energy produced), along with predicted growth.

![Graph showing photovoltaic cell production growth](image)

Figure 2: Photovoltaic Cell Production Growth

This increase in demand outweighs current production capability and therefore causes inflation of the cost of solar grade silicon.
Figure 3 shows 2006 solar grade silicon manufacturers and their market share. Renewable Energy Corporation (REC) makes solar grade silicon via the Siemens process, and is in the process of developing fluidized bed reactor technology at their Moses Lake Plant in Washington. Wacker Chemie AG has separated out their photovoltaics business into a separate company named Siltronic AG, and their silicon is produced mainly for the semiconductor industry. Hemlock makes solar grade silicon by the Siemens process, as do Tokuyama, Mitsubishi and MEMC. Newer manufacturers (such as Timminco and Reaction Sciences Inc. (RSI)) are going with new processes, many of which are proprietary. Most of these new process plants are behind schedule.

![Figure 3: Polysilicon Producers (2006)](image)

Figure 3: Polysilicon Producers (2006)$^{2}$

Costs of production for Siemens-produced silicon is $25-$30 per kilogram.$^{3}$ RSI claims that they can produce silicon for $7-$9 per kilogram with a new proprietary process. Their plant was supposed to start up in Q2 of 2010 and, despite missing their deadline, they have not issued any press releases with an update. Timminco claimed in 2007 that, through a proprietary process, they could produce solar grade silicon at the very low cost of $10/kg$^{6}$, and made plans to produce 3,600 tonnes in 2010 with expansion capability to 14,000 tonnes.$^{7}$ Timminco stock rose from pennies up to over $30$$^{7}$ per share on the announcement, only to drop back down to $1$ once it
became clear that Timminco had greatly underestimated the production cost of their solar grade silicon along with a crash in solar grade silicon demand and price that coincided with the market crash in September 2009. They have since sold 49% of their solar grade silicon subsidiary company, Becancour Silicon Inc, to Dow Corning Corporation in order to recoup some of their losses on the project.\textsuperscript{8}

Ideally, a process could be found to produce solar grade silicon energy and cost-efficiently without relying on the wastes from the semi-conductor silicon industry. The reaction of aluminum monochloride with silicon tetrachloride is being suggested as an alternative to current solar grade silicon production. AlCl\textsubscript{3} is proposed as a reducing agent for the silicon tetrachloride because it is a very strong reducing agent, and the by-product of this reaction would be AlCl\textsubscript{3}, which can then be recycled to produce more AlCl. In the next Chapter, different methods of producing AlCl will be analyzed.
Chapter 2

Background

Aluminum monochloride will be made by reacting aluminum trichloride with aluminum metal via the following reaction, reaction 8:

$$\text{AlCl}_3(g) + 2\text{Al}(s) \rightarrow 3\text{AlCl}(g)$$  \[8\]

The volatile aluminum monochloride will then be used to create pure silicon by reacting with silicon tetrachloride, shown by reaction 9:

$$2\text{AlCl}(g) + \text{SiCl}_4(g) \rightarrow \text{Si}(s) + 2\text{AlCl}_3(g)$$  \[9\]

This reaction is favourable due to the fact that aluminum monochloride is a strong reductant and is extremely reactive.

As seen in the flowsheet of Figure 4, the by-product AlCl$_3$ can also be recycled to produce more AlCl and the silicon metal should drop out as a powder, while the AlCl$_3$ will remain in a gaseous state. Using metal chlorides to produce pure metals is common in the metal production industry and much research has been done into new processes using chlorination to replace using metal oxides, which are difficult to separate and purify.
2.1 Volatile Metal Chlorides

Metal extraction and purification processes often start with metal oxides or sulphides which are then converted to oxides. The problem is then finding a way of extracting the metal of interest from the mixture of metal oxides and converting it to the pure metal. Typically the extraction of the metal oxide of interest is done through leaching, electrolysis or heating to high temperatures with a slag. For metals such as aluminum, molten salt electrolysis is used due to the fact that light metals react with water which is fairly energy intensive. One solution for hard-to-purify metal oxides (such as tantalum) is chlorination followed by either selective condensation, fractional distillation or commonly a mixture of both.

Metal chlorides are often formed during the metal refining process as an intermediary step between the oxide and pure metal. Chlorination of metal oxides or metal oxide-containing
ores is accomplished through the addition of chlorine gas in the presence of a reducing agent. By chlorinating the metal oxides they can be selectively condensed to remove other metal impurities. A major issue with the processing of metal chlorides as intermediates is that they are extremely corrosive, which necessitates the use of corrosion-resistant materials in all handling equipment. Also, any moisture in the air will react with volatile metal chlorides to produce hydrogen chloride gas, which both adds to the corrosiveness and requires scrubbing operations.

Carbochlorination is the dominant method of chlorination of metal oxides for purification, for example in the extraction of tantalum from ore; the following metal oxides are carbochlorinated prior to separation via fractional distillation:

\[
\begin{align*}
\text{Fe(TaO}_3\text{)}_2 + 6\; C + 6\; \frac{1}{2}\; Cl_2 \rightarrow 2\; TaCl_5 + FeCl_3 + 6\; CO \\
\text{Fe(NbO}_3\text{)}_2 + 6\; C + 6\; \frac{1}{2}\; Cl_2 \rightarrow 2\; NbCl_5 + FeCl_3 + 6\; CO \\
\text{Mn(TaO}_3\text{)}_2 + 6\; C + 6\; Cl_2 \rightarrow 2\; TaCl_5 + MnCl_2 + 6\; CO
\end{align*}
\]

Carbochlorination has environmental issues, mainly because it produces a lot of CHCs like dioxins and furans, as well as the formation of carbon monoxide (CO), all of which are worse greenhouse gases than CO\(_2\). The advantage of using carbon as a reducing agent is mainly that it is very cheap and does not interfere in the reaction or produce by-products and is also effective, unlike many other reductants.

The most readily chlorinated metal oxides are chlorinated first, and then can be removed through a fractional distillation step utilizing the much lower boiling point of metal chlorides compared to metal oxides. A large number of metal oxides can be separated this way in alternating selective chlorination and fractional distillation steps (see Figure 5), often with selective condensation steps in between (if cooling prior to chlorination is required this increases the efficiency).
Figure 5: Selective Chlorination in Series for AlCl₃ Production

Figure 5 shows a selective chlorination process with selective condensation for AlCl₃ product. First iron oxides are chlorinated using HCl(g) as the chlorinating agent and then the gas mixture is run through a condenser where the metal oxides are condensed and the ferric chloride is removed as a gas. After further condensing the metal oxides, the mixture is fed into another chlorination step where titanium oxide is chlorinated to TiCl₄ and then the TiCl₄ is removed as a gas in a third condenser. In the third chlorination step, the remaining metal oxides are chlorinated and removed in the final condenser. This is very similar to the purification process for SiCl₄, which is being used as a feed for the reaction with AlCl in the proposed silicon manufacturing process.
Selective condensation of metal chlorides requires very strict temperature control as it mainly relies on the difference in boiling points between all the chlorides to separate them. Selective condensation requires slowly cooling the chloride mixture, condensing out metal chlorides one at a time, allowing removal of each condensed species independently. One problem often encountered in both selective condensation and fractional distillation is occlusion of the target species by impurities. Often there exist in ores many metal chlorides with boiling points extremely close together, rendering it difficult if not impossible to remove the impurities completely or very efficiently. Depending on the ore and therefore mixture of metals some metal chlorides formed can occlude the target chloride and condense simultaneously, despite having very different boiling points. This is usually due to complexes being formed at the temperatures necessary in such operations. Due to the range of boiling points, selective condensation and fractional distillation are often used in series, removing a different impurity or set of impurities in each stage. As this includes heating and cooling in stages, it requires a lot of energy. Another expense can be additives, which are added to precipitate out impurities in selective condensation processes and can be costly (see Appendix A for further discussion on selective chlorination).

2.2 AlCl Production Reactions

There are a number of different methods of producing AlCl described in literature. All of these methods, except reaction of Al with HCl, involve AlCl$_3$ gas. The difference between these methods is therefore the chemical used as the reducing agent to remove the two chlorides from the AlCl$_3$. The most common methods are carbothermic reduction of the metal chloride using carbon and reduction using a pure metal. It is proposed to follow the second method and reduce the AlCl$_3$ using pure liquid aluminum metal.

In a paper by Tacke and Schnöckel$^{11}$, AlCl was produced by the reaction:
\[ \text{Al}_{(l)} + \text{HCl}_{(g)} = \text{AlCl}_{(g)} + \frac{1}{2} \text{H}_2(g) \]  

[13]

at 1200K and <0.2 bar and yielded >90% conversion. They found that AlCl was only stable as a solid at 77K, which is much lower than the reaction, which occurs at 180K:

\[ 3\text{AlCl}_{(s)} = \text{AlCl}_3_{(s)} + 2\text{Al}_{(s)} \]  

[14]

Another method of producing AlCl is by carbochlorination of alumina. Figure 6 shows a typical lab-scale carbochlorination setup.

![Carbochlorination Apparatus](image)

**Figure 6: Chlorination Laboratory-Scale Apparatus**

The carbon and ore are mixed together and charged to the furnace while the Cl\(_2\) is pumped in as a gas. By mixing the carbon in with the ore, good mixing and reaction kinetics are obtained. The carbochlorination process is fairly straightforward, not requiring any specialized equipment besides being closed due to the gases.

A comprehensive look at the carbothermic reduction reaction can be found in Peacey’s PhD thesis\(^{12}\), where the goal of producing aluminum monochloride was to purify aluminum metal:

\[ \text{Al}_2\text{O}_3 + 3\text{C} + \text{AlCl}_3 = 3\text{AlCl} + 3\text{CO} \]  

[15]
He found 88% conversion at 2073K using this process. Other processes are also mentioned as side reactions when using impure alumina as the starting material, as the impurities can also react with the aluminum trichloride at 2073K. Alternative reactions mentioned by Peacey that happen at similar temperatures (if he used low grade bauxite, clays with impurities, etc) are:

\[
\begin{align*}
2\text{Al}(l) + \text{AlCl}_3(g) &= 3\text{AlCl}_2(g) \quad [16] \\
\frac{1}{2} \text{Al}_4\text{C}_3(s) + \text{AlCl}_3(g) &= 3\text{AlCl}_2(g) + 3/2 \text{C}(s) \quad [17] \\
\text{Fe} + \text{AlCl}_3 &= \text{FeCl}_2 + \text{AlCl} \quad [18] \\
\text{SiC} + \text{AlCl}_3 &= \text{SiCl}_2 + \text{AlCl} + \text{C} \quad [19] \\
\text{AlCl}_3 + \text{H}_2 &= \text{AlCl} + 2\text{HCl} \quad [20]
\end{align*}
\]

At even higher temperatures, yet another method of producing AlCl is possible via thermal dissociation\(^{13}\):

\[
\text{AlCl}_3 = \text{AlCl} + \text{Cl}_2 \quad [21]
\]

However, due to the high temperatures required for yield and creation of chlorine gas, it is undesirable to produce AlCl through thermal dissociation.

### 2.2.1 Thermodynamics

High yields of AlCl have only been found above 1200°C using the proposed reaction \([16]\), with very little AlCl present in equilibrium with Al and AlCl\(_3\) at lower temperatures. The thermodynamic equilibrium that yields large quantities of AlCl occurs only at high temperatures makes it difficult to determine if the AlCl\(_3\) reacting with Al is actually producing AlCl as opposed to another sub-halide such as AlCl\(_2\). There have been a couple IR spectroscopy studies undertaken to confirm that the reaction of aluminum trichloride gas with molten aluminum does produce aluminum monochloride, with all such studies managing to confirm that this theoretical path is correct.
A paper by Russell et al\textsuperscript{14} investigated rates of reaction and yield of AlCl\textsubscript{3} as a function of AlCl\textsubscript{3} gas flow and as a function of temperature and pressure. The temperature and pressure relation with respect to yield can be seen in Figure 7.

![Figure 7: Temperature vs Pressure with Curves for Fraction of AlCl\textsubscript{3} Reacting\textsuperscript{14}](image_url)

As can be seen in Figure 7, the reaction favours high temperature and low pressure. Low pressure is favoured because the reaction results in an increase from one molecule of gas to three molecules of gas. To achieve >90% conversion at 1 atm of pressure (AlCl\textsubscript{3} and AlCl combined) temperatures in excess of 1400°C are required.

As can be seen in Figure 8, the data of which was obtained from FactSage\textsuperscript{15}, increasing the temperature increases the yield of AlCl and decreases the yield of the unwanted by-product AlCl\textsubscript{2}.  

23
As the AlCl formation reaction will be taking place between 1250°C and 1300°C, the gas composition from 1300°C was used from Figure 8 to calculate the yield of silicon over a range of operating temperatures, which can be seen in Figure 9. The yield decreases as the temperature increases, this is because SiCl$_2$ and SiCl$_4$ form in the gas phase. To get good yields, you have to go to low temperature ~1200°C and now you are competing with the formation of Al metal from the reverse reaction with AlCl.

Figure 8: Fraction of AlCl$_3$ Reacted vs Temperature$^{15}$
2.2.2 Kinetics

The effect of flow rate on the amount of AlCl$_3$ reacting with liquid aluminum can be seen in Figure 10.

The amount of AlCl$_3$ that reacts goes down with increasing flow rate, regardless of temperature. This makes sense as the AlCl$_3$ gas was flowing over the same amount of aluminum metal in
crucibles thus there is a limiting factor of surface area that increased gas flow rates is not going to impact. This is a problem with a reaction process that does not inject the AlCl₃ directly into Al metal and is especially important for industrial production where relatively high productivity is required.

2.3 AlCl₃ Sublimation

Since the method of producing AlCl will be reacting gaseous AlCl₃ with liquid aluminum, the rate of sublimation of AlCl₃ is an important factor to consider as it will have an impact on the length of preheating necessary prior to the reaction taking place as well as the temperatures that the sublimation needs to take place at. The sublimation of AlCl₃ takes place at 180°C, however the rate of formation of AlCl₃ gas at this temperature is quite low, and so it was important to sublimate the AlCl₃ at a temperature which would produce significant amount of gas at a rate able to sustain enough vapour pressure to bubble the AlCl₃ gas through molten aluminum. Along with experimental work done, research into other sources for the rate of formation with respect to temperature was conducted. From the literature, sublimation appears to be slow until temperatures over 350°C are reached¹⁶, so in many cases sublimation in the literature is done for long periods of time in batch reactors to ensure sublimation of all the aluminum trichloride.

2.4 Review of Apparatus in Literature

The equipment used in Peacey’s thesis consisted of a silicon carbide rod furnace capable of 1773 – 1873K temperature, recrystallized alumina tubes 1.2 m long and 32 mm bore as reaction tubes, a graphite crucible (to supply the carbon necessary for carbothermic reduction) as well as 5-20 Pt/Rh thermocouples, a H₂SO₄ bubbler for Ar and Cl and a gas meter. Peacey’s
approach to making the equipment was to attach everything together with alumina-containing cement and high temperature silicone sealant.

The equipment used in a paper by Russell et al\textsuperscript{14} detailing the reaction $\text{AlCl}_3 + 2\text{Al} = 3\text{AlCl}$, can be seen in Figure 11.

![Figure 11: Russell's Apparatus\textsuperscript{14}]

The equipment used in a spectroscopic investigation of $\text{AlCl}$ by Russell et al\textsuperscript{14} can be seen in Figure 12.
As can be seen in Figure 12, AlCl$_3$ was evaporated in a low temperature furnace connected to a high temperature furnace with two alumina boats containing aluminum with quartz windows dividing the high temperature furnace at either end from a low temperature furnace.

**2.4.1 Bubbling the AlCl$_3$ through the Liquid Al**

Bubbling gas through molten aluminum is a standard step in the aluminum recycling industry for removing magnesium. A patent$^{17}$ for treating a bath of liquid metal (aluminum in particular) by injecting gas consisted of a rotary agitator, the lower end of which rests on a gas injection plug disposed at the bottom of the bath and rises under the action of the pressure of the gas emitted by the plug rotating freely about its axis and allowing a multitude of regularly dispersed gas bubbles to escape through the space which separates the agitator from the plug. In a paper by Quan Fu et al.$^{18}$ on fluxing molten aluminum with chlorine, the following experimental set up (Figure 13) was used to bubble the chlorine into the aluminum:
The aluminum is in an alumina crucible inside a tube furnace and an alumina tube is inserted through which the chlorine is injected. The alumina tube was pre-heated prior to insertion in the aluminum and was reused for each run.

### 2.4.2 Carrier Gas

All of the papers mentioned above used argon as the carrier gas, although Peacey’s thesis mentions briefly using nitrogen gas and states it could possibly cause side reactions (depending on what impurities are in the reactants). It is important not to use air, as not only is the aluminum trichloride extremely reactive with moisture, it is also not desired to produce any alumina by reacting the aluminum with oxygen.

### 2.4.3 Chemical Analysis

Peacey’s thesis used the method of weighing the graphite crucible and the alumina tubes after calcination and gas flow rates, and compared these to calculated partial pressures to
determine efficiency. He also used XRF (x-ray fluorescence) to analyse the remaining components left as solid deposits and assumed most of the aluminum was deposited through the sub-halide reaction:

\[
\text{Al}_2\text{O}_{3(g)} + 3\text{C}_{(s)} + \text{AlCl}_{3(g)} = 3\text{AlCl}_{1(g)} + 3\text{CO}_{(g)} \tag{22}
\]

followed by rapid quenching to cause the aluminum deposition:

\[
2\text{AlCl}_{1(g)} = 2\text{Al}_{(s)} + \text{Cl}_{2(g)} \tag{23}
\]

In the experiment by Russell et al\textsuperscript{14}, spectroscopic equipment was built into the apparatus (Figure 12) to determine chemical composition without having to take a sample. In experiments done by Tacke and Schnöckel\textsuperscript{11}, AlCl was analysed by IR spectroscopy as a solid at low temperatures.

### 2.4.4 Designed Apparatus

In order to study the following reaction,

\[
2\text{Al}_{(l)} + \text{AlCl}_{3(g)} = 3\text{AlCl}_{1(g)} \tag{16}
\]

it is necessary to design apparatus capable of providing the necessary temperatures and reaction vessels:

The apparatus was designed as follows: there are to be two separate reactors in two separate furnaces connected by a pipe. The first reactor is used to sublimate the aluminum trichloride in crucibles at 250°C. The second reactor houses the liquid aluminum in another crucible and the gaseous aluminum trichloride bubbles into the liquid aluminum by flowing through a graphite pipe and exiting under the level of the liquid. This second reactor operates at 1250°C. The first reactor and connecting pipe are constructed out of stainless steel while the second reactor is constructed of alumina. This design was decided upon after review of the apparatus used in similar experimental work as outlined previously and is described in the next chapter.
2.5 Experiment Objectives

The objective of this research was to investigate producing silicon by reacting AlCl with SiCl₄. The following experiments were completed: AlCl₃ sublimation experiments, AlCl formation experiments, SiCl₄ evaporation experiments, and Si formation experiments.

The AlCl₃ sublimation experiments were done in order to determine optimum conditions for AlCl₃ sublimation, including temperature and rate. The AlCl formation experiments were done to optimize AlCl formation. The SiCl₄ evaporation experiments were done in order to determine optimum conditions for SiCl₄ evaporation, including carrier gas flow rate and rate. The Si formation experiments were used to determine if Si could be produced by the reaction of SiCl₄ and AlCl.
Chapter 3

Experimental

Aluminum monochloride has been successfully produced before, even using the same proposed mechanism of reacting aluminum trichloride and aluminum, so what makes this thesis work unique is having the apparatus set up to bubble the aluminum trichloride through the aluminum to increase yield. Previous work done has always passed the aluminum trichloride gas over the molten aluminum and has resulted in very poor yields of aluminum monochloride. In order to bubble the aluminum trichloride into the molten aluminum, a very different experimental apparatus was needed. The apparati used in previous testing that passed the gas over the molten aluminum were all arranged horizontally, with the gas flowing left to right over boats containing the aluminum sitting on the bottom. In order to bubble the gas through the aluminum, the set up would have to be designed vertically. This could be achieved easily by placing everything in a vertical tube furnace, except that the aluminum must be molten before the aluminum trichloride gas can bubble through it, which necessitated separating the aluminum and aluminum trichloride into two separate furnaces, to allow for stagewise heating. The fact that the aluminum must be molten before gas can bubble through it and the fact that the reaction and heating must take place under argon (to prevent oxidation) meant that the tube supplying argon and aluminum trichloride had to be able to be inserted and removed from the aluminum melt while everything was assembled and at high temperature. This was achieved by supporting a crucible containing the molten aluminum with a rod that extended out of the tube furnace through a swagelok fitting and adjusting it up and down.
3.1 Design of Apparatus

The experimental apparatus was designed to include two separate reactors in two separate furnaces, stacked vertically in order to allow for easy flow of the aluminum trichloride into the second reactor to bubble through molten aluminum. This can be seen in Figure 14, which shows an overview of the entire apparatus.

Figure 14: Experimental Apparatus
The bottom furnace controller is the base of the set up. The bottom furnace houses a tube reactor where the reaction between aluminum trichloride and molten aluminum is taking place, with the aluminum being melted in a crucible and the aluminum trichloride being fed into the aluminum from the top reactor through a graphite pipe. This furnace is a high temperature tube furnace made by Sentro Tech (model STT-1700-2.5-8/12) with molybdenum disilicide heating elements and is 50cm x 50cm x 50cm. The top furnace is used to sublime the aluminum trichloride, which is weighed into small crucibles and loaded into the top of the reactor. The two reactors are connected by a stainless steel pipe which is cut in the middle and held closed with latches. The top furnace is a lower temperature CRT 2C model from PSH that goes up to 1200°C. The top furnace sits on a metal table with adjustable legs, which in turn sits on the bottom furnace. The table is necessary to provide the space for the lid of the top reactor as well as the connecting pipe and has a hole in the middle to accommodate the pipe. Springs attached to the bottom of the table on either side of the hole help support the top reactor by means of hooks on the connecting pipe which sit on the springs. These hooks are welded near the middle of the pipe where it latches together. The bottom tubular reactor is also supported on the bottom by a stand.

Figure 15 shows a simplified view of the top reactor, which consists of a cylindrical chamber, compression fit lid (closed with latches, not shown) and the connecting pipe (which is actually two pieces held together with latches, one piece of which is welded to the top of the second reactor lid). The compression lid consists of a bottom ring of stainless steel which is placed on first, followed by a teflon o-ring and then a top lid of stainless steel placed on top, and the bottom and top pieces are then latched together, compressing the o-ring to form a seal. There are also 5 holes for fittings on the top of the lid, two of which were used for the thermocouple and thermowell and the gas inlet respectively, and the additional holes were capped.
Figure 16 shows a simplified view of the tube reactor where the aluminum monochloride formation reaction takes place. The reactor is an alumina tube with a 6.3 cm outer diameter and 75 cm long. The top and bottom of the tube are closed off using compression fitting lids similar to that of the top reactor. Inside the tube are a crucible containing the aluminum, and a graphite pipe which acts as a lance to inject aluminum trichloride vapour into the molten metal. The crucible is supported from the bottom by another tube (not shown) which sits on the bottom lid and the graphite pipe is threaded in order to screw into the bottom of the top lid. The connecting pipe is off-centred on the top lid of the reactor to allow for two additional holes for fittings, which were used for a thermocouple and a pressure gauge. The bottom lid has a similar layout to the top lid of the top reactor, having 5 holes for fittings, one of which was used for gas out another for a
thermocouple and a third for the support rod for the crucible to be lowered through, with the rest of the holes being capped off.

Figure 16: AlCl Formation Reactor

3.2 Assembly

The beginning of the assembly process was to get the top lid of the tubular reactor set up, as it was the first piece to be attached. First the graphite tube was screwed in, then a gauge was attached and then the thermowells and thermocouples were inserted. 140 g of aluminum was weighed out for the initial run, with more aluminum added to achieve a constant volume as subsequent runs depleted the aluminum. The aluminum was placed in the crucible (weight of aluminum, crucible and crucible + aluminum were all recorded). The next step was to lower the tubular reactor into the furnace but lifted up enough to allow for access at the bottom. The
crucible containing aluminum was placed on the support tube and inserted into the furnace along with the shielding which consisted of an alumina crucible that goes over the support rod, and alternating crucible pieces and graphoil discs. Then the bottom lid was attached to support the tube and crucible. The bottom lid was supported with a stand, and then the top lid was attached.

Once assembly of the bottom reactor was completed, the next step was assembly of the top reactor. The supporting table was placed on top of the furnace and then the upper furnace was placed on the table, lining up holes. Before placing the top reactor in the furnace, the reactor needs to be loaded. In the glove box, weigh out 10 g aluminum chloride into a 50mL crucible and 5 g into each of two 20mL crucible and seal all three crucibles with parafilm. Crucibles were placed into the top reactor, not removing the parafilm – this will be allowed to burn off so that no air can react with the aluminum chloride. Next the lid was prepared by inserting thermowell and thermocouple and attaching the gas-in tube to the lid. Then the top reactor was sealed with the lid and the top reactor was lowered into the top furnace and set on springs. The springs help support the top reactor separate from the bottom reactor. Then the top reactor was attached to the top lid of tube reactor via the supporting pipe and the latches closed. The next step was to leak test the apparatus. Once it was clear that there were no leaks (by sealing the outlet and checking the gauge shows an increase in pressure), the gas out tube was placed in the bubbler gas trap and the apparatus purged of air with argon.

3.3 Commissioning

The first step in the commissioning process was to assemble the equipment in the furnaces and do dry runs with each furnace to ensure that the compression seals held. Next was to determine at what pressure the lids can hold using the bottom lid stand at room temperature. Once the room temperature maximum pressure was found, the next step was to heat the entire system to
temperature and cool it to make sure that the seals hold using the bottom stand. During a dry run of the high temperature furnace, the top seal failed and slid off the tube. This was thought to be because the entire apparatus was being supported by this lid and therefore a stand was made to support the tube from the bottom. In order to verify that the seals were holding, a bubbler and dry trap on the off-gas line was used. Once the maximum pressure at room temperature was determined, it was necessary to find the maximum pressure at operating temperatures. Thus, the entire system was heated to temperature and the pressure test was performed again to determine the maximum pressure at temperature. This is important because, if there was ever a clog it was important to make sure that the pressure of the inlet gas was below this mark. It was noticed during these high temperature runs that the alumina tube was glowing hot and in order to cool the bottom of the tube to allow for deposition, shielding was installed in the bottom of the tube using graphoil and alumina crucible pieces. The next step was to use a small amount of aluminum trichloride in the top reactor and sublime. The goal of this step was to get experience in cleaning up the system. Three tests were done, two at 15 minutes in length once the top reactor reached 250°C and once a 25 minute run was completed. The first 15 minute long run was done using saran wrap to cover the crucibles. The reasoning was that Saran Wrap was thinner than parafilm and would therefore burn off faster. Unfortunately the Saran Wrap did not burn as there was no oxygen and instead covered the crucibles with a thin black film, preventing any AlCl$_3$ from subliming. In the second run, parafilm was used and, although it also didn’t burn, it did melt harmlessly down the sides of the crucible, not impeding sublimation. The 25 minute run was done once it was determined that 15 minutes was only long enough to sublime 50% of the AlCl$_3$ and more time was needed. This concluded the commissioning process and experiments began after this.
3.4 Analysis

A major issue with analyzing for the formation of aluminum monochloride is that the equilibrium is only in favour of the monochloride at temperatures above 1200°C and the design of the apparatus and the fact it must all remain under argon means it is impossible to take a sample during the run. This means that it is not possible to get a sample of the aluminum monochloride. In order to verify that the aluminum monochloride was formed, the powder left in the bottom of the reactor and in the dry trap needed to be analyzed for aluminum metal. Since the aluminum metal is contained in the crucible and the vapour pressure of aluminum is very low, the only reason there would be aluminum metal at the bottom of the reactor would be from the back reaction of any aluminum monochloride formed during the reaction. In order to determine the amount of aluminum metal in samples obtained from the reactor, the samples were analyzed using hydrogen evolution. By adding concentrated hydrochloric acid to the samples, any aluminum contained in the samples will react to form hydrogen gas via [24].

\[ 2\text{Al} + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 6\text{H} \]  

[24]

The hydrogen evolved can then be captured in an inverted graduated cylinder filled with water. By measuring the volume of the displaced water, the amount of aluminum in the sample can be determined. The problem with this method is that it was discovered that AlCl$_3$ in the samples was also producing some sort of gas that was displacing the water in the graduated cylinder. A sample of pure AlCl$_3$ was treated in the same way as the experimental samples and also evolved a gas. This meant that the aluminum and the aluminum trichloride could not be differentiated using the hydrogen evolution method as they both would displace water in the cylinder with evolved gas. In order to prevent the aluminum trichloride from interfering with the hydrogen evolution, samples with large beads of aluminum were washed with water first. This worked well, however samples
with fine powder can’t be washed as the dissolving aluminum chloride forms an acidic solution and would dissolve any fine aluminum powder. In order to get rid of the aluminum trichloride in samples with fine powdered aluminum the samples were heated in a kettle to sublime the AlCl$_3$. The cooled sample was then analyzed using hydrogen evolution. This is not ideal as heating the aluminum and aluminum trichloride mix can produce alumina, which is more difficult to do hydrogen evolution on. In order to produce samples without such a fine powder, a cold finger was introduced.

The cold finger, see Figure 17, is simply a stainless steel tube placed inside another, upside down stainless steel tube, with stainless steel discs welded to the upside down tube. Cold air is supplied through the tube and then runs back down the outside of the tube and out through the upside down tube.

Figure 17: Cold Finger
Chapter 4
Experimental Results

Once equipment was designed and fabricated, experiments could begin, and results of these experiments are detailed in this chapter. The first experiments were simple commissioning steps to ensure safety and to determine if the equipment worked as designed. A few bugs were worked out in the commissioning stages and then sublimation experiments were done using aluminum trichloride to optimize the reaction time so all aluminum trichloride could be assumed to have been available for reaction. Once the sublimation was optimized aluminum was added to react with the aluminum trichloride and aluminum monochloride formation experiments began.

4.1 Equipment Commissioning

The purpose of these experiments was to ensure safe operation of the equipment and to see if the equipment worked as expected.

Pressure Test Summary

A high temperature pressure test was conducted to determine the maximum pressure that could be applied before the top lid on the top furnace popped off. This was done at operating temperature, with the bottom furnace heated to 1250°C and the top furnace to 250°C. Halfway through the test it was discovered that the new gauges needed to have the caps pulled off and the pressure released before use. Previous to this, the gauges were reading around 14 kPa, after fixing the gauges, the pressure reading jumped up to 41 kPa. The pressure was slowly increased until the lid popped off at ~110 kPa. Another pressure test was done at ambient temperature. First the pressure was taken to 34 kPa and held for 5 minutes, and there was no decrease in pressure, indicating no major leaks. Then the pressure was gradually increased until the lid popped off. The lid popped at
around 62 kPa. A shield-testing run was done to determine if the graphoil shielding decreased the
temperature of the bottom lid significantly. The shielding was determined to work fine.

Conclusion

The commissioning tests were deemed a success and the equipment was declared safe and
working as planned.

4.2 AlCl₃ Sublimation Experiments

Sublimation tests were done prior to any aluminum monochloride formation experiments
in order to optimize the amount of aluminum trichloride to be added and the length of the
experiment required to ensure all aluminum trichloride would sublime within the experiment and
be able to react.

The first sublimation test was run with only AlCl₃ in the apparatus in order to determine
how long it would take to sublime all the AlCl₃ and ensure both that the AlCl₃ would not cause
leaks and that it could be recovered from the bottom of the furnace. The apparatus was taken
apart and a plug was found in the valve on the gas-out line.

A run was done using parafilm instead of plastic wrap to cover the crucibles. The furnace
was turned on and the crucibles were loaded with 20 g AlCl₃. The reactors were attached 1.5
hours later. Another change in procedure was to move the dry trap to in front of the valve for the
vacuum apparatus. This was to keep the valve from clogging. The experiment was run for 15
minutes after the top furnace reached a temperature of 250°C on the thermocouple. Parafilm
appeared to work as it did in the kettle test, with no residue covering the crucible. 50% of the
AlCl₃ sublimed.

Another sublimation run was done, this time running for 25 minutes to sublime more
AlCl₃. 6.8 g of the 20 g of AlCl₃ was left in the crucibles, meaning that most of the AlCl₃
sublimed in the 25 minute interval. It was decided that this was acceptable and the next runs would include aluminum. The bottom lid was sent to be machined before any experiments were run with aluminum.

**Conclusion**

Figure 18 shows the results from the three experiments conducted. The 20% sublimed value at the 15 minute point was the first experiment where a film was formed by the plastic wrap used. The point above it, at 15 minutes and ~65% sublimed, is the second run done with parafilm instead. The last run was done for 25 minute interval and a slightly higher amount was sublimed in the 25 minutes compared to the previous 15 minute run. It was determined through these sublimation experiments and prior experiments (see Appendix B) that 20 g of AlCl₃ would sublime within 25 minutes.

![Figure 18: Sublimation Experiment Results](image)
4.3 AlCl Formation Experiments

These formation experiments were done to try to reach 90% or more of the theoretical yield of aluminum monochloride via the reaction:

\[ 2\text{Al} + \text{AlCl}_3 = 3\text{AlCl} \]  \[16\]

The theoretical yield at 1300°C is 75% as seen in Figure 8. The yield of AlCl was increased over the course of the experiments by varying the length of the run, the ratio of AlCl\(_3\) to Al, the temperature of the furnace and various other operating conditions which were determined to be factors as the experiments continued.

The results from the AlCl formation experiments can be seen in Table 1. Tests F1 and F2 are missing as no samples were taken since they were simply commissioning runs. The theoretical yield of AlCl at 1300°C is around 75% as can be seen in Figure 8. This was achieved in test F7.

<table>
<thead>
<tr>
<th>Test</th>
<th>AlCl(_3) sublimed</th>
<th>Al difference in crucible</th>
<th>Al from Hydrogen Evolution</th>
<th>% AlCl(_3) Reaction</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>F3</td>
<td>28.4</td>
<td>0.2</td>
<td>0.059</td>
<td>2%</td>
<td>29%</td>
</tr>
<tr>
<td>F4</td>
<td>28.5</td>
<td>0.2</td>
<td>NA</td>
<td>2%</td>
<td>NA</td>
</tr>
<tr>
<td>F5</td>
<td>25.5</td>
<td>4.3</td>
<td>0.068</td>
<td>48%</td>
<td>2%</td>
</tr>
<tr>
<td>F6</td>
<td>26.3</td>
<td>4.9</td>
<td>0.462</td>
<td>53%</td>
<td>9%</td>
</tr>
<tr>
<td>F7</td>
<td>24.3</td>
<td>6.1</td>
<td>0.543</td>
<td>71%</td>
<td>9%</td>
</tr>
<tr>
<td>F8</td>
<td>33.3</td>
<td>1.1</td>
<td>NA</td>
<td>9%</td>
<td>NA</td>
</tr>
<tr>
<td>F9</td>
<td>37.6</td>
<td>5.3</td>
<td>0.050</td>
<td>40%</td>
<td>1%</td>
</tr>
<tr>
<td>F10</td>
<td>24.3</td>
<td>6.9</td>
<td>0.137</td>
<td>80%</td>
<td>2%</td>
</tr>
<tr>
<td>F11</td>
<td>34.4</td>
<td>3.8</td>
<td>NA</td>
<td>34%</td>
<td>NA</td>
</tr>
</tbody>
</table>

**Test F1**

The first experiment including molten aluminum along with AlCl\(_3\) was run. The high temperature furnace was turned on and four hours later the upper furnace was turned on. The rod that
supported the crucible containing aluminum could not be raised at 800°C and this had to be attempted again. At 1240°C the rod was successfully raised and bubbling could be felt through the rod indicating that argon gas was flowing through the graphite rod and bubbling into the molten aluminum. The dry gas trap was placed in an ice bath to try to get more deposition in the dry trap. The tubing at the outlet was observed to be much hotter than during previous runs without any aluminum although the bottom lid of the tube reactor was still cool to the touch. When the thermocouple in the top reactor read 200°C, white vapour was observed coming out of the wet trap which was in the fume hood. There was no more increase in pressure and bubbling in the wet trap continued for the entire run. After 25 minutes, the furnaces were shut off and allowed to begin to cool down. The support rod for the crucible was lowered. It was observed that the rod was sticky and it was impossible to tell if the crucible was also lowered.

**F1 Results**

After taking apart the apparatus, it was observed that the flow rate had been much too high, as the molten aluminum had bubbled so vigorously that it had welded most of the interior parts together and welded the crucible containing the aluminum to the tube reactor. The cracking noise had been the graphite rod breaking and the bottom piece was stuck in re-solidified aluminum in the bottom of the crucible. In order to remove the crucible, the tube and crucible were heated to 800°C, at which point the aluminum melted and the crucible slid out of the tube. The tube was cleaned with acid and was able to be reused. There was an attempt to clean the crucible but it cracked during cleaning.

**Test F2**

The furnace was started and reached temperature four hours later. The support rod was pushed up until bubbling was felt and the top furnace was turned on. The thermocouple read 250°C 20
minutes after the furnace was turned on and the run was considered to have been started at this point. This time a flow meter was used to keep the flow of argon into the system much lower, to prevent splashing the molten aluminum out of the crucible. The flow meter was set to 200 mL/min. Previously the flow was controlled through a regulator and it was calculated to be flowing at 4 L/min when the regulator was set to 34 kPa. There was a slight pressure increase noted on the gauges shortly after the run began but there was still bubbling at the wet trap. The run was stopped after 25 minutes and the furnaces were allowed to cool.

F2 Results
The furnaces were cooled under inert atmosphere and the parts were weighed. It was determined that all but 1.73 g of AlCl$_3$ had sublimed from the top reactor, which was good since the flow rate had been lowered and there were concerns that the lower flow rate might slow the rate of sublimation. The crucible containing aluminum lost only 1.4 g of aluminum. Using FactSage, it was determined that this meant 4.42 g of AlCl should have been formed and 1.14 g of aluminum should be recoverable at the bottom of the furnace. However, the parts were all washed before a sample was taken.

Test F3
The high temperature furnace was turned on and reached 1250°C four hours later. This time 30 g of AlCl$_3$ were loaded into the top reactor in hopes of increasing the amount of aluminum reacting. When the furnace reached 1027°C the support rod was pushed up so the graphite would be under the level of the aluminum. The top furnace was then turned on. It was noted that, before the rod was raised, the temperature inside the furnace had increased to 1315°C and, upon raising the rod, it immediately decreased to 1295°C, probably due to cold argon bubbling through the aluminum. The Ar was flowing at a rate of 200 mL/min and the top furnace set point was 265°C. There was
good bubbling in the wet trap throughout the run and there was no increase in pressure at either
gauge. After the top furnace reached 250°C on the thermocouple, the run was timed to last 45
minutes. It was decided to run longer as there was not much of a reaction last time, and it was
hoped that by giving it a longer run time, more of a reaction might occur.

F3 Results

All the parts were weighed and it was determined that 0.2 g of aluminum was lost from the
crucible and 1.6 g of AlCl₃ was left in the crucibles (28.4 g of AlCl₃ sublimed, see Table 2).
Scrapings were collected from the parts in the lower section of the tube reactor and these, along
with the material in the dry trap, were used to test hydrogen evolution (results of all hydrogen
evolution tests can be found in Appendix E).

Table 2: Test F3 Mass Balance

<table>
<thead>
<tr>
<th>Name of Piece</th>
<th>Weights before run</th>
<th>Weights after run</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al crucible + Al</td>
<td>561.2</td>
<td>561.4</td>
<td>0.2</td>
</tr>
<tr>
<td>AlCl₃ crucibles + AlCl₃</td>
<td>101.8</td>
<td>103.4</td>
<td>1.6</td>
</tr>
</tbody>
</table>

It was determined through hydrogen evolution (see Appendix D for sample calculation) that
0.059 g of aluminum was in the scrapings and dry trap of the 0.67 g of powder collected. Based
on theoretical calculations using the amount of aluminum missing, we should have been able to
collect 0.132 g of aluminum from the back reaction. If the amount of AlCl₃ sublimed all reacted
with the aluminum, 9.5 g of aluminum should have been missing from the crucible. Based on the
very poor reaction with aluminum, and the difficulties with the support rod, it was concluded that
the graphite tube was probably not sufficiently deep in the aluminum melt and for the next run
more aluminum should be added.
Test F4

Based on the previous run, one concern was that the graphite tube was not submerged or not submerged deep enough into the aluminum. As raising the aluminum-containing crucible was limited due to the length of the support rod, more aluminum was added in order to ensure that the graphite was under the aluminum level. Enough aluminum was added to submerge the graphite approximately 5 cm into the molten metal (100 g Al is approx. 2.5 cm depth, so 200 g were added). This gave a total weight of 762.3 g for the aluminum and crucible combined.

30 g of AlCl$_3$ was added and the experiment was run for 45 minutes. During this run the fume hood was observed to be not working and an additional wet trap was added to ensure no AlCl$_3$ vapour escaped into the room while the fume hood was repaired.

F4 Results

The support rod was not raised during this experiment and so there was no bubbling. This experiment did determine the reaction extent achieved (see Table 3) if the AlCl$_3$ is passed over the Al without bubbling. Approximately 1 g of Al reacted.

<table>
<thead>
<tr>
<th>Name of Piece</th>
<th>Weights before run</th>
<th>Weights after run</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al crucible + Al</td>
<td>762.3</td>
<td>762.1</td>
<td>-0.2</td>
</tr>
<tr>
<td>AlCl$_3$ crucibles + AlCl$_3$</td>
<td>101.8</td>
<td>103.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Test F5

The experiment was run again with same amount of Al and AlCl$_3$ as the previous experiment. The support rod was successfully raised until only 2 cm of the rod was left out of the fitting (in order to be able to lower the rod later). It was noted during this run that, when the top furnace reached approximately 180°C, bubbling in the wet trap increased and the temperature began to increase faster, indicating AlCl$_3$ probably began subliming at this temperature.
F5 Results

For this run, all the loose powder was collected, weighed and analyzed using hydrogen evolution to determine the Al content (see Table 4). 4.3 g of aluminum left the crucible, however the graphite tube weighed an additional 4.4 g.

0.07 g of Al was determined through hydrogen evolution and only 4.5 g of AlCl$_3$ was unreacted.

<table>
<thead>
<tr>
<th>Name of Piece</th>
<th>Weights before run</th>
<th>Weights after run</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al crucible + Al</td>
<td>762.1</td>
<td>757.8</td>
<td>-4.3</td>
</tr>
<tr>
<td>AlCl$_3$ crucibles + AlCl$_3$</td>
<td>101.8</td>
<td>106.3</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Test F6

As only 4.4 g of aluminum left the crucible in the previous run, no more aluminum was added for this run. In the last run it was observed that there was a significant amount of AlCl$_3$ in the connecting tube between the two furnaces, and this had been observed in all previous runs. In an attempt to increase the reaction extent by preventing deposition of AlCl$_3$ before it bubbled through the aluminum, the connecting tube was wrapped with heating tape for this run. The heating tape was also insulated. 30 g of AlCl$_3$ was added and the run was 45 minutes long. The heating tape was set to 200°C and the temperature was varied from 200°C up to 250°C during the run.

F6 Results

The hydrogen evolution yielded 0.5 g of aluminum from the powder samples (see Error! Not a valid bookmark self-reference.). 4.9 g of aluminum was missing from the crucible. This gives a reaction extent of 53% and a recovery of aluminum of 9%. 3.7 g of AlCl$_3$ was unreacted.
When the equipment was taken apart it was observed there were beads of aluminum metal stuck to the graphoil shielding as well as to the bottom lid. This is the first time that this had been observed. In the previous experiment it was observed that pure AlCl$_3$ put through the hydrogen evolution steps gave off a gas of some sort, which meant that Al and AlCl$_3$ could not be differentiated via hydrogen evolution. In order to analyze the powder collected from this run, the powder samples were washed with water in filter paper to react the AlCl$_3$ prior to hydrogen evolution. The samples were then dried in a furnace overnight.

**Test F7**

The rod was successfully raised at 1050°C and bubbling was felt through the rod. The set point for the high temperature furnace was held at 1169°C. As in previous runs, the temperature overshot. The low temperature furnace was turned on once the bottom furnace reached 1232°C. When the bottom furnace hit 1250°C, grey particles were observed dropping out of the gas at the outlet tube and in the dry trap. An ice bath was added for the dry trap to try to collect all the particles in the dry trap as many were being pulled past the trap into the tubing between the dry and wet traps. The ice bath did not seem to help; the particles were so light that the low argon flow pushed them vertically up the tube towards the wet trap.

**F7 Results**

Washing the powder collected as before was not possible due to concerns about the fine particles of aluminum dissolving, as acid will evolve when the AlCl$_3$ reacts with the water. Instead the powder was heated to vapourize the AlCl$_3$.

### Table 5: Test F6 Mass Balance

<table>
<thead>
<tr>
<th>Name of Piece</th>
<th>Weights before run</th>
<th>Weights after run</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al crucible + Al</td>
<td>758.2</td>
<td>753.3</td>
<td>-4.9</td>
</tr>
<tr>
<td>AlCl$_3$ crucibles + AlCl$_3$</td>
<td>101.8</td>
<td>105.5</td>
<td>3.7</td>
</tr>
</tbody>
</table>
The remaining powder was then used for hydrogen evolution. The mass balance showed that 71% of the aluminum reacted (see Error! Not a valid bookmark self-reference.) and it was estimated 9% was recovered based on Al measured by hydrogen evolution.

### Table 6: Test F7 Mass Balance

<table>
<thead>
<tr>
<th>Name of Piece</th>
<th>Weights before run</th>
<th>Weights after run</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al crucible + Al</td>
<td>751</td>
<td>744.9</td>
<td>-6.1</td>
</tr>
<tr>
<td>AlCl₃ crucibles + AlCl₃</td>
<td>101.6</td>
<td>107.3</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Test F8

In order to try to increase the aluminum recovery, a cold finger was fabricated and added to the apparatus. The cold finger was air-cooled and shielding was welded to it. This run was the first run with the cold finger. At the time of the experiment there was no scale available and AlCl₃ weights had to be estimated and then weighed by difference later, which is why for this run 48.5 g of AlCl₃ were used.

**F8 Results**

Heating the sample to vapourize the AlCl₃ prior to hydrogen evolution seemed to work well and so the procedure was repeated with this sample. The weight after heating gave 0.3 g of aluminum (see Error! Not a valid bookmark self-reference.), which is 29% recovered, however the actual hydrogen evolution was unsuccessful as there was an undetected hole in the tube and the gas escaped.

The mass balance showed only 10% of the aluminum reacted. This is due to the fact that it was a new aluminum melt and the melt was not deep enough.
Table 7: Test F8 Mass Balance

<table>
<thead>
<tr>
<th>Name of Piece</th>
<th>Weights before run</th>
<th>Weights after run</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al crucible + Al</td>
<td>684.0</td>
<td>683.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>AlCl$_3$ crucibles + AlCl$_3$</td>
<td>101.9</td>
<td>117.2</td>
<td>15.3</td>
</tr>
</tbody>
</table>

Test F9

More aluminum was added to the melt so the graphite would be deep enough in the aluminum for good reaction. However, at the beginning of the run a fuse blew on the temperature controller for the heating trace and so the majority of the AlCl$_3$ condensed in the connecting tube between the two reactors. 45.8 g of AlCl$_3$ were placed in the top reactor, however only 37.5 g sublimed.

F9 Results

Even though the majority of the AlCl$_3$ condensed in the connecting tube, the mass balance showed that 43% of the aluminum reacted and 1% was recovered (see Error! Not a valid bookmark self-reference.).

Table 8: Test F9 Mass Balance

<table>
<thead>
<tr>
<th>Name of Piece</th>
<th>Weights before run</th>
<th>Weights after run</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al crucible + Al</td>
<td>762.4</td>
<td>757.1</td>
<td>-5.3</td>
</tr>
<tr>
<td>AlCl$_3$ crucibles + AlCl$_3$</td>
<td>101.9</td>
<td>110.2</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Test F10

The fuse in the controller was replaced for this run. The glove box was moved to the new laboratory and a mass balance was placed inside, so that the weights were more consistent.

F10 Results

The mass balance shows that 87% of the aluminum reacted and 2% of the aluminum was recovered via hydrogen evolution (see Table 9). However, there was overflow of aluminum from the crucible, so the results are most likely inaccurate.
Table 9: Test F10 Mass Balance

<table>
<thead>
<tr>
<th>Name of Piece</th>
<th>Weights before run</th>
<th>Weights after run</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al crucible + Al</td>
<td>757.1</td>
<td>750.2</td>
<td>-6.9</td>
</tr>
<tr>
<td>AlCl₃ crucibles + AlCl₃</td>
<td>101.9</td>
<td>112.6</td>
<td>10.7</td>
</tr>
</tbody>
</table>

Test F11

Because, in the previous run, aluminum overflowed out of the crucible, the argon flow rate was reduced by half (200 mL/min to 100 mL/min) to prevent the same occurrence in this run. However, at some point during the cooling down process the graphite rod became clogged with aluminum and the resulting pressure popped the lid on the top reactor, which allowed air in and oxidized all the AlCl₃ remaining in the reactors.

F11 Results

It was discovered later, when modifying the cold finger, that a ferrule was missing, which added to the oxidation problems and could have been the reason that the graphite clogged.

No hydrogen evolution could be done as there was no way to collect a sample. However the mass balance of missing aluminum showed that 34% of the aluminum had reacted (see Error! Not a valid bookmark self-reference.).

Table 10: Test F11 Mass Balance

<table>
<thead>
<tr>
<th>Name of Piece</th>
<th>Weights before run</th>
<th>Weights after run</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al crucible + Al</td>
<td>750.2</td>
<td>746.4</td>
<td>-3.8</td>
</tr>
<tr>
<td>AlCl₃ crucibles + AlCl₃</td>
<td>101.9</td>
<td>102.5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Test F12

Although previous results with the graphite lance were very good, it was decided to determine if modifying the lance into a sparger would further improve results. A new graphite lance, identical
to the others previously used, was modified by threading a graphite plug into the bottom and drilling 0.08 cm holes around the circumference in two parallel lines, with the holes evenly spaced. It was discovered, upon assembly of the apparatus, that one fitting on the cold finger was missing a ferrule, which could explain any oxidation/clogging in the previous run.

F12 Results
During the run it was observed that the internal thermocouple in the high temperature furnace was reading 300°C lower than the furnace thermocouple and set point, which was unusual. In all previous runs the thermocouple read 50°C or higher than the furnace thermocouple. Also during the run, no white gas or vapour was observed in the dry or wet traps, unlike previous runs. When the support rod was lowered at the end of the run, the crucible stayed up, stuck. Argon was diverted to a port on the middle lid to prevent the top reactor lid from popping off once the aluminum solidified inside the graphite. The apparatus was remelted the next day to remove the crucible, however it broke during the process and aluminum coated the bottom lid. This was later melted off and the lid was cleaned and saved. However no results were obtained as the weight of the crucible after the run could not be determined.

4.4 SiCl$_4$ Evaporation Rate Tests
Prior to flowing SiCl$_4$ into the apparatus to react with the AlCl, rate tests needed to be done to ensure a steady flow of SiCl$_4$ over the duration of the run. The container designed to hold the liquid SiCl$_4$ is shown in Figure 19:
The long tube in the centre is what contains the SiCl$_4$, the 0.3 cm tube at the top is inserted into the tube containing SiCl$_4$ once the valve is opened and argon is bubbled into the SiCl$_4$. Argon is also flowed over the SiCl$_4$ through the tube running left to right across the top of the SiCl$_4$ container. There is a regulator and flow meter on the carrier gas to ensure that it is at a lower pressure than the argon that bubbles into the SiCl$_4$, so that no SiCl$_4$ can be sucked up the 0.3 cm tube. As the boiling point is only 58°C and the vapour pressure of SiCl$_4$ at room temperature is 0.26 atm, it readily evaporates without heating. The length of time needed to evaporate all 10 mL
(volume of container) of SiCl$_4$ was calculated for 4 different flowrates based on the vapour pressure. The results can be seen in Table 11.

**Table 11: Predicted SiCl$_4$ Evaporation Rates**

<table>
<thead>
<tr>
<th>Gauge Reading</th>
<th>Flowrate (mL/min)</th>
<th>SiCl$_4$ gas</th>
<th>SiCl$_4$ liquid</th>
<th>Time for 10 mL to evaporate (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>278.5</td>
<td>55.7</td>
<td>0.07</td>
<td>149</td>
</tr>
<tr>
<td>40</td>
<td>558.15</td>
<td>111.63</td>
<td>0.13</td>
<td>74</td>
</tr>
<tr>
<td>60</td>
<td>906.65</td>
<td>181.33</td>
<td>0.22</td>
<td>46</td>
</tr>
<tr>
<td>70</td>
<td>1114.05</td>
<td>222.81</td>
<td>0.27</td>
<td>37</td>
</tr>
</tbody>
</table>

These flowrates were then tested, with two flowrates per experiment, with the lower flowrate being tested first and then the flowrate was increased after a period of time to the higher flowrate. The carrier gas flowrate was kept consistent across all runs at 100 mL/min of argon. As the carrier gas can be considered additive to the bubbler, the 100 mL/min flowrate was added to the argon flow from the bubbler in Table 11 to predict the time required to evaporate 10 mL of SiCl$_4$.

The volume of SiCl$_4$ in the container was measured using a differential pressure gauge in inches of water.

**Test E1**

The flowrates tested in this run were 278.5 mL/min argon to start and then 1114 mL/min argon. The flowrate was set at 278.5 mL/min for 40 min, and then it was changed to 1114 mL/min and run until there was no SiCl$_4$ remaining. The differential pressure gauge read 22.5 cm of water at the beginning of the run.

**E1 Results**

During the first flowrate part of the run, near the switching point (35 minute mark), the system began pressuring up. The differential pressure gauge was closed off with a valve and argon flow into the system was stopped and the SiCl$_4$ container sealed off after the bubbler was raised. The
clog was discovered to be in the outlet tube, at the point where it entered the water. SiCl₄ was reacting with the water to produce Si powder, which was clogging the tube. An additional wet trap where the silicon tetrachloride gas merely passed over the water was added prior to the tube being immersed in water and the outlet tube was replaced. The run was then started again at the higher flowrate of 1014 mL/min and run until all the SiCl₄ evaporated, which took 11 minutes.

Test E2
Another test was done with another two flowrates. This time 558 mL/min argon and 907 mL/min argon flow rates were tested. The new setup with two wet traps was used again, as it was successful with the previous test, resulting in no clogs.

E2 Results
The run was completed with no incidents. The flow rate was set at 558 mL/min argon for 15 minutes and then switched to 907 mL/min until all the SiCl₄ evaporated (which took 20 minutes).

E1 and E2 Results
As can be seen in Figure 20, 906.7 mL/min argon and 1114.1 mL/min argon flow rate tests had identical rates of pressure drop and were the fastest, while the 278.5 mL/min argon flow rate produced a slow pressure drop and 558.2 mL/min was in-between. This makes sense as the higher flow rates should cause increased evaporation.
The length of time it would take to evaporate all 10 mL of SiCl₄ was calculated for each flowrate using the data collected during the runs (see Table 12). As the AlCl₃ formation experiment takes 45 minutes, the flow rate closest to this time was preferred. The rates were a bit higher than the calculated rates as the SiCl₄ evaporated faster than anticipated. The closest flow rate was 558 mL/min argon, taking 40 minutes to evaporate all 10 mL of SiCl₄ and this rate was used in the silicon formation experiments.

Table 12: SiCl₄ Evaporation Test Results

<table>
<thead>
<tr>
<th>Flowrate (mL/min argon)</th>
<th>slope (in water/min)</th>
<th>Start</th>
<th>Finish</th>
<th>Change</th>
<th>Run</th>
<th>For all 10 mL (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>278.5</td>
<td>-0.05</td>
<td>9</td>
<td>7.5</td>
<td>1.5</td>
<td>30</td>
<td>180</td>
</tr>
<tr>
<td>558.15</td>
<td>-0.2075</td>
<td>8.5</td>
<td>5.5</td>
<td>3</td>
<td>14</td>
<td>40</td>
</tr>
<tr>
<td>906.65</td>
<td>-0.2627</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>11</td>
<td>18</td>
</tr>
<tr>
<td>1114.05</td>
<td>-0.2627</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>11</td>
<td>18</td>
</tr>
</tbody>
</table>

![Figure 20: SiCl₄ Evaporation Rate](image)

The length of time it would take to evaporate all 10 mL of SiCl₄ was calculated for each flowrate using the data collected during the runs (see Table 12). As the AlCl₃ formation experiment takes 45 minutes, the flow rate closest to this time was preferred. The rates were a bit higher than the calculated rates as the SiCl₄ evaporated faster than anticipated. The closest flow rate was 558 mL/min argon, taking 40 minutes to evaporate all 10 mL of SiCl₄ and this rate was used in the silicon formation experiments.
4.5 Si Formation Experiments

Once the rate of SiCl$_4$ evaporation was determined and the optimum flowrate decided, SiCl$_4$ was ready to be introduced to the main apparatus to react with AlCl and form Si metal. In order to determine the expected silicon yield, the rate of evaporation of SiCl$_4$ needed to be compared to the formation rate of AlCl. As it is not possible to see what is occurring in the AlCl formation apparatus, nor is it possible to take periodic samples, it is impossible to calculate a rate of formation and therefore one must be estimated. AlCl$_3$ sublimation is what is causing any sort of rate of reaction to occur as it is lanced into the aluminum over the period of the run. Of 30 g introduced to the reactor, generally around 25 g sublimed over the course of a 45 minute run. As the temperature is kept steady at 250°C, slightly above the sublimation temperature of 180°C, the rate of sublimation of AlCl$_3$ can be assumed to be fairly consistent throughout the run. 25 g over 45 minutes gives a rate of sublimation of 0.6 g/min. As the maximum AlCl$_3$ reaction was 71%, assuming 70% reaction gives 0.4 g/min AlCl$_3$. 0.4 g/min AlCl$_3$ will react to form approximately 0.6 g/min AlCl or 0.01 mol/min AlCl, based on how much AlCl was formed in test F7. The evaporation rate of SiCl$_4$ was determined to be 0.25 mL/min liquid SiCl$_4$ in the evaporation rate tests. This corresponds to 0.35 g/min of SiCl$_4$ or 0.002 mol/min SiCl$_4$. Silicon yield was determined to be 75% at 1300°C based on AlCl formation at 1300°C (see Figure 9). This gives 0.04 g/min Si or 0.0015 mol/min Si. The results are summarized in Figure 21.
Figure 21: Predicted Rate of Formation of Si

After 45 minutes, 1.89 g of silicon should be formed, based on the rate of evaporation of SiCl₄ and the rate of formation of AlCl when 30 g of AlCl₃ is used and 10 mL of SiCl₄ is added at 1300°C.

Test S1:

In this first experiment attempting to make silicon metal, the experiment was run as before when AlCl was being formed, with the addition of a SiCl₄ feed line. The feed line was connected to the bottom lid and run up a tube inside to discharge above the cold finger. The experiment was running smoothly until 10 minutes in, when a pressure buildup on the SiCl₄ inlet line was noticed on the differential pressure gauge. The lines were traced from the SiCl₄ bubbler to the inlet and the pressure buildup was found and fixed, however by this point most of the SiCl₄ had vented and AlCl₃ would have sublimed. The run was continued until 45 minutes had elapsed anyway.

Test S1 Results:

The results of test S1 are shown in Table 13:
Only 5 g of aluminum metal were missing from the crucible, indicating only 59% AlCl$_3$ reaction.

At the beginning of the run it was noted that the thermocouple inside the furnace was reading significantly lower than the furnace thermocouple, so the issue may have been one of lack of heat. Metallic spheres were found on the bottom lid after the apparatus was taken apart. These were analysed by ICP (inductively coupled plasma mass spectrometry) and the results are summarized in Table 14.

### Table 14: Test S1 ICP Analysis Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>[B] %</th>
<th>[Si] %</th>
<th>[Al] %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shiny ball</td>
<td>0.16</td>
<td>0.26</td>
<td>100</td>
</tr>
<tr>
<td>Big ball</td>
<td>0.03</td>
<td>0.09</td>
<td>97.4</td>
</tr>
<tr>
<td>Loose Material</td>
<td>0.11</td>
<td>1.95</td>
<td>52.5</td>
</tr>
<tr>
<td>Scraped Material</td>
<td>0.02</td>
<td>0.59</td>
<td>97.6</td>
</tr>
</tbody>
</table>

The metal balls were aluminum (with some pre-existing impurities). The aluminum used was 99.5% aluminum in lump form and 0.5% was impurities, the most common being silicon, thus 0.3% Si is within the range of impurities present. This indicates that no reaction between the AlCl and SiCl$_4$ occurred. However some silicon is in the loose and scraped material from the crucible, potentially from reaction having occurred. 0.05 g of Si and 1.5 g of Al were collected in total from the samples. This is 3% of the Al that was collected, which is about 30 times the impurity level of silicon typically in aluminum.
Test S2:

To prevent another clog on the SiCl$_4$ inlet, the SiCl$_4$ inlet was moved to the lid on the top of the tube from the bottom of the tube for this run. Additional gauges were also added at the inlet and outlet of the apparatus to better detect the position of any clogs or leaks that may occur.

Test S2 Results:

The results from S2 can be found in Table 15:

<table>
<thead>
<tr>
<th>Name of Piece</th>
<th>Weights before run</th>
<th>Weights after run</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al crucible + Al</td>
<td>778.4</td>
<td>775.8</td>
<td>-2.6</td>
</tr>
<tr>
<td>AlCl$_3$ crucibles + AlCl$_3$</td>
<td>101.9</td>
<td>108.5</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Only 2.6 g of aluminum were missing from the crucible, which corresponds to 31% AlCl$_3$ reaction. Five minutes into the run, an o-ring caught on fire, causing a large leak at the top of the tube, and most of the AlCl formed after this would have vented out of the leak. After the o-ring stopped burning, the experiment was run for the normal amount of time, however large amounts of gas were vented out of the top lid. After everything cooled down, samples were taken and analysed for silicon and aluminum by ICP analysis (see Table 16).

<table>
<thead>
<tr>
<th>Sample</th>
<th>[B] %</th>
<th>[Si] %</th>
<th>[Al] %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Lid</td>
<td>0.06</td>
<td>1.84</td>
<td>73.7</td>
</tr>
<tr>
<td>Bottom Lid</td>
<td>&lt;DL</td>
<td>1.70</td>
<td>30.6</td>
</tr>
<tr>
<td>Loose material in crucible</td>
<td>0.04</td>
<td>1.27</td>
<td>77.2</td>
</tr>
</tbody>
</table>

There is significantly more silicon in the samples than exists as an impurity in the aluminum or aluminum trichloride (0.3-0.5%), indicating that some silicon tetrachloride reacted. However, due to the leak, it is impossible to determine if the silicon is silicon oxide from SiCl$_4$ reacting with
oxygen that may have entered the reactor or if it is silicon metal that then oxidized after. 0.02 g of Si were collected in total and 1 g of Al was collected representing 2% of the aluminum.

Test S3:

The test was run again the same as in test S2, but with more care taken to ensure that insulation was located under the lid and not covering the lid, so as to prevent another fire and subsequent leak. There were issues with the furnace temperature, and during the run bubbling in the wet trap ceased for a time, indicating that either a clog or a leak formed.

Test S3 Results:

The results from test S3 are located in Table 17.

Table 17: Test S3 Mass Balance

<table>
<thead>
<tr>
<th>Name of Piece</th>
<th>Weights before run</th>
<th>Weights after run</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al crucible + Al</td>
<td>587.4</td>
<td>583.6</td>
<td>-3.8</td>
</tr>
<tr>
<td>AlCl₃ crucibles + AlCl₃</td>
<td>101.9</td>
<td>106.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

After the apparatus cooled down overnight, everything was taken apart, weighed and samples were taken. It was discovered that the tube had cracked in several places at some point, but this was not visible because the cracks were in the furnace. It is not possible to determine when the cracks formed, so it must be assumed that any material in the furnace during the run might have been exposed to oxygen. Only 41% of the AlCl₃ reacted during the run based on the amount of aluminum missing from the crucible (see Table 18).

Table 18: Test S3 ICP Analysis Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>[B] %</th>
<th>[Si] %</th>
<th>[Al] %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top wall of tube</td>
<td>&lt;DL</td>
<td>2.95</td>
<td>23.8</td>
</tr>
<tr>
<td>Bottom wall of tube</td>
<td>0.09</td>
<td>1.63</td>
<td>26.1</td>
</tr>
<tr>
<td>Bottom Lid</td>
<td>0.03</td>
<td>1.41</td>
<td>21.9</td>
</tr>
</tbody>
</table>
The analysis results show the presence of significant amounts of silicon, but again it is impossible to determine if this is because of the reaction with AlCl or due to the influx of oxygen owing to the cracks in the alumina tube. The low levels of aluminum are to be expected as there should also be a significant amount of chloride in the samples as well as oxygen from the leak. It was also determined that only 5 mL of 10 mL of SiCl\(_4\) had evaporated. 1.07 g of Al and 0.07 g of Si were collected in total. As 3.8 g of Al was missing from the crucible, 12.4 g of AlCl were formed, however, of this, 3.5 g of AlCl back reacted (to get the 1.07 g of Al at the end). This means that around 9 g of AlCl either reacted with the SiCl\(_4\) or vented to the atmosphere.

**Test S4:**

Another test was run, this time removing the cold finger, as it was making it difficult to move the support rod up and down. Additionally, a graphite cap was made for the top of the rod, as sometimes the rod would get stuck between the crucible and the tube wall on an angle, making it impossible to move. The graphite cap was a disc 5 cm in diameter and 2.5 cm deep, with a hole in the middle the size of the rod 1.3 cm into the disc. This meant it added another 1.3 cm of height to the rod.

**Test S4 Results:**

During the run, the pressure increased on all gauges, maxing out the gauge limits, but reading 28 kPa on the one higher pressure gauge. This happened immediately when the rod was raised up and the graphite was in the aluminum, and another pressure increase occurred once the SiCl\(_4\) feed line was opened and flowing. It was later determined that the SiCl\(_4\) line plugged with AlCl\(_3\) prior to flow starting. The graphite was stuck in the aluminum, holding the crucible up and impossible to remove, even when the temperature was increased. It is not known why this occurred. This made it impossible to calculate the amount of aluminum that reacted, if any. As the SiCl\(_4\) line
plugged up immediately, little to no SiCl₄ made it into the reactor, with 7 mL remaining in the container and approximately 2 mL being removed from the line where it recondensed. Of the 30 g of AlCl₃ in the top reactor, only 14.5 g sublimed, where, typically, 25 g or more sublimes during a run. Some small metal beads were removed from the bottom of the reactor and analyzed.
Chapter 5

Discussion

Based on the results shown in Chapter 4, it is clear that the AlCl formation reaction was taking place and AlCl was being formed in the quantities predicted from thermodynamics. While there was poor initial recovery of the Al metal and AlCl$_3$ powder at the bottom of the tube reactor, there was significant aluminum missing from the crucible that cannot be accounted for other than by having reacted with the aluminum trichloride. Powder scrapings that were obtained did contain aluminum metal along with aluminum trichloride, as would be expected after aluminum monochloride backreacted upon cooling.

When SiCl$_4$ was introduced to the reactor in the hopes of forming Si metal, very little reaction was observed. A significant increase from the amount of silicon present in the aluminum as an impurity to the amount found in the sample was observed, but not in the quantities predicted.

5.1 AlCl Formation

As previously discussed, the predicted AlCl formation at 1250°C (from Figure 8) is 65% and at 1300°C is 75% which correlate with 80% and 85% AlCl$_3$ reaction (see Table 19). The reason the predicted reaction and formation rates are not 100% is due to the thermodynamics.

<table>
<thead>
<tr>
<th>Test</th>
<th>Actual</th>
<th>% of Predicted (75%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F3</td>
<td>2%</td>
<td>3%</td>
</tr>
<tr>
<td>F4</td>
<td>2%</td>
<td>3%</td>
</tr>
<tr>
<td>F5</td>
<td>52%</td>
<td>70%</td>
</tr>
<tr>
<td>F6</td>
<td>58%</td>
<td>77%</td>
</tr>
<tr>
<td>F7</td>
<td>75%</td>
<td>100%</td>
</tr>
</tbody>
</table>
Table 19 shows the actual AlCl formation as an actual percentage and as a percentage of the predicted AlCl formation, taken as the predicted at 1300°C (the furnace was nominally set at 1250°C for most runs but the internal thermocouple showed it reading 50°C above for all runs). This was calculated by using Excel’s solver to solve for the amounts of AlCl and AlCl$_2$ formed by the simultaneous reactions using the stoichiometry of the reactions along with the amount of aluminum that reacted and the predicted ratio of AlCl$_3$/AlCl from the thermodynamics (calculated using FactSage). The following knowns and unknowns were used:

<table>
<thead>
<tr>
<th>Knowns:</th>
<th>Unknowns:</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl$_3$ + 2Al $\rightarrow$ 3AlCl</td>
<td>AlCl$_3$ going to each reaction</td>
</tr>
<tr>
<td>2AlCl$_3$ + Al $\rightarrow$ 3AlCl$_2$</td>
<td>Al going to each reaction</td>
</tr>
<tr>
<td>AlCl$_2$/AlCl = 0.11 (see Figure 22)</td>
<td>AlCl$_3$ formed</td>
</tr>
<tr>
<td>Total Al reacted</td>
<td>AlCl$_2$ formed</td>
</tr>
<tr>
<td>Total AlCl$_3$ available to react</td>
<td></td>
</tr>
</tbody>
</table>

Two columns were set up in excel, one for each reaction, and the aluminum used in each one was summed and the sum set to the total aluminum used. Then the AlCl$_3$/AlCl ratio was calculated in one cell and solver was used to force the ratio to be equal to 0.11 by varying the AlCl and AlCl$_2$ amounts formed. Constraints of AlCl and AlCl$_2$ amounts being greater than zero and the total aluminum being equal to the amount used were added. The amounts of aluminum and aluminum trichloride going to each reaction were calculated using the AlCl and AlCl$_2$ amounts calculated by solver and the stoichiometry of the reactions.

Figure 22 shows the AlCl$_3$/AlCl ratio as a function of temperature. As the temperature was around 1300°C, 0.11 was the ratio used. The amount of AlCl formed is the actual and the
percentage of predicted is calculated by dividing the actual percentage reacted by the predicted amount that reacts based on the thermodynamics.

![AlCl2/AlCl Ratio as a Function of Temperature](image)

**Figure 22: AlCl₂/AlCl Ratio as a Function of Temperature**

As before, when comparing the percent reaction of AlCl₃, run F7 produced almost exactly the amount of AlCl predicted.

### 5.1.1 Experiment Optimization

In order to achieve the good results obtained in run F7, modifications were made to both the experimental conditions and apparatus. The first modification necessary was after test F1, when it was discovered after the run that the argon flow rate had been so high that it caused the molten aluminum to splash over the inside of the alumina tube. For all the following runs, the argon flow rate was set much lower. After the second run, test F2, there was still not very much reaction, so the amount of AlCl₃ was upped from 25 g to 30 g, as it was thought this might increase the amount of reaction. At the same time, the experiment was run for longer – 45 minutes instead of
30 minutes, in order to give the extra AlCl$_3$ more time to sublime and react. The results from test F3 were still not very good, and it was determined from the graphite rod that there was not enough aluminum depth in the crucible to get good reaction with the AlCl$_3$. For all following runs, the amount of aluminum in the crucible was carefully monitored and calculations ensured that enough aluminum was added to the crucible to submerge the graphite tube. After it was observed during test F5 that a lot of the AlCl$_3$ was recondensing on the connecting tube between the furnaces, heating tape was wrapped around the connecting tube in order to ensure more AlCl$_3$ reached the aluminum in order to increase the reaction. Finally after all these modifications, there was good reaction for runs F6 and F7. However, even though test F7 showed that predicted AlCl$_3$ reaction could be obtained, the amount of powder being recovered at the bottom of the alumina tube was still very poor, with only 10% of the reacted aluminum being recovered. In order to increase the aluminum recovery, a cold finger was added to the apparatus. By cooling the cold finger with compressed air, it was hoped that aluminum and AlCl$_3$ would condense on the cold finger, rather than condensing on the lid or escaping as gas out the outlet tube. While the cold finger did cause the powder to preferentially condense on the cold finger rather than on the lid, there was not any extra condensation, and the amount of aluminum recovered was still only 10% for the runs using the cold finger. The final modification done before the SiCl$_4$ was introduced to the reactions was to exchange the graphite lance for a graphite sparger. It is unknown what effect the sparger had, as the crucible was damaged during the test run and could not be weighed after to determine how much aluminum reacted. Changes made during the silicon formation runs included moving the silicon inlet port from its initial location on the bottom lid to the middle lid (top of the tube reactor) and removing the cold finger. The cold finger was making it difficult to move the support rod up and down, resulting in the crucible becoming frequently stuck. The
initial run in the silicon formation experiments had problems with the outlet line clogging, thought to be due to the location of the SiCl₄ inlet, thus it was relocated to the top lid of the tube. A bypass valve was also added to allow for pressure release and purging of the SiCl₄ line prior to the SiCl₄ flow being turned on. Additionally, a graphite cap was added to the top of the support rod, in order to facilitate keeping the crucible aligned parallel to the alumina tube and preventing the rod from wedging up against the side of the crucible.

5.1.2 Heat Balance Comparison

As the goal of these experiments was to come up with a method of producing solar grade silicon as an alternative to the Siemens process, it would be good at this point to compare the results achieved in this study to the commercially used process. The Siemens process consists of two reactions:

\[
\text{Si} \quad \text{(l)} + 3\text{HCl} \quad \text{(g)} \rightarrow \text{HSiCl}_3 \text{(g)} + \text{H}_2 \text{(g)}
\]

\[
\text{SiHCl}_3 \text{(g)} + \text{H}_2 \text{(g)} \rightarrow 3\text{HCl} \text{(g)} + \text{Si} \quad \text{(s)}
\]

First metallurgical grade silicon is melted and reacted with hydrogen chloride gas at 350°C to form trichlorosilane gas and hydrogen gas. The trichlorosilane gas is then reacted with a pure stream of hydrogen gas at 1100°C to react with any impurities. This step recycles many times until the trichlorosilane is 99.99999999% pure (8N). The trichlorosilane is then deposited on heated silicon seed rods. For the heat balance on the Siemens process, only one cycle was used in the trichlorosilane purification step and it was assumed to go 80% to completetion. The first reaction to make trichlorosilane was also assumed to have 80% yield. In order to properly compare the two processes, a base of 20 kg of Si metal produced was used, which yielded the following masses (Figure 23).
Using these mass values and calculating the moles of each substance, along with heats of formation for each substance, the heats of reaction for both reactions were calculated. The energy required to bring all the substances to temperature was calculated using the heat capacities, molar masses and change in temperature. These energies were all added together to find the overall energy input required for the process, which was 128 GJ.

For the method attempted in these experiments, there are two important reactions.

\[
2\text{Al}_{(l)} + \text{AlCl}_3_{(g)} \rightarrow 3\text{AlCl}_{3(g)}
\]

\[
2\text{AlCl}_{3(g)} + \text{SiCl}_4_{(g)} \rightarrow \text{Si}_{(s)} + 2\text{AlCl}_3_{(g)}
\]

First, aluminum trichloride is sublimed and then bubbled through molten aluminum at 1250°C to produce aluminum monochloride. Next, the aluminum monochloride is reacted with silicon tetrachloride to form silicon metal and aluminum trichloride, also at 1250°C. The yield for the first step was calculated to be 85% during the experiments and the yield of the second step was taken as 75% as previously calculated. In order to make 20 kg of silicon metal, the following masses were calculated (see Figure 24).
The heats of reaction for both reactions were calculated using the heats of formation and moles of each substance. The energy required to heat the chemicals to 1250°C was also calculated, using the moles of each substance along with the heat capacity and temperature change. These were all added together to get the total energy input needed for the system, which was 120 GJ.

Overall, the Siemens process uses 8 GJ more per 20 kg of silicon produced.

5.1.3 Issues with Scale Up

When scaling up to industrial scale from lab scale, the lessons learned during the lab scale optimization process will predict what problems are likely to be encountered. A major issue during lab scale tests was controlling the flow rate through the lance to minimize any splashing of aluminum. Any residual aluminum on the side of the tube cause the crucible to stick, which meant that, when the furnace was cooled, aluminum solidified inside of the graphite lance, pressuring up the system and popping off the top reactor lid (weakest point). Once the lid popped off, all the contents oxidized. Another issue that was encountered during lab scale tests was the difficulty of collecting powder samples from the bottom of the reactor. Even with the addition of the cold finger, only 10% or less of the residue was successfully collected. This will continue to be an issue as the system is scaled up. Either a better cold finger would need to be designed or some sort of filter should be placed at the outlet to increase recovery. One problem encountered during lab scale tests that will probably not be an issue during scale up was the amount of

<table>
<thead>
<tr>
<th>Substance</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃ input</td>
<td>99.30 kg</td>
</tr>
<tr>
<td>Al input</td>
<td>80.37 kg</td>
</tr>
<tr>
<td>AlCl produced</td>
<td>118.56 kg</td>
</tr>
<tr>
<td>SiCl₄ input</td>
<td>235.52 kg</td>
</tr>
<tr>
<td>Si produced</td>
<td>20.00 kg</td>
</tr>
<tr>
<td>AlCl₃ produced</td>
<td>189.91 kg</td>
</tr>
</tbody>
</table>

Figure 24: Mass Basis for Heat Balance of AlCl Process
material to react and length of experiment. Once the system has been scaled up, more material will be used, and as long as sufficient time is allowed for reaction, neither of these issues should be a problem.

5.1.4 Recoverable Material
As previously stated, even with good reaction as evidenced by aluminum missing from the crucible, very little aluminum was recovered from the apparatus at the end of any of the runs. Only 9% of the aluminum was recovered even in the reaction with 100% of the predicted aluminum reacting (test F7). In order to try to increase the amount of aluminum recovered, a cold finger was introduced through the bottom lid and cooled with compressed air. While the cold finger did cause preferential condensation, it did not cause more condensation than previously, with only ~10% of the aluminum condensing on the cold finger. One potential issue causing the lack of recoverable powder is that a lot of gas is observed in the dry and wet traps and leaving the wet trap during and after the runs. Most likely this is AlCl₃, but some of the gas could also be AlCl that has not back reacted, which could account for the low amounts of aluminum recovered. Another observation was that in many runs powder was collected in the tubing and dry trap, and sometimes small particles were even blown out the outlet tube and down the tubing, which could account for some of the aluminum not being recovered. The other possibility is that aluminum is reacting to form alumina, which would not form hydrogen gas during the hydrogen evolution analysis of the powder residues. The problem with this hypothesis is that the total powder residue collected from each run still does not total the amount of aluminum which should be recovered. Most likely the recovery problem is a combination of the above.
5.2 Si Formation Experiments

The results from the silicon formation experiments are summarized in the experimental section. Overall there was a noted increase in silicon in samples taken from the reactor, from 0.3% Si in the aluminum used (which is a typical level of impurity for primary aluminum) to 1-2% Si in the sample. This can be assumed to have resulted from silicon forming due to reaction of SiCl$_4$ and AlCl as, if there had been no reaction, the SiCl$_4$ would not remain in the reactor due to its volatility. The only other way for silicon to be present would be as SiO$_2$ formed as a result of oxygen present in the system reacting with the SiCl$_4$. This may have been the case in test S3, however the experimental apparatus was set up to preclude any oxygen content in the system, and in tests with no leakage it can be assumed there is no oxygen and thus no SiO$_2$. In none of the experiments was pure silicon metal discovered, as either a powder or as beads. All silicon found was mixed in with the aluminum metal powder formed upon back reaction from the AlCl, and any aluminum beads found were pure aluminum with only 0.3% silicon from pre-existing impurities.

5.2.1 Expected Si Yield

The expected yield of Si was discussed in detail in the experimental section, where it was predicted that, with the input of 30 g of AlCl$_3$ and 10 mL of SiCl$_4$, 1.89 g of silicon metal should form. This assumed the rate of SiCl$_4$ evaporation and AlCl formation were similar (or that the AlCl produced always exceeded that of SiCl$_4$), meaning that the amounts of each substance needed to react to form silicon would be present in the minimum ratio for the duration of the test. The rate of SiCl$_4$ evaporation and the rate of AlCl$_3$ sublimation were previously determined, however the rate of AlCl formation was uncertain, although it was assumed to be constant throughout the run. An assumption was made that the formation of AlCl would be constant and
steady over the course of the experiment and a graph was made illustrating the amounts of AlCl and SiCl₄ over time and the predicted amount of Si thus formed, as seen in Figure 21, which shows cumulative masses generated. What was not taken into account was the rate of back reaction from AlCl to AlCl₃ and Al. The predicted silicon formation was 1.89 g of silicon, which should equate to around 30% of the collected sample when analyzed. What was actually obtained was 2% silicon and the majority aluminum, with any remainder assumed to be chloride, or in the case of leakage, oxygen. The biggest observable problem was that it was very difficult to control the flow of SiCl₄ and AlCl₃ into the reactor. The two flows caused backpressure issues in the system, with backpressure observed when one flow was set higher than the other. This made it very hard to ensure a steady rate of evaporation of SiCl₄ and consistent bubbling of AlCl₃ into the aluminum. This promoted clogging leading to some unreacted feed. As the SiCl₄ was being evaporated using argon flow and high vapour pressure, the SiCl₄ being introduced to the reactor was cold and not preheated, and this could have caused a cold zone right where the AlCl was being formed, preventing any significant reaction due to freezing of the aluminum surface or prompting back reaction of the AlCl. This was observed in test S4 when the SiCl₄ inlet immediately clogged with AlCl₃ at the point it entered the reactor. This could have been avoided had the SiCl₄ flow been preheated or higher in volume than the carrier gas for the AlCl₃, but then it would have been possible for the SiCl₄ flow to force AlCl₃ back into the top reactor, which was also undesirable. In the last experiments there were many issues with temperature and trying to maintain the furnace at 1250°C for the formation of AlCl. Another issue developing from this is that increasing the temperature would form more AlCl but would drive down the formation of Si, which is more favourable at lower temperatures. The various formation rates that have been discussed in this section are summarized in Figure 21. Even in tests where there was significant
silicon in the sample, it was entrained in the aluminum metal, which means that the purity desired for solar grade material would be impossible to achieve via this method. As both the aluminum metal and silicon metal were fine powders and mixed together, it would be very difficult to separate them mechanically, and remelting them would be very energy intensive.
Chapter 6

Conclusions and Recommendations

6.1 Conclusions

The purpose of this work was to a) form AlCl by reacting AlCl$_3$ with Al by bubbling AlCl$_3$ through the Al to increase yield and b) form Si by reacting AlCl with SiCl$_4$. Both of these goals were met, albeit the second goal met with very limited success. By bubbling the aluminum trichloride into the molten aluminum, much better kinetics were achieved than in previous experiments where the aluminum trichloride flowed over the surface of the aluminum. In those experiments, reaction at the temperature range used in these experiments (1250-1300°C) yielded less than 80% AlCl (Russell et al$^{14}$). By bubbling the AlCl$_3$ into the molten aluminum, yield was increased to in excess of 85%, previously only possible by increasing the temperature. This method of lancing is a viable commercial option, as the technology already exists in the steel industry. Based on the amounts of aluminum used in the plant scale extrapolation, a lance depth of up to 4 m would be reasonable. Potential operating problems for this process would be corrosion of the lance due to the AlCl$_3$, wear due to the high temperatures, clogging of the lance due to uneven heating in the melt, and poor reaction due to mixing issues, depending on the volumes of aluminum used per ladle.

For this work, a carrier gas was required to flow the AlCl$_3$ from the top reactor into the aluminum. The vapour pressure formed by the aluminum trichloride appeared to be insufficient on its own to overcome the back pressure of the aluminum based on the depth that the lance was placed in the melt. Argon was chosen since nitrogen would react to form aluminum nitrides. The presence of argon in the system caused dilution of the AlCl$_3$, as well as cooling of the top reactor,
as the argon was not preheated. As the furnace was well above the sublimation temperature of AlCl₃ and the flow of argon was fairly low, there was no issue with condensation of the AlCl₃ in the reactor due to cold gas. Also, flowing in through the top reactor allowed for preheating of the argon prior to injection in the aluminum, which prevented freezing at the surface. The argon carrier gas could be recycled through the process at industrial scale.

Silicon metal was formed by introducing SiCl₄ into the reactor while AlCl was being produced, with resulting silicon levels in the powder samples being 10 times more than the silicon present in the lump 99.5% aluminum (3% versus 0.3%). While the silicon levels were well below what was hoped for, the reaction was shown to work. Because SiCl₄ has a very high vapour pressure, it was decided that heating was not necessary to evaporate the silicon tetrachloride. Instead, the argon carrier gas was used alone to evaporate the silicon tetrachloride, taking advantage of its volatility. There were a couple of drawbacks to this approach. Because no heat was used, the silicon tetrachloride was not preheated before entering the 1250°C reactor. This caused issues with freezing on the top of the molten aluminum, as well as condensation in the lines feeding the SiCl₄, which was especially evident when there was any clogging. The cold SiCl₄ also caused AlCl to back react and condense at the SiCl₄ inlet port, leading to clogging and pressuring up the system. The difficulty with the process seems to be in the relative reactions of AlCl converting to AlCl₃ and aluminum versus SiCl₄ reaction with AlCl. From this work, the rate of reaction of SiCl₄ with AlCl appears to be similar to that of AlCl producing Al metal and AlCl₃. There is also an issue with temperature control and the injection point of the SiCl₄. The cold SiCl₄ might be cooling the AlCl and promoting the decomposition reaction to produce Al and AlCl₃. Temperature was difficult to control in the laboratory setup and, while it might be more straightforward in a commercial reactor, it is still a major issue with the process. Even had this issue
been addressed, the fast back reaction of AlCl could mean that there would be issues with impurity of any silicon formed. All of this makes difficult the control of where and how much SiCl$_4$ enters the reactor.

In order to achieve the results eventually obtained, modifications were made to both the experimental conditions and apparatus. The first modification necessary was after the first test, when it was discovered after the run that the argon flow rate had been so high that it caused the molten aluminum to splash over the inside of the alumina tube. For all the following runs, the argon flow rate was set much lower. After the second run, there was still not very much reaction, so the amount of AlCl$_3$ was upped from 25 g to 30 g, as it was thought that this might increase the amount of reaction. At the same time, the experiment was run longer 45 minutes instead of 30 minutes, in order to give the extra AlCl$_3$ more time to sublime and react. After it was observed during testing that a lot of the AlCl$_3$ was recondensing on the connecting tube between the furnaces, heating tape was wrapped around the connecting tube in order to ensure that more AlCl$_3$ reached the aluminum in order to increase the reaction. Changes made during the silicon formation runs included moving the silicon inlet port from its initial location on the bottom lid to the middle lid (top of the tube reactor). A bypass valve was also added to allow for pressure release and purging of the SiCl$_4$ line prior to the SiCl$_4$ flow being turned on. Finally, a graphite cap was added to the top of the support rod, in order to facilitate keeping the crucible aligned parallel to the alumina tube and preventing the rod from wedging up against the side of the crucible. Many modifications were needed in order to optimize the experiment and achieve the desired results for AlCl production. However, more modifications would be necessary to improve Si production.
As the powder samples collected from the bottom of the reactor were very fine and mixed together, the samples were analysed by hydrogen evolution. Hydrogen evolution was done by adding concentrated HCl to the powder samples and collecting the gas evolved. By using the volume of the collected gas, the aluminum content can then be calculated by determining the number of moles of hydrogen, dividing this by three and multiplying by two to get the number of moles of aluminum. The mass of aluminum is then simply calculated by multiplying the number of moles of aluminum by the molar mass of aluminum (26.98 g/mol). It was observed that adding HCl to pure AlCl$_3$ evolved some gas, and so a modification was made to the procedure to first remove any AlCl$_3$ present in the sample in order to get an accurate measure of the aluminum metal content. Washing was tried at first, but there were concerns that the acidic solution produced by this would dissolve some of the aluminum in the sample. The final method used was to heat the samples first under argon and allow the AlCl$_3$ to condense in a separate chamber.

Additional information was also achieved during the course of experiments. The rate of sublimation of AlCl$_3$ at different temperatures was determined, with the rate used being 0.5 g/min at 250°C and 50 mL/min argon flow (see Appendix B), as was the rate of evaporation of SiCl$_4$ under different argon flow rates. Rates of formation of AlCl and Si were intuited from the data collected as well, and the yields studied under different conditions.

The point of these experiments was to prove silicon metal could be formed by reacting AlCl with SiCl$_4$, but the purpose of proving this was to eventually commercialize the process. A commercial flowsheet was proposed and cost analysis done. However there were many issues discovered that would make the process difficult to scale up. Purification using AlCl was not able to be investigated. A small amount of AlCl should be able to preferentially react with boron and phosphorous impurities in the SiCl$_4$ gas, however, this might promote the decomposition of AlCl.
Without some method for purification of the SiCl$_4$ gas, any solar grade silicon would likely not meet the purity specifications required. This presents a barrier to the commercial use of this method. Morphology and extraction of the product from the reactor are two other issues that would cause difficulties for the commercial system as more than one form of silicon would make it difficult to separate the silicon and aluminum efficiently, which would already be difficult as the silicon was in a fine powder form and intermingled with the aluminum powder. Had silicon beads formed, much higher purity could have been expected.

The process as originally proposed is not feasible at this point as an industrial method of producing solar grade silicon. While the first step of producing AlCl from bubbling AlCl$_3$ into Al worked as predicted, the second step, of reacting SiCl$_4$ and AlCl, did not produce the expected results. There were a lot of issues with SiCl$_4$ addition to the reactor, either due to plugging of the inlet or freezing of the aluminum. There were also issues with backpressure in the system and trying to maintain constant bubbling. More work is needed to resolve these issues before scale up could be considered. Another major issue with the possibility of using this process commercially is the fact that the silicon that was formed was a very fine powder mixed in with fine powdered aluminum and aluminum trichloride. It would be both hard to collect and hard to separate out the silicon, and as a fine powder, it would be hard to get the purity needed. Unless all these issues can be resolved, this process could not be used to commercially produce solar grade silicon. It was proven that AlCl could be made with very high yield by bubbling the aluminum tricholide through a lance into the aluminum metal, which could be very useful for other applications where a strong reductant is needed or where volatile chlorides are used. It was also proven that silicon could be produced, albeit in very small amounts, through the reaction of AlCl with SiCl$_4$. 
Although cost analysis of this process at industrial scale is very favourable, the low yield and purity issues encountered mean this process is not a feasible method of producing solar grade silicon at this point. Further study may improve this.

6.2 Recommendations

While it was shown that AlCl could be formed successfully and in the predicted quantities, many difficulties were encountered when attempting to form silicon by reacting SiCl$_4$ with the AlCl formed. Most of these difficulties encountered would also be an issue at larger scales. The problem of controlling the flows of AlCl$_3$ and SiCl$_4$ into the reactor would continue to pose a problem, as would issues related to back pressure in the system. The rate of back reaction of AlCl into AlCl$_3$ and Al, and the possibility that it is faster than the reaction with SiCl$_4$ to form Si, would also be an issue at larger scale. Temperature control and fluctuation issues in the reactor might also continue to be a problem at large scale. While larger industrial furnaces could just increase the temperature to produce more AlCl, higher temperatures are not favourable for forming Si. Even attempting to form the AlCl at high temperature and then flowing the gas to a second, cooler furnace could cause AlCl to back react before having a chance to react with the SiCl$_4$. The issue of silicon dissolution in the aluminum would also continue to pose a problem. Further work in this area would need to solve these issues before committing to increasing the scale.
References


   http://www.factsage.com


Appendix A

Selective Chlorination Examples

Selective Condensation of Chlorinated Bauxite Ore to Recover Aluminum

One ore that is suitable for selective condensation due to the great number of different metal impurities is bauxite. Bauxite is mined for aluminum production, but usually also contains iron, titanium and silicates. In order to separate out the aluminum, the current industrial method is to use the Bayer process, followed by the Hall-Heroult process. The Bayer process involves oxidizing the bauxite to obtain alumina, which is then leached out into solution using sodium hydroxide, leaving most of the other metal oxides formed as a solid sludge to be settled out in a clarifier.

Before the condensation process, the bauxite is first chlorinated in an oxidizing atmosphere, which selectively chlorinates the iron chloride, which is vaporized and removed. Then the remaining metals are chlorinated in a reducing atmosphere which chlorinates and vaporizes the aluminum, silicon, titanium and any residual iron. The metal chlorides are then separated and recovered through selective condensation. Additives such as silicon tetrachloride can be added during the reducing chlorination step to prevent chlorination of siliceous material, allowing easier separation during the condensation step.

In the selective condensation process, the volatile metal chlorides are fractionally condensed at three different operating temperatures to produce different fractions containing the different metal chlorides. The theory is that due to the different volatilities, the iron, aluminum, titanium and silicon chlorides can be separated in a series of cooled condensers, with the metals with higher boiling points condensing out first. The first step is to condense out the iron (III) chloride, which can be done by cooling the gases to 220°C. Some of the aluminum chloride may also co-
condense at this stage, but as aluminum chloride is the product, purity of the iron chloride is not as important as the loss of aluminum chloride in this step. The next step is to condense out the aluminum chloride at 90°C\textsuperscript{20}, aluminum chloride produced in this step is pure enough for commercial sale, as the titanium and silicon chlorides will not condense at this temperature. To remove the titanium and silicon chloride from the remaining gas, the gas is run through a condenser operating at -20°C.\textsuperscript{20} The titanium and silicon chloride can be separated later through fractional distillation.

The aluminum chloride obtained through selective condensation is of high purity and can then be recovered using molten salt electrolysis via the Hall-Heroult process, along with the usual feed of alumina.

Figure 25 shows a selective condensation and fractional distillation process for producing AlCl\textsubscript{3}. The process starts with feeding in clay, chlorine and carbon to a reactor where carbochlorination takes place. Following a quenching step, the process feeds into a series of condenser/distillation steps, first distilling off the TiCl\textsubscript{4}, which is removed for further treatment. By the end of the second step, all the TiCl\textsubscript{4} is removed and the third step begins separating the AlCl\textsubscript{3} from the FeCl\textsubscript{3}. The “AlCl\textsubscript{3} product” feeds into a fourth distillation column in Figure 26.
Figure 25: Selective Condensation and Fractional Distillation in Series²¹
Figure 26: Selective Condensation and Fractional Distillation in Series Part 2

The AlCl₃ concentrated gas mixture still has impurities in it, and so it is run through a further three condensation/distillation steps for further purification. The reason TiCl₄ is being added to Distillation Column D is that the patent Figure 25 and Figure 26 are from is proposing an alternate method of fractionally distilling AlCl₃ that avoids condensing AlCl₃ inside the distillation column, which can happen due to the range of temperatures the columns operate at. They proposed to solve this by adding in TiCl₄ to wash the column, preventing any crystal formation. TiCl₄ is used because its boiling point is much lower than AlCl₃ and FeCl₃, and also it is being produced earlier in the process and is therefore readily available already at the necessary temperatures.
Fractional distillation of metal chlorides also requires very strict temperature control as it mainly relies on the difference in boiling points between all the chlorides to separate them. Fractional distillation relies on heating up the chloride mixture slowly so each chloride vaporizes sequentially, allowing separation of the gaseous metal chlorides. Often there exist in ores many metal chlorides with boiling points extremely close together, rendering it difficult if not impossible to remove the impurities completely or very efficiently. Depending on the ore and therefore mixture of metals some metal chlorides formed can occlude the target chloride and vaporize simultaneously, despite having very different boiling points. This is usually due to complexes being formed at the temperatures necessary in such operations. For example, in fractional distillation of aluminum chloride, a hexachlorinated complex of iron and aluminum often forms at the volatility temperature of aluminum chloride.\(^9\)

**Fractional Distillation of Metal Chlorides to recover Aluminum Chloride**

Starting with a mix of metal chlorides, generally from the chlorination of an aluminum containing ore or clay (bauxite or kaolin or other), the mixture can be heated up in stages in a series of distillation columns thereby fractionally distilling out the chlorides in sequence due to their relative volatilities. Such a mixture of metal chlorides is usually assumed to contain ferric chloride, aluminum chloride, titanium tetrachloride and silicon tetrachloride. Fractional distillation of these metal chlorides requires at least three separate distillation columns operating at different temperatures.\(^{22}\) Such a process is demonstrated above in Figure 25 and Figure 26. The first lowest temperature column volatilizes titanium tetrachloride and silicon tetrachloride, as they have similar boiling points and both are much more volatile than ferric chloride and aluminum chloride. The second column operates at higher temperature and volatilizes the aluminum
chloride, leaving the iron chloride as a liquid which is then volatilized in the third column. The volatile chlorides obtained from the distillation columns are then quenched to form solid powders.
Appendix B

Sublimation Experiments

In order to determine the rate of sublimation of AlCl$_3$ a series of experiments were run at different temperatures and carrier gas flow rates at durations of one hour and thirty minutes, keeping a consistent mass of 50 g of AlCl$_3$ in the reactor. The experimental setup used was a Pyrex reactor and condenser, with a Pyrex connector all of which was wrapped with heat traces and insulated. A heating mantle was used to heat the reactor and three temperature controllers were used to control the temperature of the reactor heating mantle, reactor heating trace and connector heating trace, with an additional thermocouple monitoring the internal reactor temperature.

The experimental setup can be seen in Figure 27 the reactor is on the left and the condenser is on the right. Graphite foil was used to seal the lids of both the condenser and the reactor. Missing in Figure 27 is the additional gas condenser, which can be seen in Figure 28.
Also seen in Figure 28 are the insulated reactor and the gas flow meter. The experiment consisted of assembling the apparatus as shown, bringing the apparatus up to temperature, adding the AlCl₃ powder, letting the powder sublimate for the length of time specified in the experiment and then after the apparatus has been cooled down, weighing the amount of AlCl₃ powder remaining in the reactor and the amount condensed in the condenser. The results of the experiments have been summarized in
Table 20.
Table 20: Sublimation Experiment Results

<table>
<thead>
<tr>
<th>Run</th>
<th>Reactor Temp °C</th>
<th>Ar Flow Rate mL/min</th>
<th>Wt in Reactor G</th>
<th>Wt in Condenser G</th>
<th>Efficiency %</th>
<th>Time Min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>50</td>
<td>36.9</td>
<td>negligible</td>
<td>26.2</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>250</td>
<td>50</td>
<td>2</td>
<td>1</td>
<td>96</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>280</td>
<td>50</td>
<td>1.3</td>
<td>23.6</td>
<td>97.4</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>280</td>
<td>150</td>
<td>0.9</td>
<td>15.4</td>
<td>98.2</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>280</td>
<td>250</td>
<td>0.84</td>
<td>33.33</td>
<td>98.32</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>200</td>
<td>50</td>
<td>25.18</td>
<td>0.25</td>
<td>49.64</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>230</td>
<td>50</td>
<td>13.8</td>
<td>0.14</td>
<td>72.4</td>
<td>60</td>
</tr>
<tr>
<td>8</td>
<td>250</td>
<td>50</td>
<td>12.2</td>
<td>0.45</td>
<td>75.6</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>280</td>
<td>50</td>
<td>6.64</td>
<td>1.04</td>
<td>86.72</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>250</td>
<td>0</td>
<td>5.45</td>
<td>0.19</td>
<td>89.1</td>
<td>60</td>
</tr>
</tbody>
</table>

Ten runs were done at varying temperatures, run times and gas flow rates to determine the optimum temperature at which to run the final reactor for the AlCl formation experiments using 50 g of AlCl$_3$ and a reasonable amount of time (between 30 min and 2 hours is considered reasonable). The first seven runs were conducted at a run time of 60 min with varying temperature (200-280°C) and gas flow rate (50-250 mL/min Argon). An additional 2 runs at 50 mL/min at a run time of 30 min and varying temperature (250, 280°C) were conducted because the one hour experiments at these two temperatures showed the AlCl$_3$ to be completely sublimated and therefore a rate could not be determined. The effect of temperature can be seen in
Figure 29. The gas flow rate was seen to have negligible effect at the run times and temperatures used, so 50 mL/min was deemed to be sufficient.

As can be seen in Figure 29, efficiencies in excess of 75% were achieved at temperatures of 250°C and higher at both 30 and 60 min. Therefore, 250°C was determined to be the optimum temperature at which to operate the final reactor, as increases in temperature beyond 250°C do not increase the efficiency any appreciable amount (especially in the 60 min run time).

Based on the results from the sublimation experiments, the final reactor for AlCl₃ sublimation in the AlCl formation reactions can be run at 250°C and 50mL/min argon carrier gas flow. This means the reactor can use Teflon or similar o-rings and does not require the complicated lid as previously designed.
Appendix C

Experimental Procedure

Set-up

1. Weigh all components
2. Screw graphite tube into top lid of formation reactor
3. Insert thermowells and thermocouples into top lid of formation reactor
4. Insert support rod, SiCl₄ feed tube (SS ¼”) and cold finger with shielding into bottom lid of formation reactor and tighten Swageloks
5. Insert formation reactor tube into MoSi₂ furnace from the top
6. Insert support rod, SiCl₄ feed tube and cold finger with shielding into formation reactor tube while holding aluminum-containing crucible on top of support rod and line up bottom lid with tube
7. Seal formation reactor tube with bottom lid
8. Support bottom lid with large screws
9. Attach top lid to formation reactor tube
10. Place table on top of the furnace
11. Put resistance furnace on table, lining up holes in table and resistance furnace
12. In glove box, weigh out 10 g aluminum chloride into 50 mL crucible and 5 g into 2 each 20 mL crucible and seal with parafilm
13. In positive pressure glove box, using a syringe, inject 15 mL of SiCl₄ into stainless steel tube (held by a retort stand and placed in containment vessel) and tighten Swagelok fitting on top, making sure all valves are closed. Add in slowly to prevent overflow.
14. Place small crucibles into the bottom of sublimation reactor
15. Connect to feed tube and Ar and purge container with Ar, then lower 1/8” tube bubbler into SiCl₄ tube, and purge again
16. Insert thermowell and thermocouple into lid of sublimation reactor
17. Attach gas in tube to lid
18. Seal sublimation reactor with lid
19. Lower sublimation reactor into resistance furnace and set on springs
20. Attach sublimation reactor to top lid of formation reactor via pipe latches
Leak test apparatus

21. Pressurize to (TBD by leak test) 2 psi
22. Hold pressure for 15 min
23. If gauge shows pressure drop, use soap to find and fix leaks until it holds for 30 min
   1. Begin leak test procedure over again

Purge

24. Connect gas out tube to off-gas system in fume hood
   1. Gas out connects to dry trap (2 L)
   2. Dry trap connects to wet trap (500 mL)
   3. Wet trap vents into fume hood
25. Flow Ar 50 mL/min

Pre-Experiment Checklist before Heating

1. Is Ventilation on?
2. Did the apparatus pass the leak test?
3. Has the apparatus been purged?
4. Are the temperature controllers programmed/set properly and the thermocouples attached to controller/reader?
5. Is everything insulated/shielded?
6. Is the tube supported from the bottom?
7. Is the gas out line connected to the off gas system?
8. Is the off gas system in the fume hood?
9. Is the fume hood on?
10. Is the apparatus grounded?
11. Is the Ar running at 50 mL/min?

26. Attach grounding wire to latch on connecting tube
27. Insulate top furnace
28. Wrap connecting pipe with heating tape
29. Plug resistance furnace into temperature controller
30. Plug thermocouples into reader and temperature controllers
31. Begin heating up MoSi\textsubscript{3} furnace to 1250°C

Then begin heating up bottom furnace to 1250°C using the following procedure.

1. Turn on the Main Power at the Disconnect Switch. The green light on the Controller Panel should be on and indicating the power is on, cooling fan starts running.
2. Turn the power locking switch on, Temperature Controller show “power on”.
3. Temperature Controller should be on measuring only mode: PV showing small digital number and SV flashing “stop”. If Controller is not in this mode, press the up button
4. Set up the program in Temperature Controller
5. Press < for just one second, controller shows C01, should be set as 0°C
6. Press scroll button, controller shows t 01, 250 min
7. Scroll again, controller shows C 02, 1250°C
8. Scroll again, controller shows t 02, 120 min, which is the time the furnace will soak at 1250°C
9. Press scroll again, controller shows C 03, 1250°C
10. Scroll again, controller shows t 03, 250 min, which is how long it will take to get to the next temperature
11. Scroll again, controller shows C 04, 0°C (furnace to room temperature)
12. Scroll again, controller shows t 04, -121, program end automatically
13. After setting up the temperature profile program, wait 30 seconds or press < and scroll at the same time and controller will return to measuring mode automatically, the press the down button to run the program.

Experiment

32. Check for leaks once bottom furnace is at high temperature but not yet at operating temperature
33. When MoSi\textsubscript{3} furnace is at 1250°C, pause program on furnace
34. Begin heating top reactor to 250°C
35. Turn on heating tape (SP 200°C)
36. Open valves on SiCl\textsubscript{4} bubbler and turn on Ar flow to bubbler once top reactor reaches 200°C
37. When top reactor reaches 250°C start recording temperature, pressure and observations for 45 min
38. After the 45 min, close bubbler valve on SiCl₄ tube and pull bubbler up, closing valve on SiCl₄ tube
39. Cool down furnaces to room temperature overnight with Ar running, leaving Ar purge on SiCl₄ running overnight.

Dismantling
40. Detach all inlet and outlet tubes from apparatus, including cold finger and SiCl₄ container
41. Detach sublimation and formation reactors and remove sublimation reactor from resistance furnace
42. Immediately cover both ends of connecting tube with parafilm
43. Place sublimation reactor in fume hood
44. Take lid off top reactor and remove crucibles
45. Quickly cover crucibles with parafilm and weigh
46. Remove resistance furnace from table
47. Remove table from MoSi₃ furnace
48. Place paper under formation reactor
49. Remove top lid from formation reactor
50. Remove crucible from formation reactor, cover with parafilm and place in fume hood
51. Remove support rod and shielding from formation reactor and place in fume hood
52. With one person lifting tube up, remove bottom lid from tube
53. Cover bottom of formation reactor tube with parafilm
54. Remove formation reactor from furnace by lifting straight up
55. Place formation reactor in fume hood
56. Move bottom lid to fume hood
57. Collect all AlCl₃ residue into containers and weigh
58. Weigh all components
59. Analyze wet trap for Al and try mass balance

Waste Disposal Procedure
60. To dispose of AlCl₃ after use, dissolve in excess amounts of water and dispose down drain

Personal Protective Equipment

- Gas mask
- Gloves (Nitrile and heat resistant)
- Safety Glasses
- Steel toed shoes
- Lab coat
Appendix D

Hydrogen Evolution Sample Calculation

After the sample has been collected and the sample pre-treated to remove any residual AlCl₃ (either by washing or heating), the samples are analysed by hydrogen evolution. The first step is to place the powder in a small vacuum flask and cap with a soft plastic cap. A tube is connected to the vacuum nozzle which runs under water into a water-filled inverted graduated cylinder. The water in the experiment was dyed pink in order to assist with reading the volumes off the graduated cylinder. The initial volume of water in the graduated cylinder was recorded and then 40 mL of concentrated HCl (excess) were added by a syringe inserted into the soft cap. The HCl and any aluminum in the sample react via reaction [25]:

\[
2\text{Al} + 3\text{H}_2\text{O}^{\text{acidic}} = \text{Al}_2\text{O}_3 + 3\text{H}_2
\]

The volume of hydrogen that evolves once the concentrated HCl is added can be determined by recording the final volume of water in the graduated cylinder and subtracting the initial water volume. The aluminum content can then be calculated by calculating the number of moles of hydrogen, dividing this by three and multiplying by two to get the number of moles of aluminum. The mass of aluminum is then simply calculated by multiplying the number of moles of aluminum by the molar mass of aluminum (26.98 g/mol).

Example:

Starting Volume: 40 mL
Ending Volume: 136 mL
Volume of Hydrogen: 136 – 40 = 96 mL

Moles of Hydrogen: \[ n = \frac{PV}{RT} = \frac{(1\text{atm} \times 96\text{mL})}{(0.082\text{atmL/molesK} \times 298\text{K} \times 1000\text{mL/L})} = 0.0039 \text{ moles H}_2 \]

Moles of Al: \[ 0.0039 \times \frac{2}{3} = 0.0026 \]

Mass of Al: \[ m = nM = 0.0026 \times 26.98 = 0.07 \text{ g of Aluminum} \]
### Appendix E

#### Hydrogen Evolution Results

**Table 21: Test F3 Hydrogen Evolution**

<table>
<thead>
<tr>
<th>Name</th>
<th>Starting Volume</th>
<th>End Volume</th>
<th>Volume Change</th>
<th>Acid Volume Added</th>
<th>Mass of Acid</th>
<th>mol H₂</th>
<th>mol Al</th>
<th>g Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Trap</td>
<td>26 mL</td>
<td>92 mL</td>
<td>66 mL</td>
<td>60 mL</td>
<td>2.16 g</td>
<td>0.00270</td>
<td>0.00180</td>
<td>0.040858</td>
</tr>
<tr>
<td>Scrapings</td>
<td>20 mL</td>
<td>84 mL</td>
<td>64 mL</td>
<td>10 mL</td>
<td>0.36 g</td>
<td>0.00087</td>
<td>0.00038</td>
<td>0.01031</td>
</tr>
</tbody>
</table>

**Table 22: Test F5 Hydrogen Evolution**

<table>
<thead>
<tr>
<th>Name</th>
<th>Starting Volume</th>
<th>End Volume</th>
<th>Volume Change</th>
<th>Acid Volume Added</th>
<th>Mass of Acid</th>
<th>mol H₂</th>
<th>mol Al</th>
<th>g Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Trap</td>
<td>40 mL</td>
<td>40 mL</td>
<td>0 mL</td>
<td>30 mL</td>
<td>0.108 g</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Scrapings from Shields</td>
<td>32 mL</td>
<td>64 mL</td>
<td>22 mL</td>
<td>20 mL</td>
<td>0.072 g</td>
<td>0.00059</td>
<td>0.00036</td>
<td>0.01619</td>
</tr>
<tr>
<td>Scrapings from Middle</td>
<td>64 mL</td>
<td>134 mL</td>
<td>70 mL</td>
<td>30 mL</td>
<td>0.108 g</td>
<td>0.00286</td>
<td>0.00191</td>
<td>0.05153</td>
</tr>
</tbody>
</table>

**Table 23: Test F6 Hydrogen Evolution**

<table>
<thead>
<tr>
<th>Name</th>
<th>Starting Volume</th>
<th>End Volume</th>
<th>Volume Change</th>
<th>Acid Volume Added</th>
<th>Mass of Acid</th>
<th>mol H₂</th>
<th>mol Al</th>
<th>g Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inside of Al Crucible</td>
<td>15 mL</td>
<td>162 mL</td>
<td>147 mL</td>
<td>40 mL</td>
<td>8.712 g</td>
<td>0.006</td>
<td>0.004</td>
<td>0.1082</td>
</tr>
<tr>
<td>Alumina Tube</td>
<td>15 mL</td>
<td>35 mL</td>
<td>20 mL</td>
<td>40 mL</td>
<td>8.712 g</td>
<td>0.0008</td>
<td>0.0005</td>
<td>0.0147</td>
</tr>
<tr>
<td>Bottom Lid and Alumina Rod</td>
<td>22 mL</td>
<td>164 mL</td>
<td>142 mL</td>
<td>40 mL</td>
<td>8.712 g</td>
<td>0.0058</td>
<td>0.0039</td>
<td>0.0891</td>
</tr>
<tr>
<td>Graphite Tube and Middle Lid</td>
<td>33 mL</td>
<td>373 mL</td>
<td>340 mL</td>
<td>40 mL</td>
<td>8.712 g</td>
<td>0.0139</td>
<td>0.0093</td>
<td>0.2503</td>
</tr>
</tbody>
</table>

**Table 24: Test F7 Hydrogen Evolution**

<table>
<thead>
<tr>
<th>Name</th>
<th>Starting Volume</th>
<th>End Volume</th>
<th>Volume Change</th>
<th>Acid Volume Added</th>
<th>Mass of Acid</th>
<th>mol H₂</th>
<th>mol Al</th>
<th>g Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Trap</td>
<td>26 mL</td>
<td>264 mL</td>
<td>238 mL</td>
<td>20 mL</td>
<td>8.64 g</td>
<td>0.0097</td>
<td>0.0065</td>
<td>0.1752</td>
</tr>
<tr>
<td>Shield Pieces</td>
<td>40 mL</td>
<td>136 mL</td>
<td>96 mL</td>
<td>40 mL</td>
<td>17.28 g</td>
<td>0.0039</td>
<td>0.0026</td>
<td>0.0707</td>
</tr>
<tr>
<td>Loose Powder</td>
<td>20 mL</td>
<td>384 mL</td>
<td>404 mL</td>
<td>20 mL</td>
<td>8.64 g</td>
<td>0.0165</td>
<td>0.011</td>
<td>0.2974</td>
</tr>
</tbody>
</table>