

**ALUMINA FROM COAL WASTES THROUGH THE
FORMATION OF ALUMINUM NITRIDE**

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FORMATION OF ALUMINUM NITRIDE

by

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A thesis submitted to the faculty of
The University of Utah
in partial fulfillment of the requirements for the degree of

Master of Science

in

Metallurgy

Department of Metallurgy and Metallurgical Engineering

The University of Utah

December 1982

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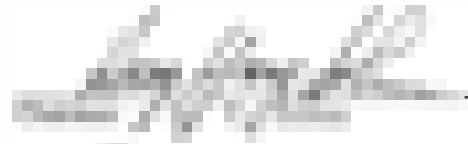
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ABSTRACT

The carbothermal reduction of coal wastes under a nitrogen atmosphere to form aluminum nitride and silicon carbide was carried out in the present study. The leaching of the aluminum nitride to subsequently produce aluminum hydroxide was also investigated. Thermodynamic and kinetic factors such as reaction time, temperature, particle size, mixing, pelletizing, excess carbon, and nitrogen flow rate were considered.

A minimum temperature of 1350°C and a reaction time of 1-2 hours were needed to produce aluminum nitride. Up to 98% of the alumina originally present was converted to aluminum nitride. When the temperature became too high, or the reaction time too long, the formation of aluminum nitride dropped off. This hindered the ability to completely leach the aluminum nitride. Optimum reaction times at various temperatures were determined.

The optimal leaching conditions were found to be one molar sodium hydroxide for two hours at boiling temperature. Approximately 70% of the aluminum nitride could be decomposed by leaching. Before precipitation of aluminum hydroxide, calcium hydroxide was added to remove the iron and silica impurities.

The overall recovery of alumina was determined to range from 40-60%. Silicon carbide and ammonia are valuable by-products of the process.

TABLE OF CONTENTS

	Page
ABSTRACT	iv
LIST OF TABLESviii
INTRODUCTION	1
THERMODYNAMIC CONSIDERATIONS	5
PREVIOUS INVESTIGATIONS ON CARBOTHERMAL REDUCTION IN A NITROGEN ATMOSPHERE	12
History of Carbothermal Reduction of Alumina	12
Reaction Mechanism	14
Carbothermal Reduction of Silica	14
Carbothermal Reduction of Aluminum Nitrate	15
Products of Reaction	16
Silicon Carbide	16
Silicon Nitride	17
Transforming Silicon Nitride to Silicon Carbide	19
Aluminum Nitride	19
Obtaining Alumina from Aluminum Nitride	20
Effect of Iron Catalyst	22
EXPERIMENTAL	24
Sample Preparation and Identification	24
Carbon Analysis	26
Apparatus for Carbothermal Reduction	27
Apparatus for Leaching	31
Analysis of the Reaction Products	31
RESULTS AND DISCUSSION	33
Preliminary Results	33
Qualitative Analysis	35
Quantitative Analysis	37
Reduction of Silica by Silicon Carbide	42
Effect of Excess Carbon	52
Weight Loss	56
Effects of Mixing	61
Surface Area Effect	62
Effect of Temperature	64

TABLE OF CONTENTS (Continued)

	Page
Effect of Pelletizing	67
Effect of Nitrogen Flow Rate	70
Leaching	70
Precipitation	82
 CONCLUSIONS	 86
Stage I: Carbothermal Reduction of Alumina in Coal Waste Under a Nitrogen Atmosphere to Produce Aluminum Nitride	 86
Stage II: Leaching of Aluminum Nitride to Obtain Aluminum Hydroxide	 87
Stage III: Desilication and Precipitation of Sodium Aluminate Solutions	 89
 RECOMMENDATIONS FOR FURTHER STUDY	 91
 APPENDIX	 92
 REFERENCES	 93

LIST OF TABLES

TABLE		Page
I.	Free Energy of Formation Values	10
II.	Initial Analysis of Material	26
III.	Preparation Plant Waste Analysis	26
IV.	Product Analysis	43
V.	Effect of Excess Carbon	53
VI.	Effect of Mixing	64
VII.	Effect of Particle Size	64
VIII.	Effect of Temperature	66
IX.	Effect of Nitrogen Flow Rate	71

INTRODUCTION

The need for aluminum is growing rapidly. It is the second most widely used metal today, with consumption exceeding that of all non-ferrous metals combined. Even though it is the third most common element in the earth's crust, only a small portion of aluminum minerals are used commercially for producing aluminum.

Currently, the Bayer process accounts for nearly all of the alumina production in the world. This process depends on bauxite ore ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), which is not readily available in the United States. In fact, the USA imports 90% of the approximately 3,500,000 tons per year of the bauxite it uses. Furthermore, the demand for aluminum resources by other industrial nations is also increasing.

Bauxite is formed in warm climates where heavy rainfall can leach other metals from the soil and leave a high concentration of alumina. Such climates are typical of tropical countries.

To avoid becoming dependent upon foreign imports, the USA must find alternative resources and technologies. Many other aluminum bearing minerals besides bauxite are abundant. These include alunite, anorthosite, halloysite, and kaolinite. Their usefulness is limited only

by economics and man's ingenuity in processing them. Several innovative processes using these non-bauxite domestic raw materials have been analyzed and reviewed by the U.S. Bureau of Mines.¹ These methods include sintering with lime (and soda ash), chlorination, and acid or alkali leaching. Although some of these methods appear promising, none has been used beyond the pilot plant stage because production costs are too great.

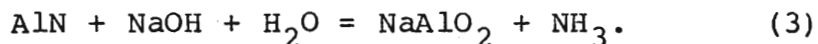
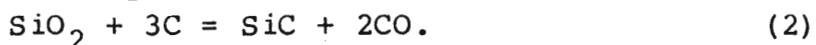
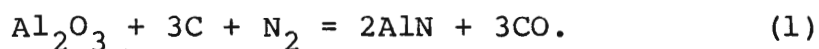
Also of concern to the USA at this time is the increasing cost and dwindling reserves of petroleum. It has become apparent that the USA must develop its own domestic energy sources in order to become independent of foreign sources for fuel. An emphasis has been put on using more coal. With this increase in coal production comes an increase in coal wastes - the overburden material and preparation plant tailings. These coal wastes cause ever increasing disposal problems. Yet coal wastes contain a significant fuel value and may even prove to be a valuable source of alumina.

In an attempt to solve both of these problems simultaneously, a process using coal waste material to produce alumina has been investigated in this work. This is attractive in that a waste containing 10-30% Al_2O_3 and 40-70% SiO_2 , which normally must be discarded, could be used as a resource. The carbon inherently present in the wastes helps reduce the alumina and silica under a nitrogen atmosphere to form aluminum nitride and silicon

carbide. The basic reaction scheme was originally patented by Serpek² using bauxite ore. Recently, Cutler³ has proposed applying the process to kaolin clay. Because clay is a component of coal wastes, the process could be applicable to these wastes. The fuel value inherent in the coal waste is expected to supply most of the energy requirements. Heat could be recovered from the hot combustion gases formed to produce electricity to satisfy the needs of the aluminum production.

The aluminum nitride is leached in a caustic solution in the form of sodium aluminate, which can subsequently be treated to produce aluminum hydroxide or alumina. Two valuable by-products are obtained: silicon carbide and ammonia. This is a major advantage of the process.

The following reactions are involved:



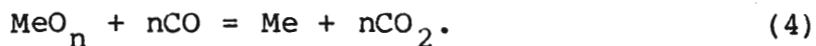
With carbon alone, the reduction of alumina is very difficult and a high temperature is required.⁴ However, in a nitrogen atmosphere, alumina can be reduced to aluminum nitride, a reaction possible at a lower temperature. Nitrogen gas also serves to flush out the carbon monoxide, helping both reactions 1 and 2 proceed as written.

Reactions 1 and 2 are examples of reaction between two solids proceeding through gaseous intermediates.

Sohn⁵ has formulated original theories to determine important reaction mechanisms for such systems. His theories will be of use in this study.

THERMODYNAMIC CONSIDERATIONS

When carried out at atmospheric pressure, it has been found⁶ that the direct reduction of many metal oxides with solid carbon usually takes place through gaseous intermediates, with the following steps:



Several examples are available in the literature supporting this type of mechanism. In particular, the reduction of silica will be discussed later in detail. Reduction can occur when the ratio between CO_2 and CO in the gas phase falls below the equilibrium value. The corresponding ratio $P_{\text{CO}_2}/P_{\text{CO}}$ is shown in Figure 1 for several oxides. Low concentrations of carbon monoxide alone can reduce the less stable oxides Cu_2O , PbO , and Fe_2O_3 . However, alumina and silica are very stable oxides. To reduce these, a gas ratio virtually free of carbon dioxide is required. The reduction process stops as soon as a small amount of carbon dioxide is formed - even if the reduction begins under a pure carbon monoxide atmosphere.

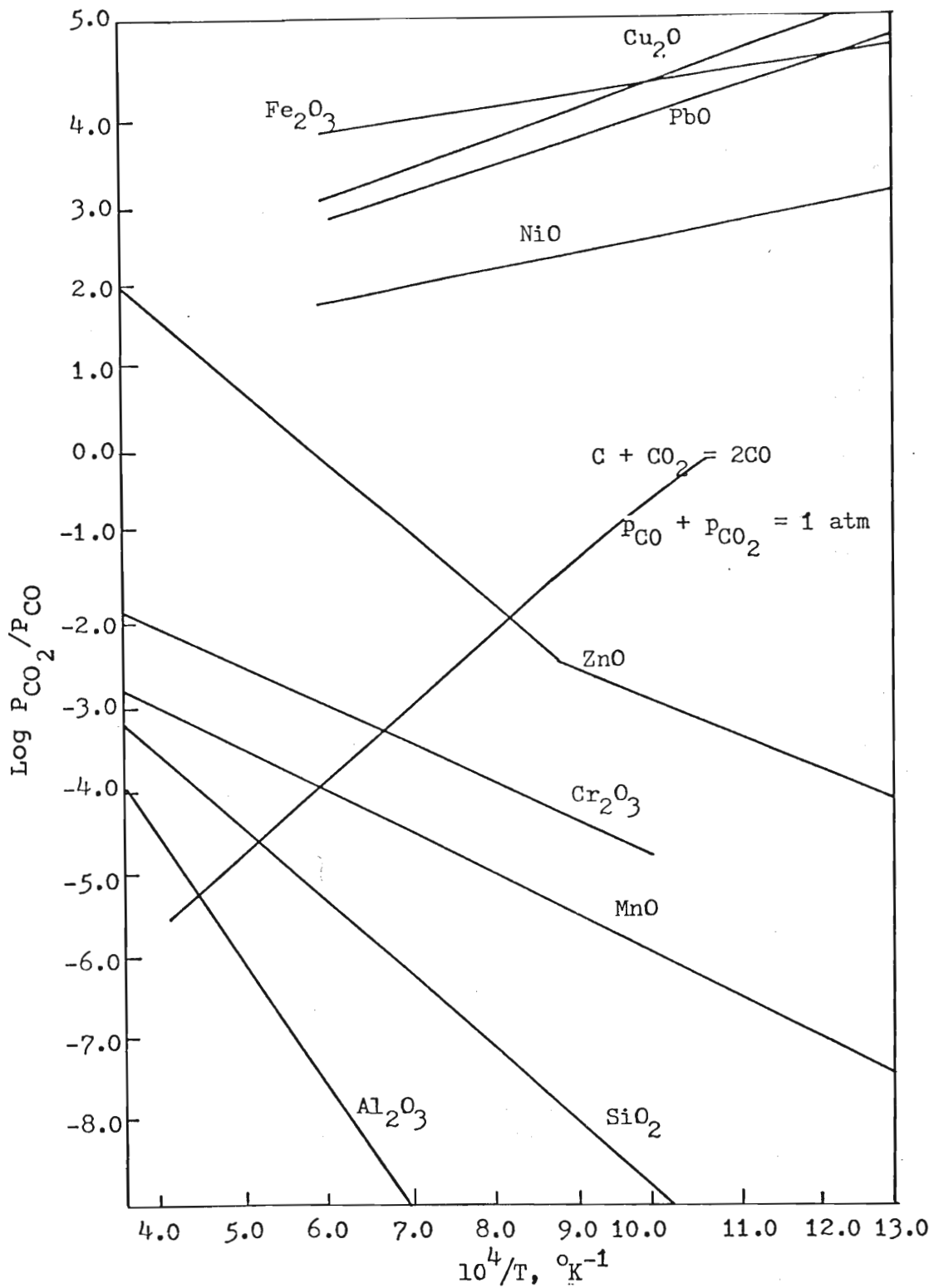
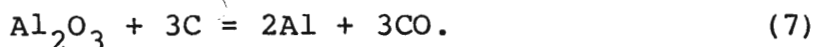


Figure 1. Equilibrium gas ratio $P_{\text{CO}_2}/P_{\text{CO}}$ for the reduction of various oxides.

Therefore, carbon is essential in the reduction of stable oxides. As seen in reaction 5, carbon can be interpreted as either a CO_2 getter or a CO generator and acts to keep the $P_{\text{CO}_2}/P_{\text{CO}}$ ratio low enough to make the reduction possible. The initial formation of carbon monoxide may occur either by the oxygen of the entrapped air in the carbon particles reacting with carbon, or by a solid-solid reaction of particle contacts between carbon and the metal oxide. Although the amount of carbon monoxide produced is small, either of these reactions would occur before any other reaction. Once carbon monoxide is present for reaction 4, carbon will regenerate carbon monoxide through reaction 5.

As seen in Figure 1, alumina can be reduced only with great difficulty at high temperatures with carbon alone.



Therefore, in order to reduce alumina, it is proposed to form aluminum nitride by having both carbon and nitrogen present (see reaction 1). In Figure 2, the free energies of formation for the reduction of alumina to form either aluminum or aluminum nitride are shown.

As seen aluminum nitride can be formed at a lower temperature than aluminum.

For the carbothermal reduction of alumina and silica under a nitrogen atmosphere, other probable products of reaction, besides aluminum nitride and aluminum are

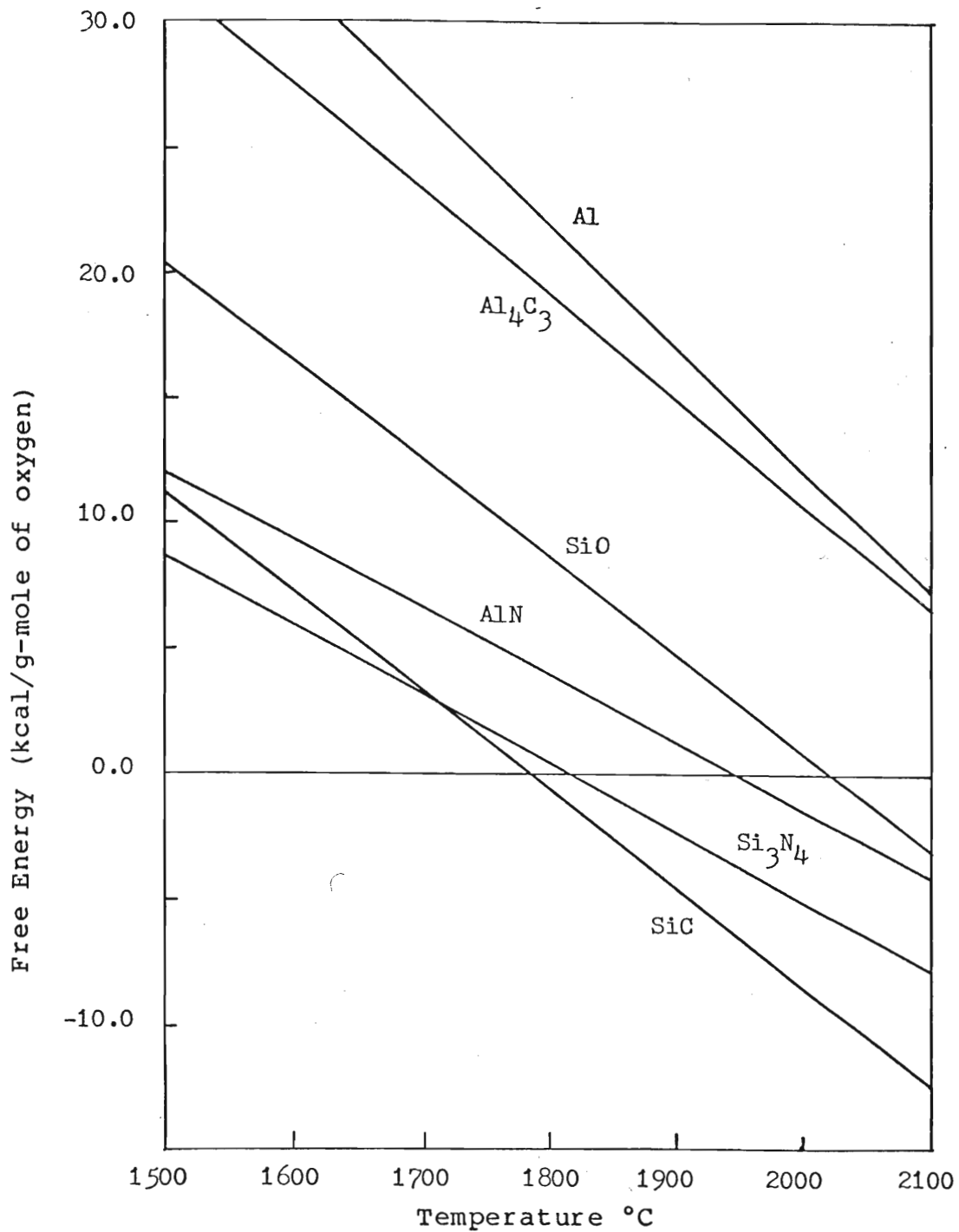
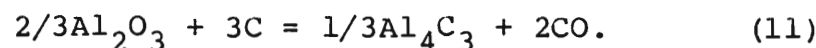
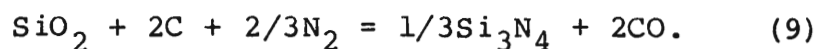
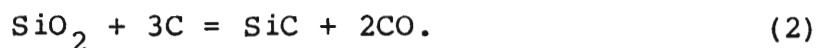


Figure 2. Free energy of formation for possible reactions in the alumina-carbon-nitrogen and silica-carbon-nitrogen systems.

silicon carbide, silicon nitride, silicon oxide, and aluminum carbide. The corresponding reactions are:



Using the standard thermodynamic data⁷ listed in Table I, Figure 2 shows the standard free energies of formation versus temperature for the above reactions. This type of information can be useful in determining if the reactions will proceed as written. For example, at 1575°C aluminum nitride, silicon carbide, and silicon nitride are all possible products of reaction. However, thermodynamic data alone are not sufficient in predicting the reaction rate or path.

Also by using the thermodynamic data, the equilibrium carbon monoxide partial pressure for the above reactions can be determined. These values are plotted in Figure 3 for various temperatures. The reactions with the higher carbon monoxide partial pressure are more likely to proceed if the pressure can be maintained as specified in the graph. As seen, the formation of aluminum nitride is favored over the other possible aluminum compounds.

TABLE I. Free Energy of Formation Values
(kcal/mole)

Compound	1600°C	1700°C	1800°C	1900°C	2000°C
AlN (s)	-33.94	-31.178	-28.420	-25.664	-22.914
Al ₂ O ₃ (s)	-276.865	-269.198	-261.557	-253.944	-246.359
CO (g)	-60.284	-62.315	-64.337	-66.349	-68.353
CO ₂ (g)	-94.739	-94.746	-94.750	-94.751	-94.752
SiC (s)	-14.548	-14.263	-13.372	-12.485	-11.597
Si ₃ N ₄ (s)	-51.850	-43.837	-34.043	-24.289	-14.572
SiO ₂ (s)	-149.791	-145.607	-140.833	-136.076	-131.338
SiO (g)	-56.244	-57.992	-59.118	-60.237	-61.340
Al ₄ C ₃	-27.028	-24.755	-22.478	-20.191	-17.909

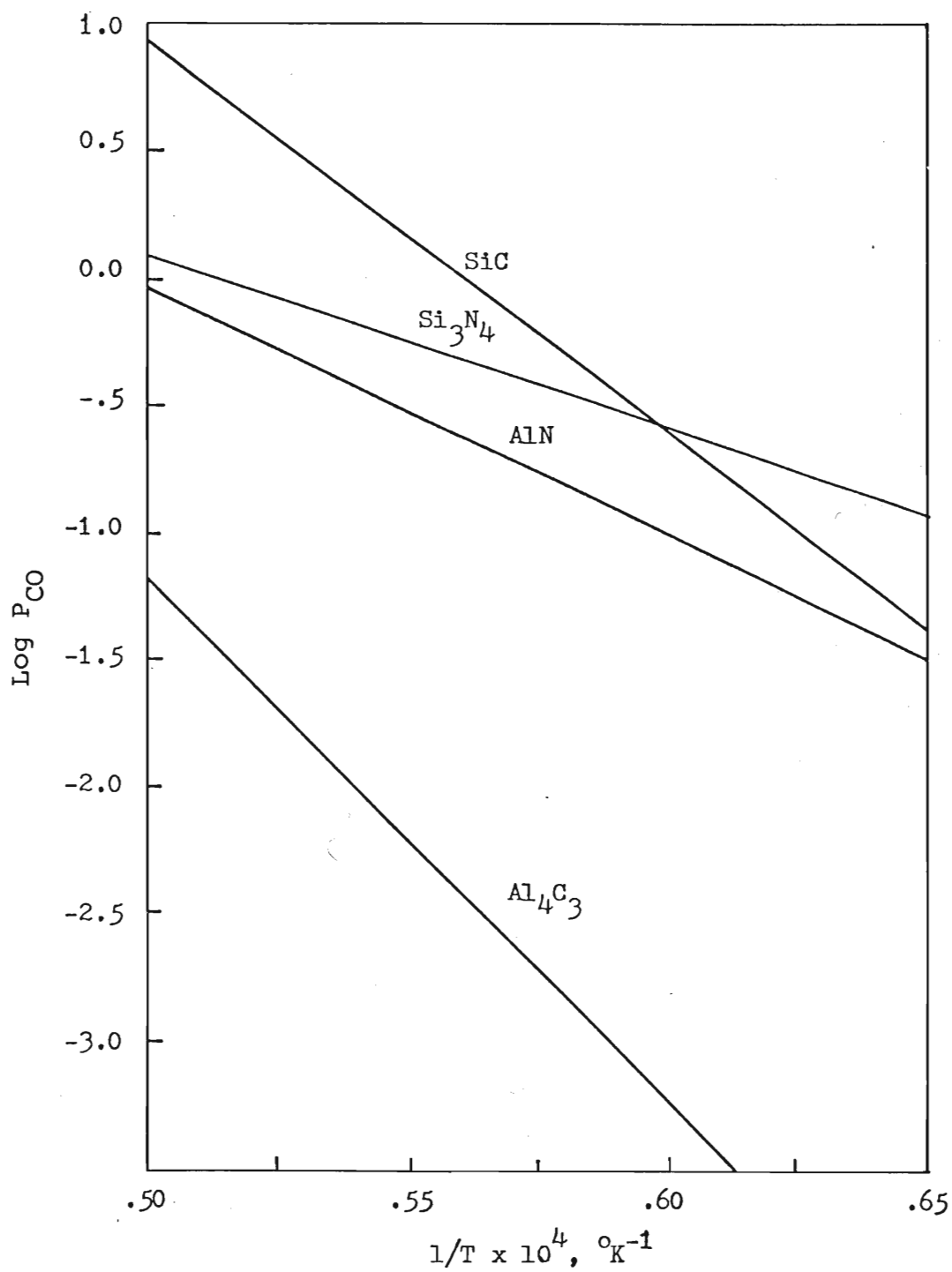


Figure 3. Equilibrium CO pressures for alumina-carbon-nitrogen, silica-carbon-nitrogen reactions.

PREVIOUS INVESTIGATIONS ON
CARBOTHERMAL REDUCTION IN
A NITROGEN ATMOSPHERE

History of Carbothermal
Reduction of Alumina

A review of the literature shows that the idea of carbothermal reduction of alumina in the presence of nitrogen is not new. As early as 1896, Willson⁸ received a patent stating that metallic nitrides can be produced by heating the oxide of the metal with carbon and nitrogen. Although he worked primarily with magnesium oxide, Willson did mention the possibility of using alumina.

In 1908, Serpek² patented a process in which bauxite and coke are heated in an electric furnace under a nitrogen atmosphere. The major objective of this process was the production of ammonia (see reaction 3). Until that time, the Haber process for producing ammonia inexpensively had not been developed. Serpek found the reaction to proceed at a temperature of 1800°C with a noticeable reaction occurring at 1100°C.

Fraenkal and Silbermann⁹ experimented with this system in 1913. They found the reaction beginning at 1400°C and proceeding readily by 1500°C. Over the next

several years, patents were issued to several researchers regarding improvements on the system.¹⁰

However, due to new methods of producing ammonia and the lack of technology in high temperature equipment, the idea was abandoned for many years. In addition, several technical difficulties were encountered which hindered successful operation of the process.⁴

It should be noted that most of these early researchers used bauxite ore as the alumina source. Recently, some researchers have taken a renewed interest in this process, especially using materials other than bauxite.

In 1962, Clair¹¹ in France obtained a U.S. Patent for a process and furnace to continuously produce aluminum nitride via reaction 1. He stipulated that the reaction temperature cannot exceed 1750°C, because at higher temperatures, aluminum carbide is formed. He does not mention the source of alumina.

In 1977, Kost, et al.,¹² showed the possibility of obtaining aluminum nitride and silicon nitride from coal wastes using the Serpek reaction. However, they did not attempt to separate the aluminum nitride from the other compounds present in the final product.

Along these same lines, Japanese investigators¹³ have patented a process for obtaining silicon nitride and silicon carbide by nitridding a mixture of diatomaceous earth with carbonaceous materials in the temperature range 1400-1700°C.

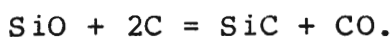
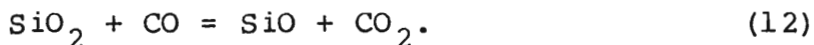
Finally, in 1978, Bechtold¹⁴ showed that clay minerals can be used to produce aluminum nitride.

Reaction Mechanism

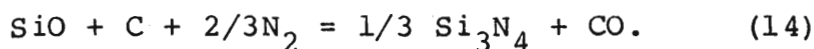
Carbothermal Reduction of Silica

The reaction between carbon and silica to form silicon carbide dates back before the turn of the century with Acheson's¹⁵ original experiments. Since that time, this system and the corresponding reaction mechanism have been studied extensively. Several authors¹⁶⁻²⁰ have concluded that the carbothermal reduction of silica occurs through the gaseous intermediate SiO.

Lee¹⁶ proposed the following gas-solid reaction scheme for the carbothermal reduction of silica in a nitrogen atmosphere:



or



Similar mechanisms have been proposed for other oxides that are less stable than silica.

Lee showed that reactions 8 and 14 are not the slowest steps. He found that SiO reacts with carbon as soon as it forms. Consequently, he proposed that reactions 12 and 13 are linked in a chain mechanism

and that together they control the overall reaction rate.

Carbothermal Reduction of Aluminum Nitride

Although it has never been extensively studied, it is supposed that the carbothermal reduction of alumina in a nitrogen atmosphere proceeds through steps similar to reactions 12, 13 and 8.

However, preliminary work by other researchers shows the formation of several intermediates. Stroup,⁴ in reviewing the process, concluded that it is doubtful if the reaction to produce aluminum nitride is as simple and straightforward as expressed in reaction 1. To the present time, efficient production of aluminum nitride has not been demonstrated and the process is probably complicated by the formation of suboxides, aluminum carbide, aluminum oxy-carbide and cyanides. Grjotheim²¹ believes the process to be too inefficient and energy intensive to be considered industrially.

Repenke, et al.,²² have investigated the conversion of a mixture of alumina and carbon at 1660-1800°C in a nitrogen atmosphere and believe the first stage of the reaction is the formation of the spinelide, Al_3O_4 , which is then converted into aluminum oxynitride and finally into aluminum nitride. Lejus²³ has obtained aluminum nitride at 1700° under a nitrogen flow from a mixture containing Al_2O_3 and carbon. When the obtained

product was heated with alumina, aluminum oxynitrides were formed.

This study does not attempt to determine the mechanism for the reaction. It will only be assumed that gaseous intermediates are involved. Perhaps the best method to determine the gaseous species would be with a mass spectrometer. This method, however, was not attempted in this investigation.

Products of Reaction

Due to rapidly advancing high temperature technology, better refractory materials are needed. Presently, a great deal of attention is being devoted to refractory materials based on nitrides and carbides, especially silicon carbide and silicon nitride. These two materials are obtained as by-products in this study. Perhaps it would be useful to expound upon the characteristics of these compounds, as well as aluminum nitride.

Silicon Carbide

Because of its high resistance to thermal shock and stress, exceptional corrosion resistance in high temperature oxidizing environments, and good stability at high temperatures, silicon carbide has found uses as semiconductors, refractories, abrasives, heating elements, rocket nozzles, combustion tubes, combustion chamber liners, linings for ball mills, and as an additive in ferrous metallurgy.²⁴ In particular, there has been

an increasing demand for silicon carbide with fine particle sizes in the grinding and polishing industry.

Currently, silicon carbide is manufactured using the Acheson process.¹⁵ Mixtures of silicon and carbon with a small percent of sawdust and common salt (to remove impurities) are heated in large trough-type electric furnaces. A centrally mounted core of graphite and coke through which a large current can pass serves as a heating element. Temperatures higher than 2000°C for two to three days are required for completion of the reaction. The product appears at the end of the process in the form of an intergrown crystalline mass of alpha silicon carbide.

Silicon carbide exists in two crystalline forms, alpha and beta. Alpha phase is hexagonal, but has many modifications based on stacking sequences in the layered structure. Beta phase is cubic. Alpha phase is stable at higher temperatures and beta transforms slowly to alpha above 1900°C. However, this transition temperature is not well defined.

Silicon Nitride

Silicon nitride has received growing interest as a ceramic material for high temperature applications. Especially attractive is its lower cost compared to the expensive refractory materials it replaces.²⁵

The desirable characteristics of silicon nitride include a low coefficient of thermal expansion, high strengths over a wide range of temperatures, good thermal conductivity and good resistance to oxidation, thermal shock, creep and corrosion.

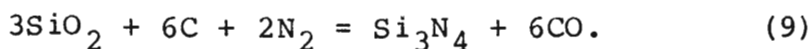
Silicon nitride is extremely stable chemically. HCl, H₂SO₄, H₃PO₄ at all concentrations, chlorine at 900°C, H₂S at 1000°C, boiling 25% NaOH solutions reportedly have no effect on it in tests of 500 hours.²⁶ However, it is decomposed by hydrofluoric acid solutions.

It has a wide variety of uses including crucibles and boats for melting and refining semiconductor materials, thin walled thermocouple protection tubes, radiant heat shields, rocket nozzle inserts, and turbine components for electricity generation and vehicle propulsion.

Silicon nitride also exists in two phases, alpha and beta.

The majority of silicon nitride is manufactured by nitridization of silicon. This is a slow process. Silicon nitride forms on the silicon surface and slows the diffusion of nitrogen. Thermodynamically, the formation of silicon nitride from metallic silicon requires very low partial pressures of nitrogen and oxygen.

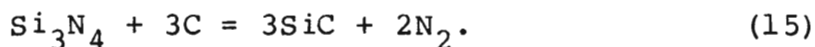
The synthesis of silicon nitride by the reaction between silica, carbon and nitrogen has been well known since a German patent was granted in 1896 to Mehner.²⁷ The reaction was more recently studied by Mah.²⁸



It promises to be a fast, inexpensive method to produce high purity silicon nitride. However, there are a few drawbacks. Mah found the reaction to be complicated by the formation of silicon carbide and the existence of unreacted silica. The major problem, however, was the difficulty in forming dense, complex shapes. Novel densification procedures have been developed²⁹ to alleviate this problem.

Transforming Silicon Nitride to Silicon Carbide

Depending on the desired product, it is possible to transform silicon nitride to silicon carbide according to the reaction



Thermodynamics indicate the reaction should proceed at temperatures greater than 1400°C. To lower the reaction temperature, nitrogen should be removed during the reaction. This is accomplished by reacting the nitride with excess carbon in a flowing inert gas atmosphere.

Aluminum Nitride

Aluminum nitride is also finding uses as a refractory material. Although first prepared many years ago, its properties have not been well known. It has been shown³⁰ that aluminum nitride is relatively inert. The material is essentially unaffected by mineral acids.³¹ Compared

to most ceramics, it has a high thermal conductivity, low thermal expansion and good thermal shock resistance. Its electrical properties are similar to those of aluminum oxide. Aluminum nitride is oxidized in air at temperatures of 700°C and higher.

Obtaining Alumina From Aluminum Nitride

For this process to be successful, the aluminum nitride formed must be decomposed to obtain a recoverable form of alumina. According to a German patent,³² aluminum nitride can be leached with strong sodium hydroxide to obtain ammonia and alkali aluminate, from which alumina is obtained by the ordinary Bayer process. The Handbook of Chemistry³³ verifies that aluminum nitride is readily soluble in hot caustic solutions.

But, as in the Bayer process, other impurities may also enter the solution. Two of the most critical impurities are silicon and iron. In fact, the main difficulties in manufacturing alumina arise from the necessity of keeping these elements at low levels. Acceptable amounts for reduction grade alumina are listed below.³⁴

SiO_2	.012-.02%
Fe_2O_3	.01-.015%
Al_2O_3	98.5-99.4%

In the Bayer process,³⁵ these impurities are eliminated as follows: soluble silica in the presence of

sodium and aluminate ions is precipitated as sodium aluminum silicate or red mud ($2\text{Na}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). This red mud is then separated and discarded. Iron tends to form colloidal iron hydroxide which can deposit during precipitation and contaminate the solids. To prevent this from occurring, a combination of settling followed by clarification is used. Once these impurities are removed, the aluminate liquor is cooled and agitated with a seed charge of fresh aluminum hydrate to precipitate aluminum hydroxide, which is calcined at 1200°C to give alumina.

But, the system investigated in this study differs from the Bayer process. These techniques for desilication and precipitation may or may not be applicable. There are theoretically two ways to obtain pure alumina - either remove the impurities first and precipitate alumina, or selectively remove the alumina leaving the impurities in solution.

Much work has been done recently in desilicating aluminate solutions. Noworyta³⁶ suggested increasing the temperature of the aluminate solution to cause precipitation of sodium aluminasilicate. However, he obtained the best results by adding a solution of calcium hydroxide to a heated aluminate solution. Once the impurities are removed, aluminum hydroxide can be precipitated. A very early English patent by LeChatelier³⁷ lists a variety of methods which may be used to precipitate

aluminum hydroxide from aluminate solutions. These include blowing in carbon dioxide, adding sodium bicarbonate or ammonium carbonate, supersaturating with alumina, and adding acid, ammonium chloride, or aluminum chloride solutions. Once a relatively pure aluminum hydroxide is formed, it can be calcined to obtain alumina.

Effect of Iron Catalyst

Early work by Cutler³⁸ showed transition metals and their compounds, particularly Fe and Fe_2O_3 , to be effective in catalyzing the carbothermal reduction of silica to form silicon carbide. More specifically, it has been shown that iron catalyzes reaction 5.^{16, 39, 40}



Although several theories have been proposed, the detailed mechanism is not clear. More important, however, is the fact that a catalyst is only effective on the rate controlling steps. If reaction 5 is the rate controlling step and if the reduction of alumina follows steps similar to reaction 12, 13 and 8 as postulated for silica, then iron should also act as a catalyst on the formation of aluminum nitride.

Portnoi, et al.,⁴¹ recently studied the influence of iron on the growth of crystals of aluminum nitride by the reduction of aluminum oxide by carbon in a nitrogen atmosphere according to equation 1. They determined

that the presence of iron is a decisive factor in the growth of crystals.

In the formation of silicon carbide, it has been observed that above a certain level, iron saturates the system. Mah²⁸ determined that above 3% by weight iron, the reaction rate is independent of the amount of catalyst added. Renlund²⁹ reported a rate increase in the clay-carbon-nitrogen system when up to 1% by weight iron was added. He also showed that in the clay-coal-nitrogen system, no rate increase occurred even with iron added. The coal obviously contained enough iron (.77%) so that additional amounts were ineffective.

The analysis of the coal wastes used in this study showed that Fe_2O_3 accounts for 2.6% of the material. Therefore, testing the catalytic effect of iron was not attempted in this study.

EXPERIMENTAL

Sample Preparation and Identification

Three different coal waste samples were obtained for use in this study: preparation plant and overburden materials from the New Mexico Canyon strip mine, and a gangue material from the Utah Sunnyside underground mine.

The materials were reduced in size by a roll crusher. Further reduction to suitable size (-200 to -65 mesh) was accomplished using a ceramic ball mill. By using a riffle splitter, a representative sample of each size fraction was taken for analysis.

Three different methods were used to determine the alumina and silica content. In the first, a weighed sample of coal waste was burned at 900°C for two hours to remove the carbon and other volatile material. The non-volatile material was then dissolved into solution using hydrofluoric acid and aqua regia. Once in solution, atomic absorption spectrometry was used for alumina analysis. Because some silica remained undissolved, a more appropriate gravimetric procedure⁴² for determining silica was used. The results for the -200 mesh material are shown in Table II.

To check the reliability of these analyses, a sample of kaolinite was analyzed using the above procedures. These results are also shown in Table II. As seen, the results agree reasonably well with the typical analysis of kaolinite.

The second method of analysis used X-ray fluorescence, a procedure which also could identify other compounds. Because the preparation plant material was shown to contain the greatest amount of alumina, it was used for all experiments in this study.

The last method is one listed in Atomic Absorption Newsletter⁴³ using lithium meta-borate. This compound combines with the inorganic material in the waste to form a melt which dissolves readily in a hydrochloric acid solution. Once in solution, atomic absorption can be used to determine the quantities of elements present. The results of the two methods are shown in Table III. As seen, the agreement is exceptional.

A mineralogical analysis was also made of the preparation plant material. X-ray diffraction analysis showed the main constituents to be quartz and kaolinite mixed with minor amounts of alumina-silicates.

Carbon Analysis

Carbon analysis of the raw material was carried out using a Leco Carbon Analyzer. This analysis showed

TABLE II. Initial Analysis of Material

Material	SiO ₂	Al ₂ O ₃
Preparation Plant	47.1%	19.5%
Overburden	63.0%	19.3%
Kaolinite	38.7%	40.6%
Kaolinite (typical analysis)	38.1%	44.5%

TABLE III. Preparation Plant Waste Analysis

Compound	X-ray Fluorescence	Atomic Absorption
Al ₂ O ₃	17.95%	18.0%
SiO ₂	52.56%	52.6%
Fe ₂ O ₃	2.62%	2.63%
CaO	1.43%	1.72%
MgO	1.02%	1.48%

the preparation plant material to contain 14% carbon, which is not enough carbon for the reaction to proceed to its stoichiometric completion. To compensate for this, excess carbon in the form of Carbon Black Raven 2000 was mixed with the coal wastes. In industrial operation, coal would be preferred over carbon black because of its availability and lower price. However, coal would introduce more impurities into the system.

Apparatus for Carbothermal Reduction

Two high temperature furnaces were used in this study. One of these, a Lindberg single zone tube furnace, Model 45543, was capable of reaching a temperature of 1450°C. It was placed in a vertical position. A mullite tube from Coors Porcelain Company was inserted through the furnace. In order to maintain a nitrogen atmosphere, a closed system was necessary. This was accomplished by attaching a pyrex extension tube with a removable cover on the top of the mullite tube and inserting a rubber stopper with a gas inlet into the bottom of the tube. The pyrex cover also served to hold the sample chain and to simplify insertion and removal of the sample.

A porcelain crucible was used as a sample holder. It was suspended into the mullite tube using a chain of 1/16 inch Kanthal A wire. Kanthal A wire was chosen after thin wires of platinum, tungsten, and molybdenum failed in this high temperature nitrogen atmosphere.

Temperature was controlled with a Lindberg Control Console Model 59545. The temperature reading was obtained using a Leeds and Northrup millivolt potentiometer with a Pt, Pt-10%Rh thermocouple.

Nitrogen gas flowed through the system at the desired flow rate. To remove any oxygen from the nitrogen, pyrogallic acid was used. Figure 4 more clearly demonstrates this set-up.

Another furnace was built to reach temperatures greater than 1450°C. This also was a vertical tube furnace with a similar setup to the Lindberg furnace. However, because of the high temperatures needed, Kanthal Super 33 heating elements from the Kanthal Corporation were used. The center tube was made of alumina, as were the crucibles to hold the samples. The kanthal wire used for hanging the samples in the Lindberg furnace could not withstand these higher temperatures. Therefore, a sample holder using tungsten wire covered with an alumina shield was designed. A high temperature cement from Chem-Thermic Industries, Inc. was used to cover the joints. Temperature was controlled by using a Research Inc. Process Controller Model 640U with an accompanying Phaser Power Controller Model 64600. A Pt, Pt-10%Rh thermocouple was used to read the temperature (see Figure 5).

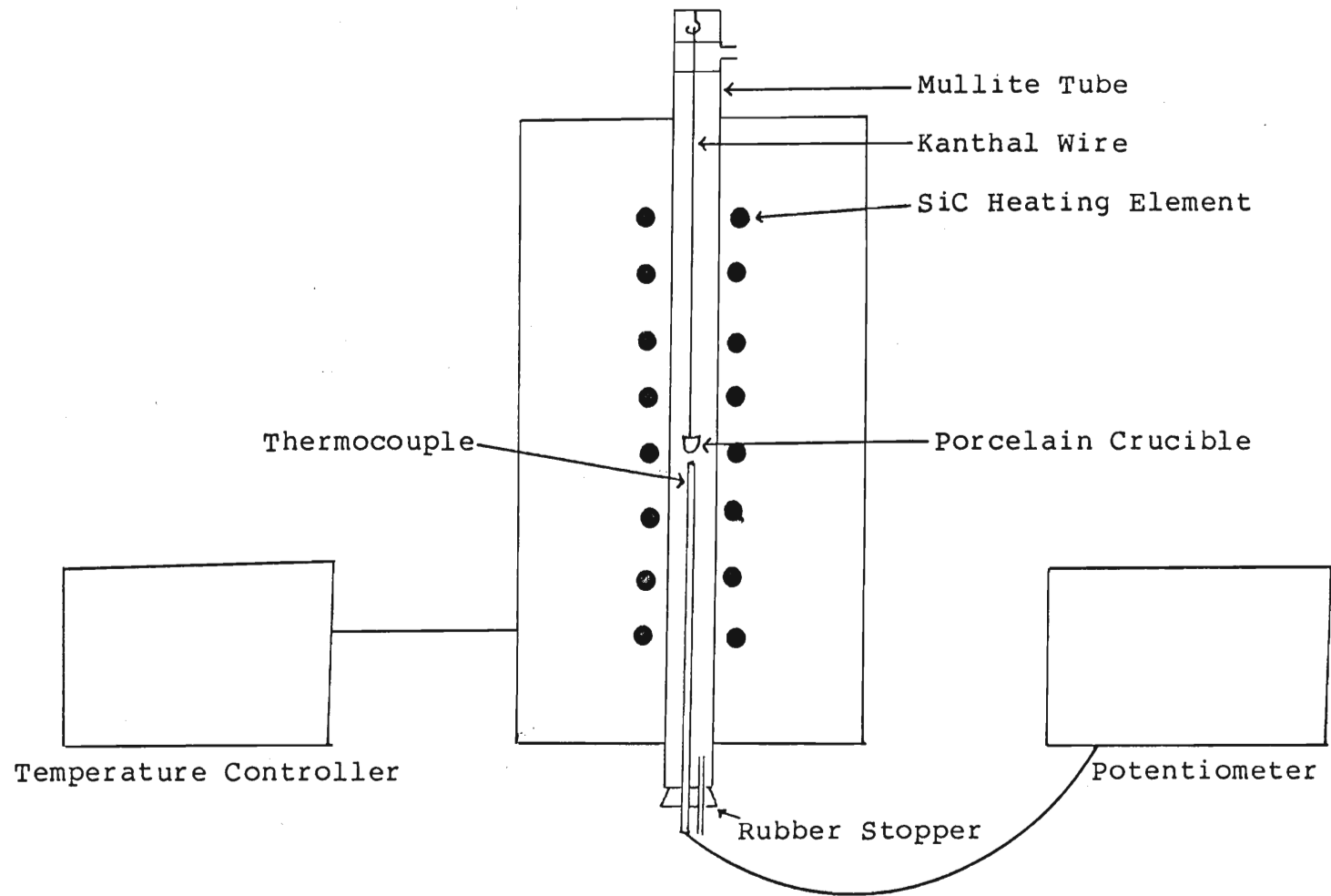


Figure 4. Schematic diagram of the furnace set-up.

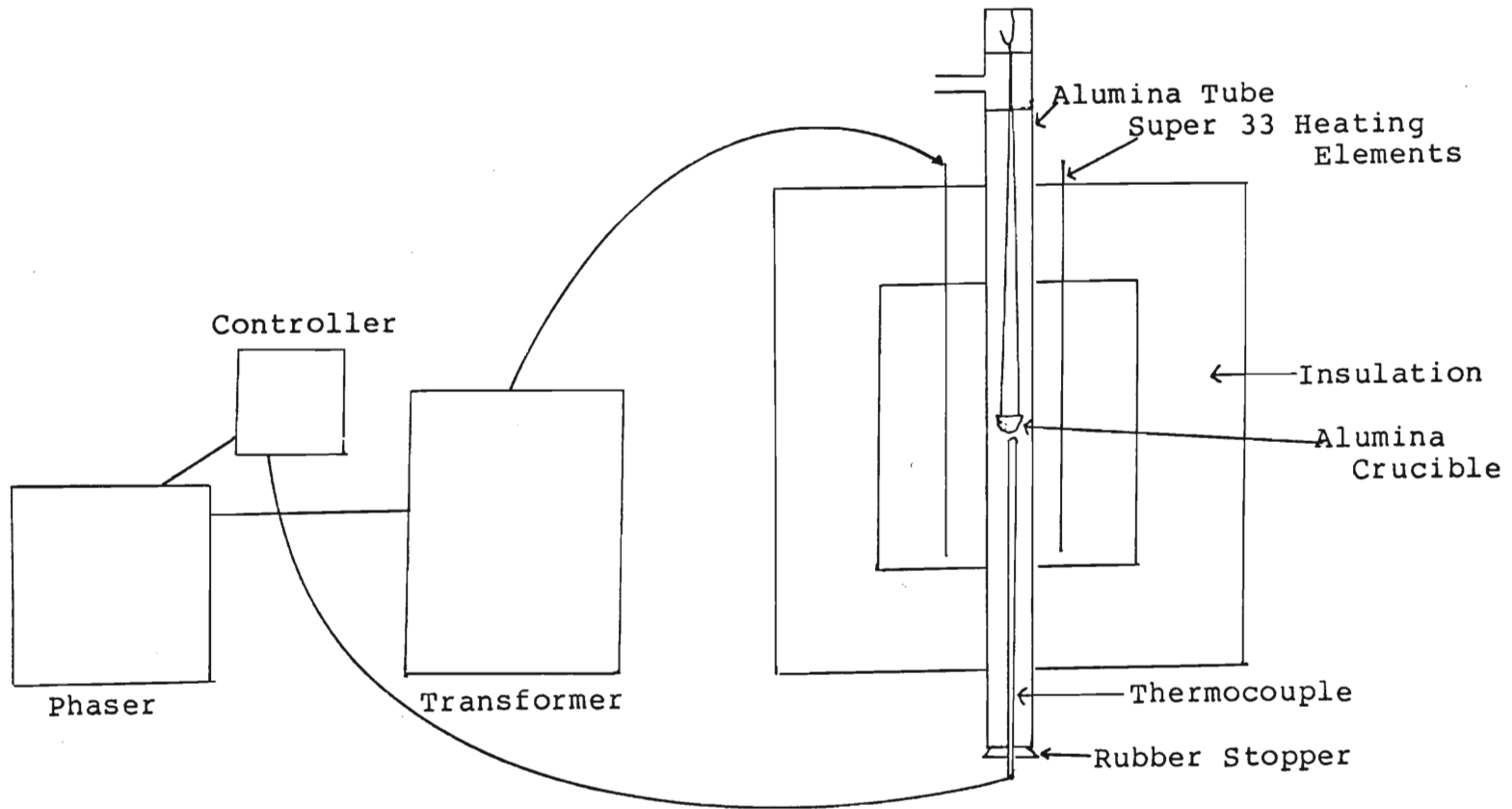


Figure 5. Schematic diagram of the high temperature furnace using Kanthal Super 33 heating elements.

Apparatus for Leaching

A leaching system was constructed consisting of a Corning Stirring Hotplate, a teflon beaker, and a condensation tube (see Figure 6). Teflon was used because it was found that caustic solutions at high temperatures leach silicon from glass ware. Silicon is an impurity in the system and should be avoided if possible.

Analysis of the Reaction Products

Sample analysis was done by X-ray diffraction using a Norelco diffractometer with CuK alpha radiation. The X-ray diffraction data for the compounds involved in this study can be found in a powder diffraction file.⁴⁴

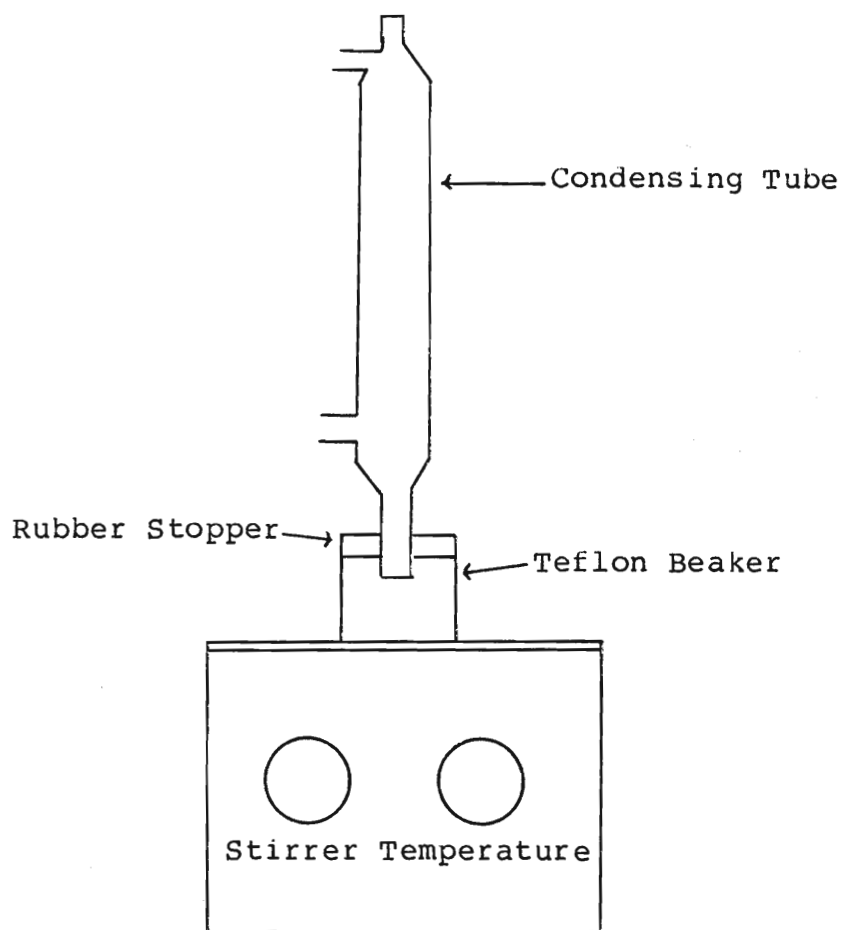


Figure 6. Schematic diagram of the leaching operation.

RESULTS AND DISCUSSION

Preliminary Results

As given by equation 1-3, the reactions to obtain alumina from coal wastes appear relatively simple. Realistically, however, the impurities in coal wastes and various possible side reactions complicate the process. To simplify matters, it would be useful to observe how the reactions proceed with fewer impurities present. This can be accomplished by using clay instead of coal waste. Earlier experiments by Renlund⁴⁵ using kaolin and halloysite clays mixed with carbon black showed that above 1400°C, under a nitrogen atmosphere, aluminum nitride and silicon carbide are formed along with silicon nitride.

To verify these results, a few experiments were done in this study using kaolin clay mixed with carbon black under the conditions listed above. X-ray diffraction analysis of the products showed that indeed, aluminum nitride, silicon carbide and silicon nitride are formed. Analysis of the coal waste showed that clay is originally present; therefore, similar results are expected in the coal waste-nitrogen system.

One of the major advantages of using coal waste in this process is having carbon inherently present. When the coal waste material in its original form was reacted under a nitrogen atmosphere at 1450°C, X-ray diffraction analysis of the product showed that mullite as well as silicon carbide was formed. Aluminum nitride was not present. The coal waste used in this study contained carbon. However, it was less than stoichiometrically needed for completion of reactions 1 and 2.

When kaolin clay alone, with no added carbon, was reacted under a nitrogen atmosphere at high temperature, X-ray diffraction showed that mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) formed. According to the literature, this is expected. Kingery, et al.,⁴⁶ states that "on heating, clay decomposes at 980°C to form mullite. Further heating of clay gives rise to increased growth of mullite crystals." This would explain the presence of mullite when using coal wastes. The fact that silicon carbide forms shows that reactions 1 and 2 do not occur simultaneously as previously thought. It appears that silicon carbide forms first.

To form both aluminum nitride and silicon carbide, sufficient carbon is needed. Some excess carbon should be used to compensate for any reducible oxide impurities in the coal waste and to assure complete reaction. Therefore, carbon in some form must be added to the waste material when it does not contain a sufficient amount of carbon.

Graphite was used in a few experiments as the carbon source. X-ray diffraction analysis of the product showed that mullite is still formed. Obviously, graphite is not reactive enough. When coal was used in a few experiments, the formation of silicon carbide and aluminum nitride was detected. However, coal can contain additional impurities which can complicate analysis. To minimize the amount of impurities, carbon black was used for all of the experiments in this study.

Qualitative Analysis

Many experiments were completed using the preparation plant coal waste material mixed with carbon black to test the feasibility and optimum conditions for this process. Analysis of the products was accomplished using X-ray diffraction.

X-ray diffraction provides a convenient and practical means for qualitative identification of crystalline compounds. By matching diffraction patterns of the unknown with the patterns of known compounds, the unknown compounds can be identified.

Through such qualitative analysis, it was determined that the major products of the reactions in this study are aluminum nitride, beta-silicon carbide, and beta-silicon nitride. This is consistent with previous research. Bechtold¹⁴ found beta-silicon carbide to be formed exclusively in a clay-carbon-nitrogen system

when a transition metal impurity is present. Some minor constituents, such as ferrosilicon (FeSi) and alpha-silicon nitride were also identified. The impurities present in the coal wastes must also exist in some form in the final product. However, X-ray diffraction does not detect such small quantities.

To verify that the X-ray diffraction patterns representing these various compounds were correctly interpreted, systematic chemical analyses were performed on the products of reaction.

The product was initially leached in a 3 molar sodium hydroxide solution. Aluminum nitride is known to be soluble in caustic solutions.³³ The solution was filtered and the remaining solids dried and re-examined using X-ray diffraction. The peaks corresponding to aluminum nitride had decreased significantly in the diffraction pattern.

These solids were then boiled in hydrofluoric acid. This acid should have no effect on silicon carbide. Silicon nitride, however, decomposes in such a solution.³³ Again the solution was filtered, the solids dried and X-rayed. The peaks corresponding to silicon nitride were greatly reduced in proportion to the silicon carbide peaks.

To verify the existence of ferrosilicon, two methods were used. First, because ferrosilicon is soluble in acid solutions, the products of reaction were leached

in a hydrochloric acid solution. After filtering and drying, X-ray diffraction analysis showed that the ferrosilicon peaks had disappeared. Second, excess iron in the form of ferric nitrate was added to the sample before reacting in the furnace. X-ray diffraction analysis of the material after reacting showed the growth of ferrosilicon peaks with respect to the other compounds.

Quantitative Analysis

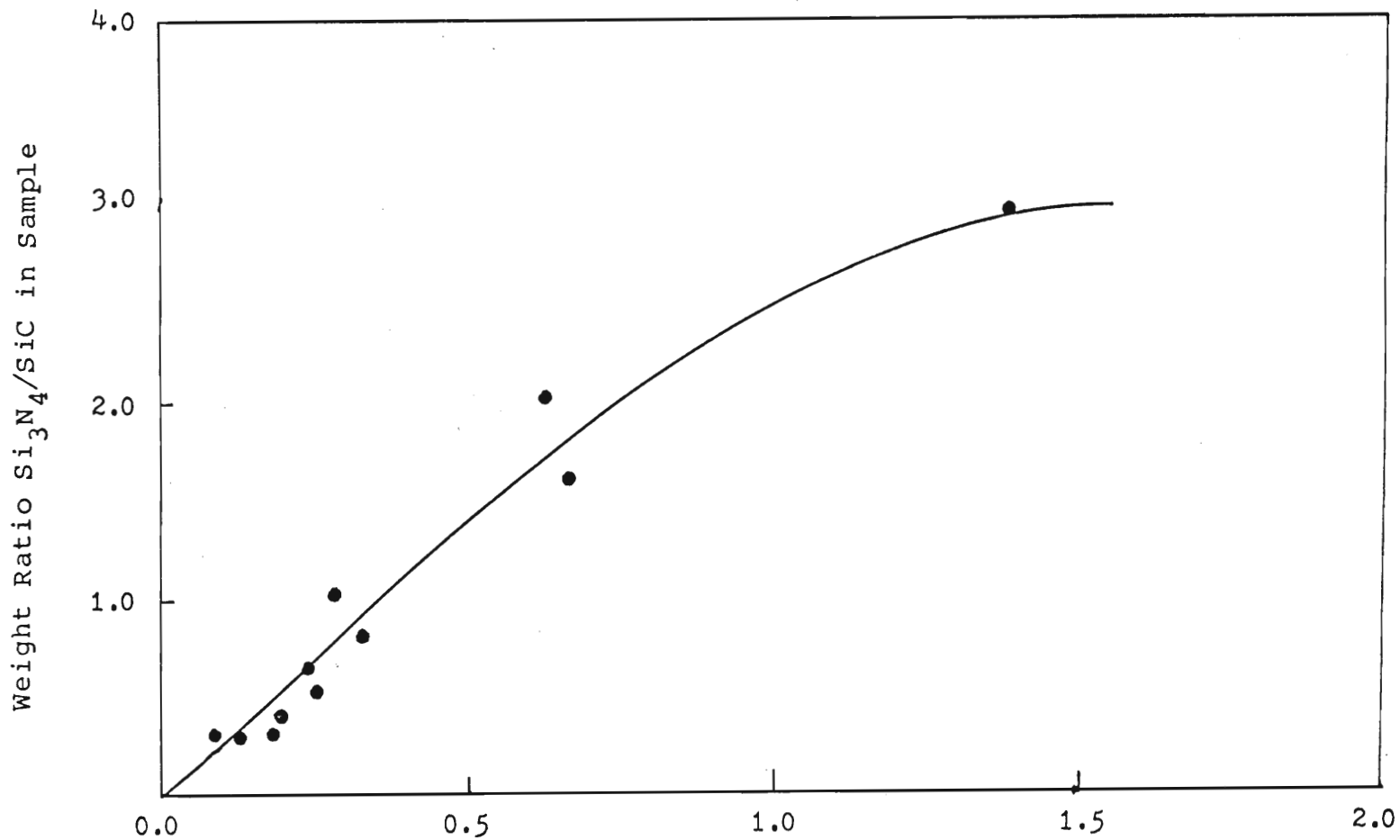
Because the intensities of the diffraction peaks of a given compound are proportional to the fraction of the material in a mixture, X-ray diffraction is adaptable to quantitative analysis. However, because of the differences in absorption coefficients of the compounds being determined and the total mixture, direct comparison of the intensities of peaks in a pattern obtained from a mixture is difficult. To correlate these intensities, correction factors are necessary. These can be determined by comparing known standards.

For this study, relatively pure samples of aluminum nitride, silicon nitride, and silicon carbide were obtained. Different proportions of these three were mixed and analyzed using X-ray diffraction. Normally, it is advisable to compare the peaks of highest intensity. However, as seen in the Inorganic Index to the Powder Diffraction File,⁴⁴ the angles at which the highest peaks for silicon carbide and beta-silicon nitride occur

overlap. Therefore, suitable non-overlapping angles were chosen for analysis, namely, aluminum nitride = 33.14° , silicon carbide = 60.02° , and silicon nitride = 26.92° .

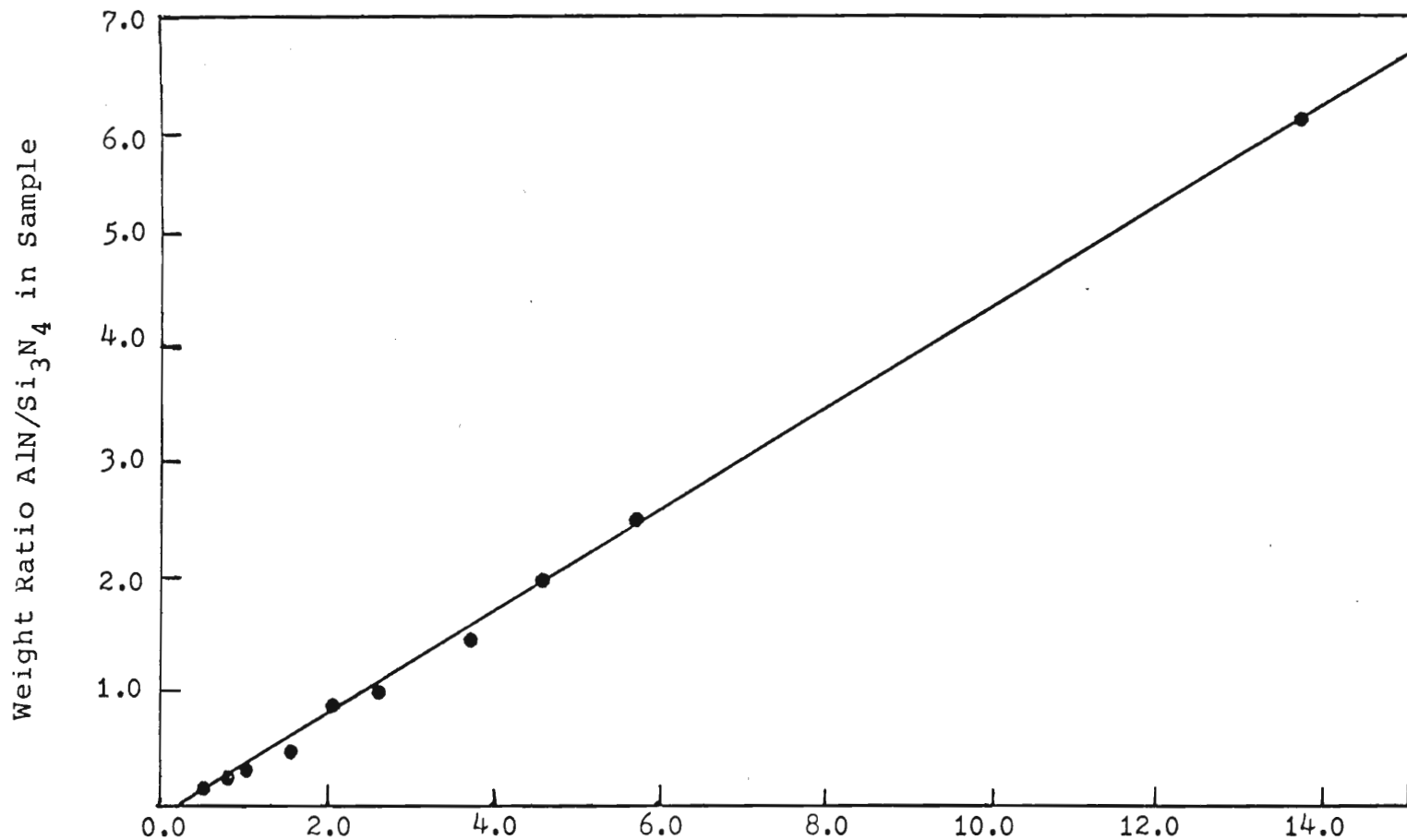
Standard X-ray calibration curves, comparing the ratio of the peak heights at these angles, were developed in Figures 7-9. From these standards, the relative amounts of aluminum nitride, silicon carbide, and silicon nitride found in the experiments can be determined. Hoggard⁴⁷ used a similar technique in determining alumina content in SIALON. This provides a quick method to determine relative amounts of products without having to perform a chemical analysis on every product.

To verify the quantitative results obtained by X-ray diffraction, chemical analysis of the products was performed. As already mentioned, aluminum nitride and silicon nitride dissolve in a boiling hydrofluoric acid solution, while silicon carbide remains undissolved. Therefore, the solids were dissolved in hydrofluoric acid, the solution filtered and analyzed for alumina and silica with atomic absorption spectroscopy. By back calculating, the amounts of aluminum nitride, silicon nitride, and silicon carbide present can be determined. However, to compare these results with the results from quantitative X-ray diffraction analysis, only the amounts of these three products are added (omitting impurities)



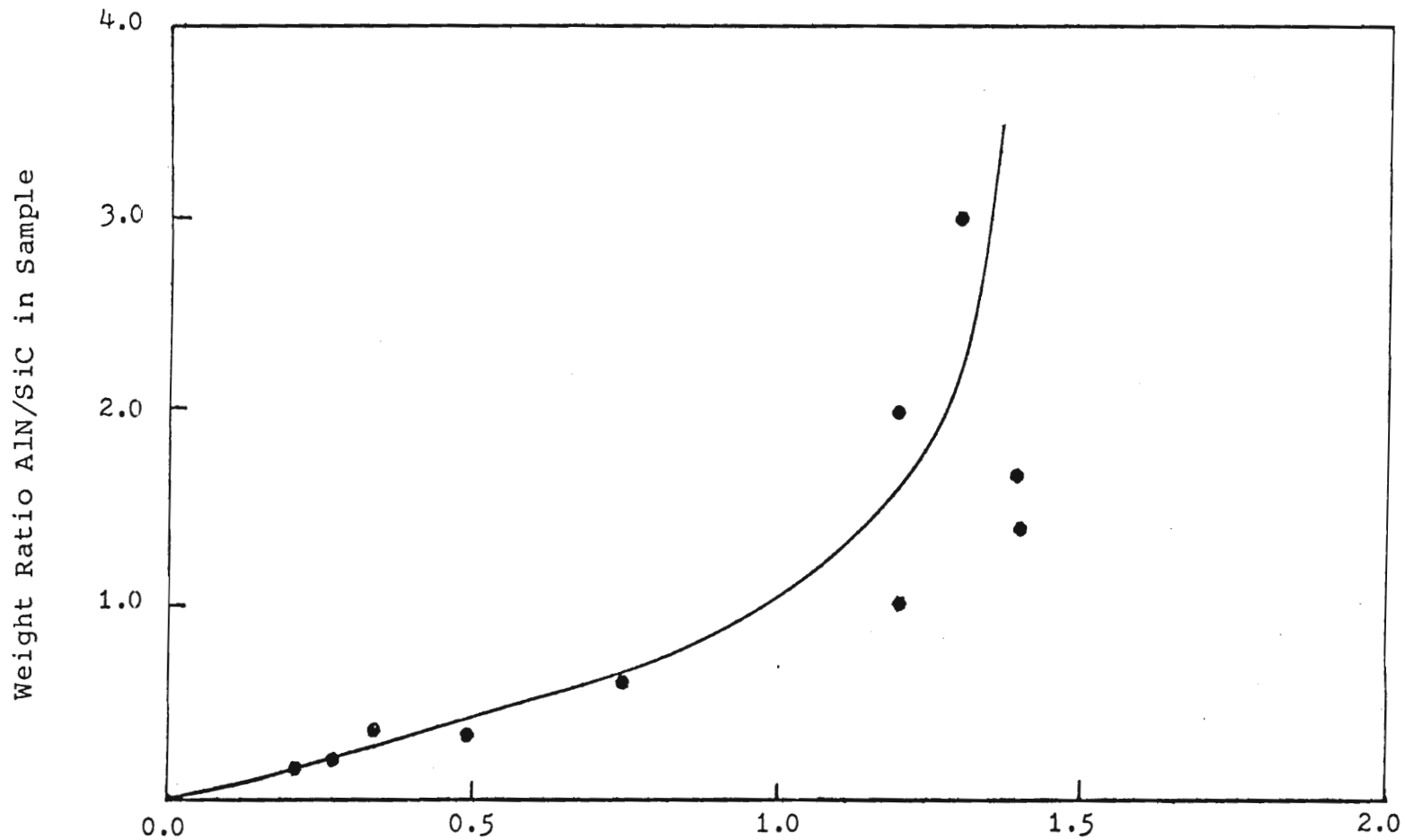
Ratio of X-ray Diffraction Peak Heights in Si₃N₄/SiC

Figure 7. X-ray diffraction calibration curve used for quantitative analysis of reaction products.



Ratio of X-ray Diffraction Peak Heights in AlN/Si₃N₄

Figure 8. X-ray diffraction calibration curve used for quantitative analysis of reaction products.



Ratio of X-ray Diffraction Peak Heights in AlN/SiC

Figure 9. X-ray diffraction calibration curve used for quantitative analysis of reaction products.

and the relative percent of each is calculated. The results are shown in Table IV.

To determine the percent conversion, the following technique is used. Knowing the amount of alumina originally present in the coal waste, the maximum possible amount of aluminum nitride formed can be calculated. This is also true of the maximum amounts of silicon carbide or silicon nitride formed. These theoretical values can be compared with the actual amounts obtained by X-ray diffraction quantitative analysis to determine the conversion of alumina to aluminum nitride.

Reduction of Silica by Silicon Carbide

Experiments showed that as the reaction proceeds, the amount of silicon carbide formed decreases while the amounts of silicon nitride and aluminum nitride formed increase. Typical examples are shown in Figures 10-13.

Lee,¹⁶ in studying the carbothermal reduction of silica, observed a similar occurrence with regards to silicon carbide. He observed two distinct stages in the reaction of silica being reduced with carbon (see reaction 2). The reaction proceeded rapidly to about 30% conversion and then tapered off considerably. This suggested that silicon carbide forms in the first stage followed by the slower reduction of silica by silicon carbide in the second.

TABLE IV. Product Analysis

Sample Condition	Dissolved in HF*			Quantitative X-ray Diffraction		
	AlN	SiC	Si ₃ N ₄	AlN	SiC	Si ₃ N ₄
1450°C 2 hours	22.7	45.0	30.0	24.4	50.4	25.3
1550°C 3 hours	32.4	17.5	50.0	30.9	8.0	55.4
Mixture of Knowns	40.0	44.0	16.0	40.0	40.0	20.0

* Analyzed by A.A. Impurities excluded to make total of AlN + SiC + Si₃N₄ = 100%

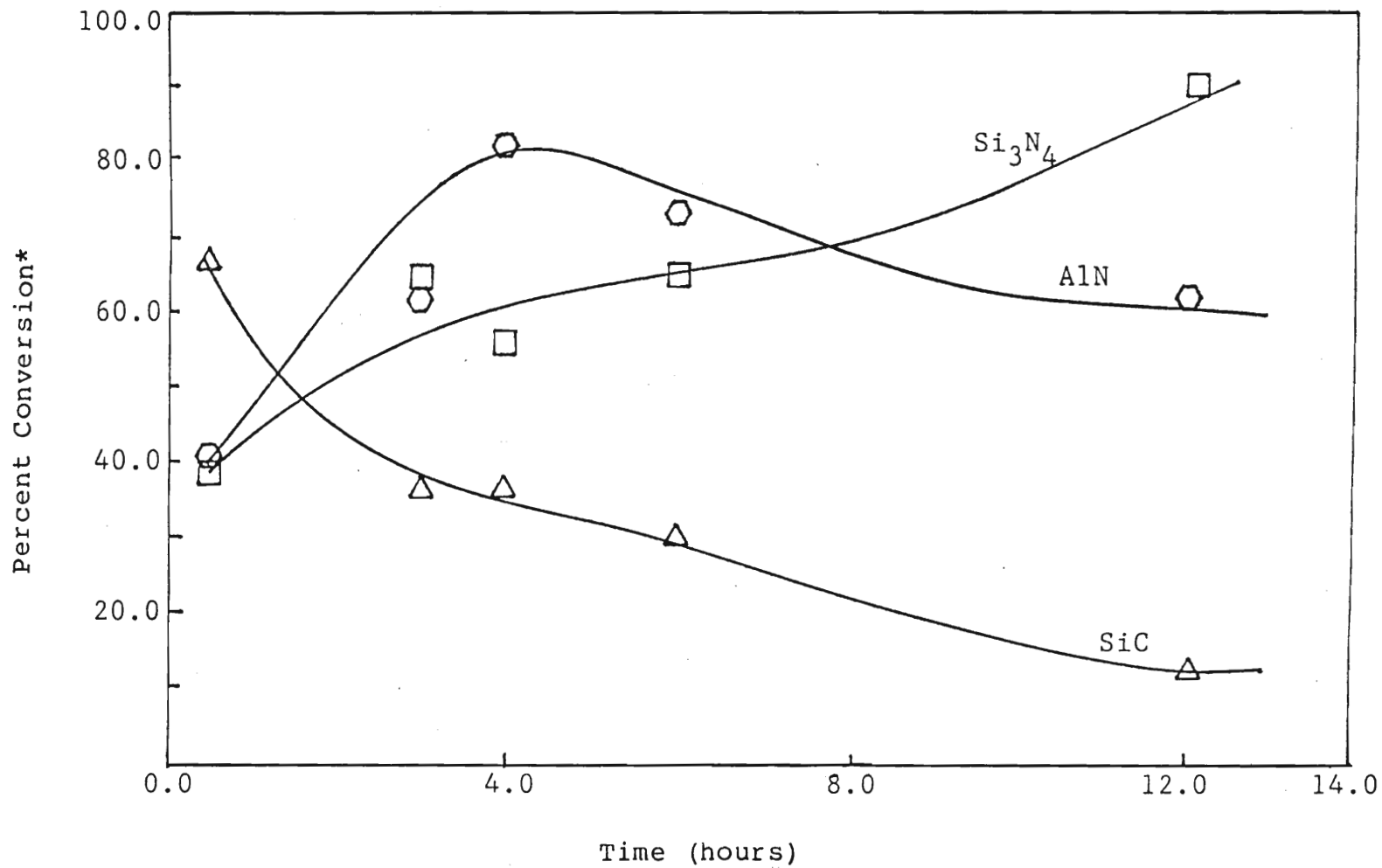


Figure 10. Formation of compounds at a temperature of 1400°C (10% excess carbon).
 *Percent of original amount in coal waste converted to product.

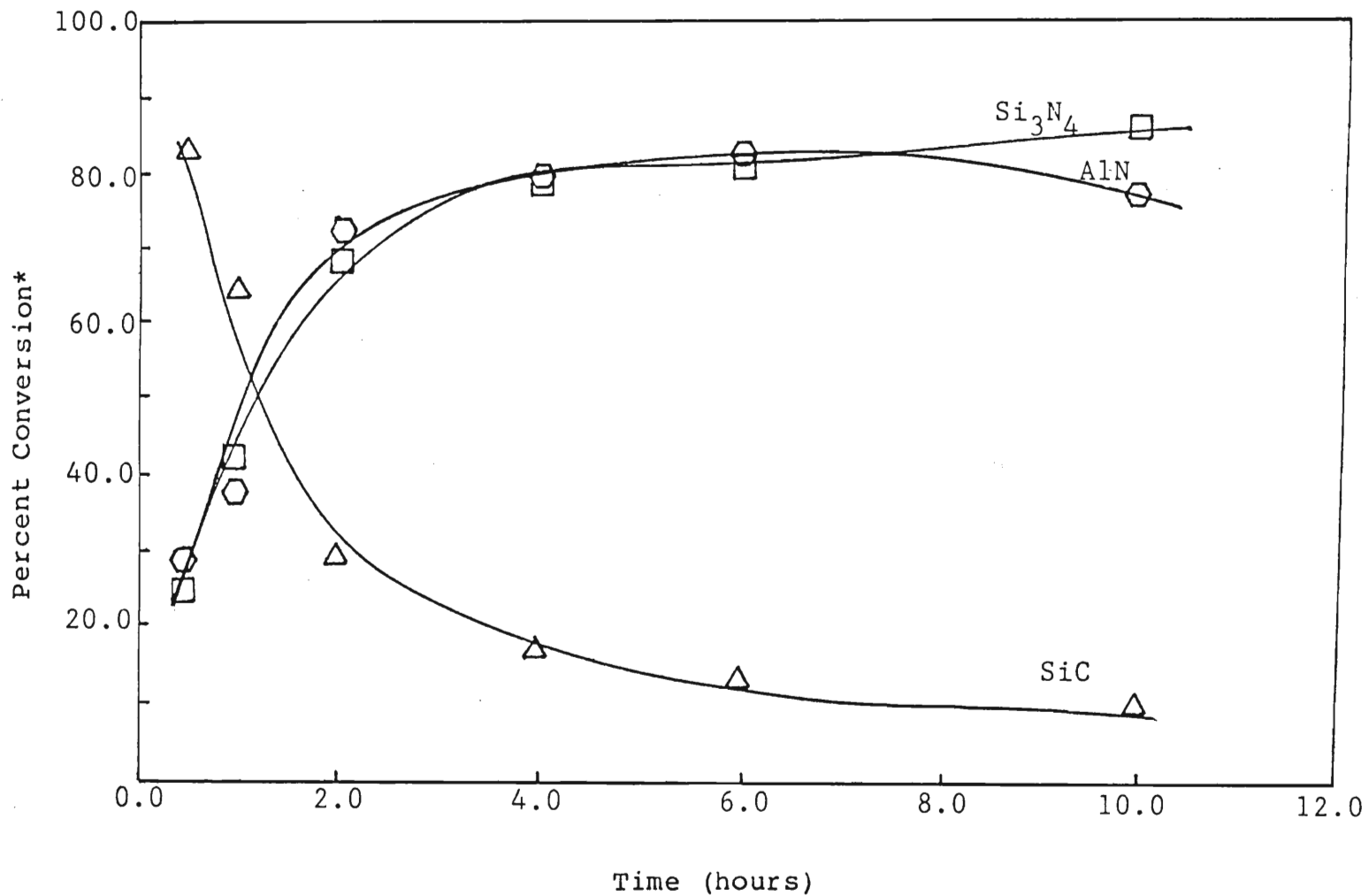


Figure 11. Formation of compounds at a temperature of 1450°C (10% excess carbon).
 *Percent of original amount in coal waste converted to product.

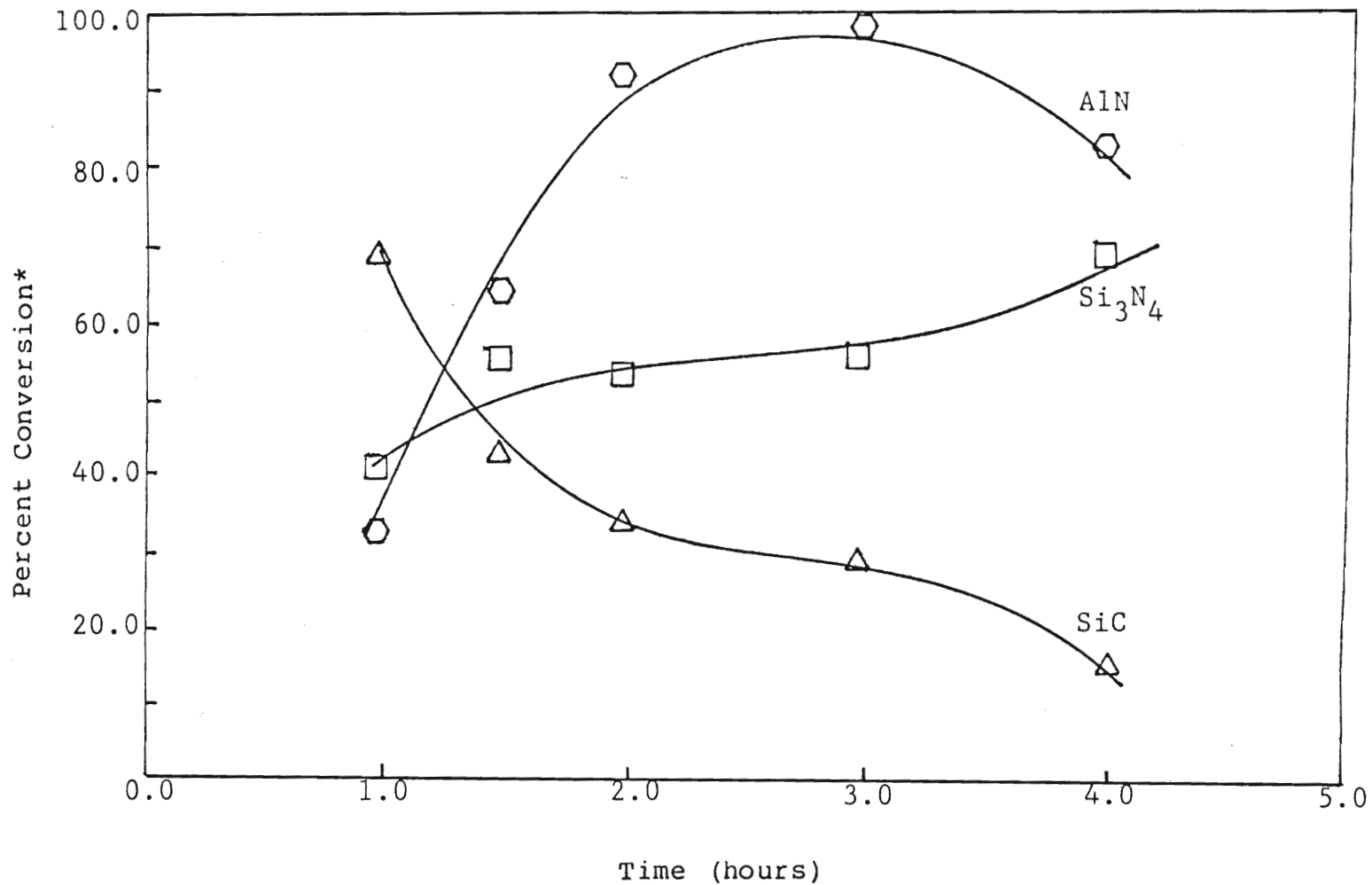


Figure 12. Formation of compounds at a temperature of 1500°C (10% excess carbon).
 *Percent of original amount in coal waste converted to product.

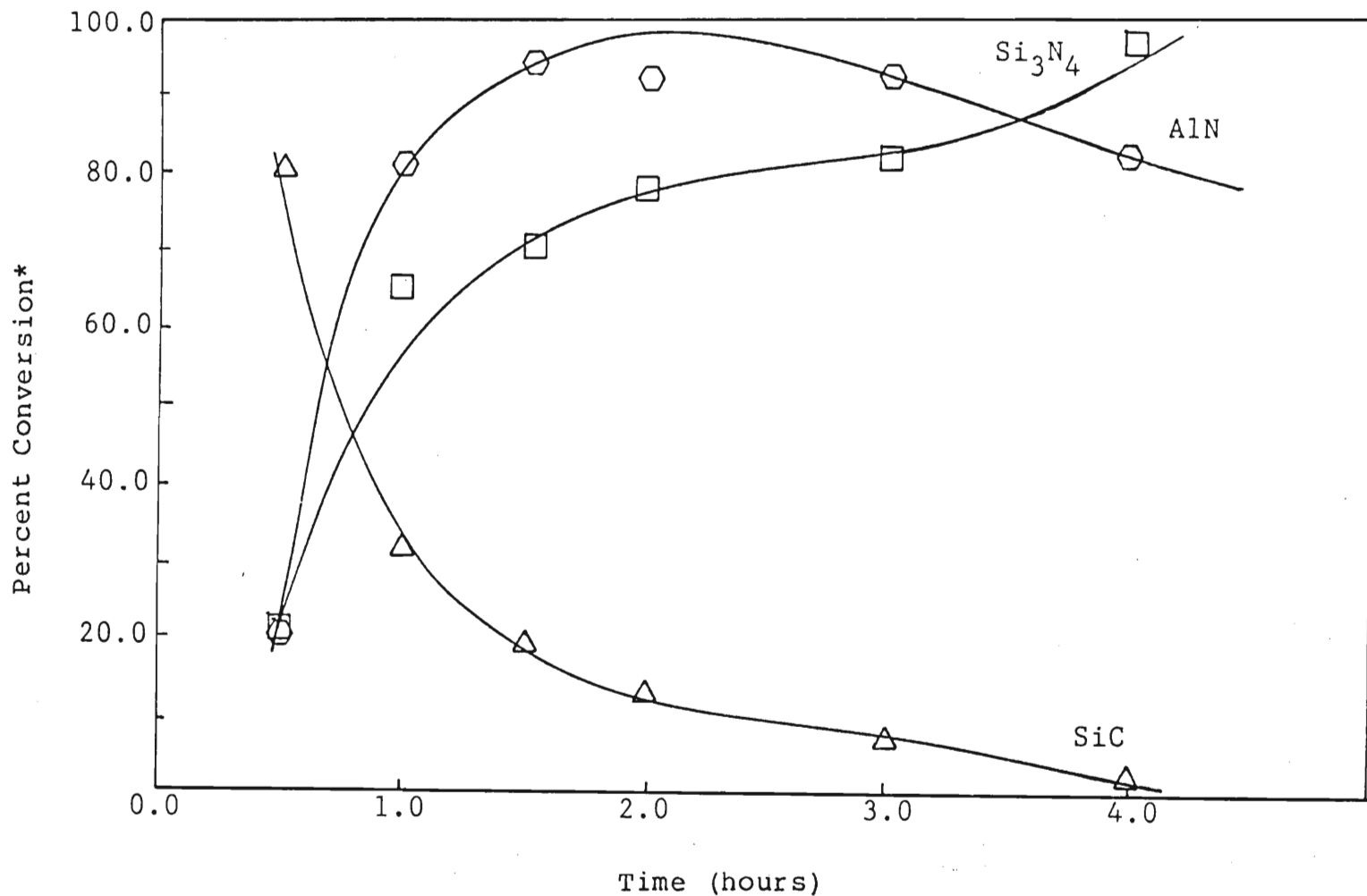
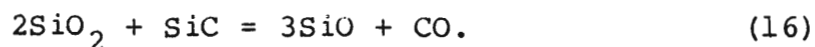
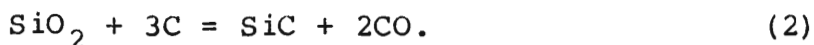


Figure 13. Formation of compounds at a temperature of 1550°C (10% excess carbon).
 *Percent of original amount in coal waste converted to product.



with the overall reaction being



Other researchers have made similar observations. Blumenthal¹⁷ concluded that the silicon carbide formed by reaction 2 is only an intermediate in a consecutive reaction mechanism that continues to SiO and CO gases. He claimed that silicon carbide rapidly reacts with silica at temperatures of 1300°C and higher to form volatile products (reaction 16). Miller⁴⁸ and Bechtold¹⁴ also maintain that silicon carbide can act as a reducing agent for silica.

The reduction of silica by silicon carbide at 1270-1430°C was studied extensively by Pultz and Hertl.⁴⁹ They observed the loss of silica in a linear fashion with time and concluded that the formation of SiO and CO is the dominating process.

As to why reaction 16 is slower than reaction 2, Lee¹⁶ considered three possible reasons:

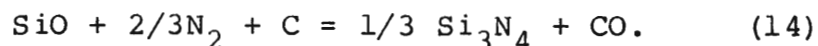
- 1) The surface area of silicon carbide is less than that of carbon. As explained previously, gas-solid reaction rates depend on the surface area of the reactants. The greater the surface area, the faster the rate. Miller,⁴⁸ in studying reaction 16 concluded that the surface area of silicon carbide is much less than the carbon from which it is formed. This difference in

surface area could easily account for the change in reaction rate.

2) There is a higher concentration of SiO gas in the sample in the absence of carbon with which it can react.

3) The reducing power of silicon carbide is less than that of carbon.

This background validates the assumption that in this investigation silicon carbide forms quickly and then acts to reduce silica, forming SiO gas. It is further postulated that this excess SiO gas reacts with nitrogen according to reaction 14 to form silicon nitride.



Even though reaction 8 is favored thermodynamically, reaction 14 requires less carbon. This could be an important factor because much of the carbon has been already consumed by reaction 13.



This will be discussed later in more detail.

This mechanism would account for the increase in the formation of silicon nitride. The overall scheme is represented in Figure 14. Nitrogen gas is transported into the reaction interfaces against the gaseous intermediates SiO and CO diffusing out. SiO reacts first to form silicon carbide, which in turn reduces silica forming more SiO gas which reacts to form silicon nitride.

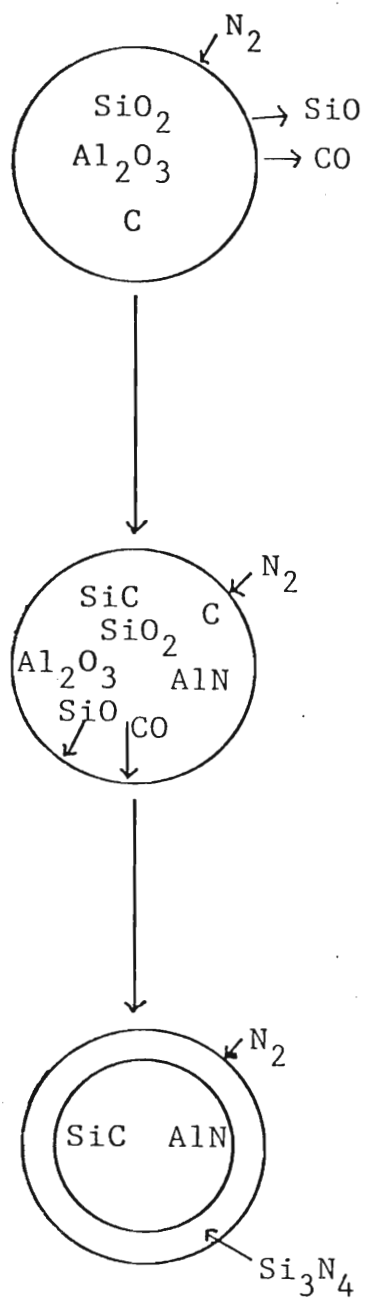


Figure 14. Direction of interface movement during reaction.

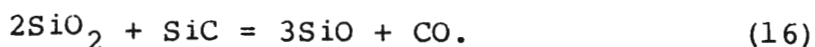
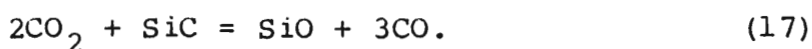
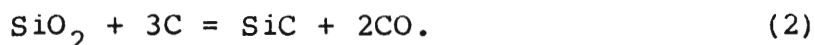
To verify this assumption, a large pellet was reacted at 1450°C for 4 hours. Outward appearance on removing the pellet showed the outside to be lighter in color than the inside. This demonstrates a distinct reaction zone moving from the outer edges inward. The two parts were separated and analyzed using X-ray diffraction. The following results were obtained.

	<u>Aluminum Nitride</u>	<u>Silicon carbide</u>	<u>Silicon nitride</u>
Outside	32.7	18.7	48.5
Inside	27.9	28.8	43.3

The outer portion has more aluminum nitride than silicon carbide, while the inside has more silicon carbide than aluminum nitride. This indicates that the proposed scheme is realistic. SiO acts as a reducing agent and leads to the increased formation of silicon nitride.

A sample of silica gel mixed with carbon black was reacted at 1500°C for 3 hours in a nitrogen atmosphere. Concurring results were obtained. The inside showed the exclusive formation of silicon carbide. The outer portion, however, showed silicon carbide and silicon nitride.

The mechanism for the reduction of silica by silicon carbide has been given by Miller⁴⁸ as follows:



Effect of Excess Carbon

To examine the effect of excess carbon, a set of samples was prepared with varying amounts of excess carbon mixed with the coal waste. These were each reacted for two hours at 1500°C under a nitrogen atmosphere. The results are given in Table V. It appears that the more carbon originally present, the more reaction 2 is favored over reactions 1 and 14. In other words, as the amount of carbon increases, so does the amount of silicon carbide formed, while the amount of aluminum nitride and silicon nitride formed decreases. An excess of carbon seems to hinder the production of aluminum nitride and silicon nitride. Therefore, the remaining experiments were performed with ten percent excess carbon. This compensates for any reducible oxide impurities that may be present in the coal waste, and also assures that enough carbon (and not an excessive amount) exists for reduction of alumina and silica. As to why silicon nitride formation is hindered with excess carbon, the following possible explanations are given:

- 1) As long as excess carbon is present, reaction 2 proceeds. When the carbon in an area is depleted, the silicon carbide begins acting as a reducing agent on the silica as explained in the previous section. With large excesses of carbon, this condition is never reached. Bechtold¹⁴ found that with increasing carbon content the point of transition from reaction 2 to reaction

TABLE V. Effect of Excess Carbon

Percent Excess Carbon	Molar Ratio $\left(\frac{\text{AlN}}{.5\text{Al}_2\text{O}_3}\right)$	Relative Percent of Products*			Percent Conversion†		
		AlN	SiC	Si ₃ N ₄	AlN	SiC	Si ₃ N ₄
10	4.0	33.8	16.9	49.3	99.0	19.7	66.6
20	3.75	31.2	22.0	46.8	93.7	25.6	63.2
50	1.9	15.8	74.0	10.3	47.4	98.2	11.9
100	1.37	11.4	86.6	2.0	34.2	98.0	1.9

* Impurities excluded to make total of AlN + SiC + Si₃N₄ = 100%.

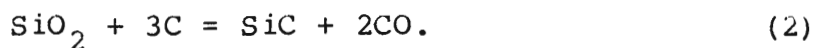
† Percent of original amount in coal waste converted to product.

Experiments run for 2 hours at 1500°C.

16 occurred after greater amounts of silicon carbide were formed. This corresponds with what was observed in this study.

2) With excess carbon, reaction 2 is favored.

Whereas, with limited carbon, reaction 10 is more probable.



3) Nitrogen gas must be transported into the reaction interfaces against the gases diffusing out. Excess carbon mixed with the waste allows for better dispersion throughout the sample and shortens the SiO and carbon monoxide gas diffusion distances while increasing the distance that nitrogen must diffuse, thus enabling larger amounts of SiO to react with the carbon inside the sample. Thus, the formation of silicon carbide is favored over silicon nitride.

To explain the decrease in the formation of aluminum nitride, a more detailed explanation is offered.

Bechtold¹⁴ observed that upon heating, kaolin decomposes to mullite and free silica in the presence of carbon. When this mixture was further reduced, X-ray diffraction analysis showed that the free silica was reduced first, followed by the reduction of the silica in mullite.

Wright and Wolff⁵⁰ observed a similar occurrence while studying the problem of refractory brick checkerwork deterioration. They found that the aluminosilicate

refractory transformed to mullite and free silica. Petrographic studies showed that at temperatures greater than 1370°C, the free silica reduced first, followed by the reduction of the silica in the mullite. Perhaps silica in aluminosilicate is inhibited by its association with alumina and therefore is less reactive than free silica.

X-ray diffraction analysis of the coal waste used in this study showed that a major portion is free silica mixed with some aluminosilicate material. As reported previously, when the coal waste with a limited amount of carbon was reacted, mullite and silicon carbide were the products of reaction. No aluminum nitride was detected. From this observation, it was concluded that reaction 2 proceeds before reaction 1. Therefore, according to the above argument, it is postulated that the free silica is reduced first followed by the reduction of alumina and silica in the silicate material.

With excess carbon, conditions remain favorable for free silica to more completely react. Consequently, the reduction of the alumina in the aluminosilicate material to aluminum nitride is delayed. This would account for the decrease in the amount of aluminum nitride formed for a set reaction time when increasing amounts of excess carbon are added. However, it is supposed that the conversion to aluminum nitride will increase to the maximum if the reaction time is increased.

Weight Loss

Observing the weight change of a sample during reaction is often useful in following the progress of the reaction. Valuable information can be inferred from a plot of weight loss versus time. Such curves for the reactions studied in this investigation are shown in Figures 15-18. Continuous weight loss during the reaction would imply that the reductions of silica and alumina take place simultaneously.

In the proposed mechanism, some of the silicon carbide initially formed acts as a reducing agent on the remaining silica producing SiO and an increase in weight loss. The SiO combines with nitrogen to form silicon nitride, leading to a decrease in weight loss. This process is represented by reactions 2 and 18, the combination of which is reaction 9. At some point in this process, aluminum nitride begins forming according to reaction 1, resulting in an increase in weight loss. It should also be remembered that coal waste contains impurities and volatile materials which are reacting in the furnace. These reactions are difficult to follow and can be contributing to either weight loss or gain. Considering all these possibilities, it would appear reasonable that the weight loss curves are not smooth and continuous.

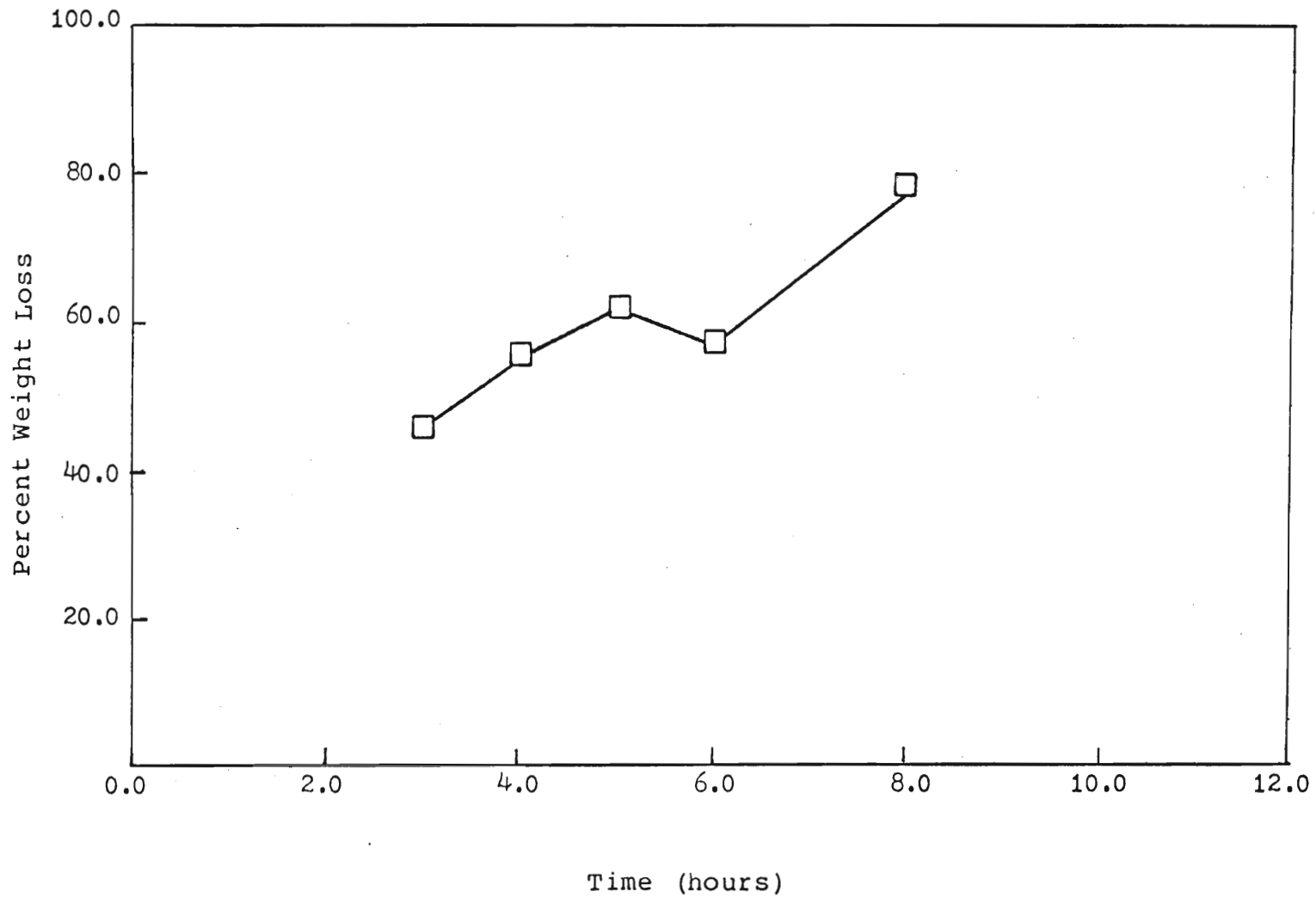


Figure 15. Weight loss during reaction at 1400°C.

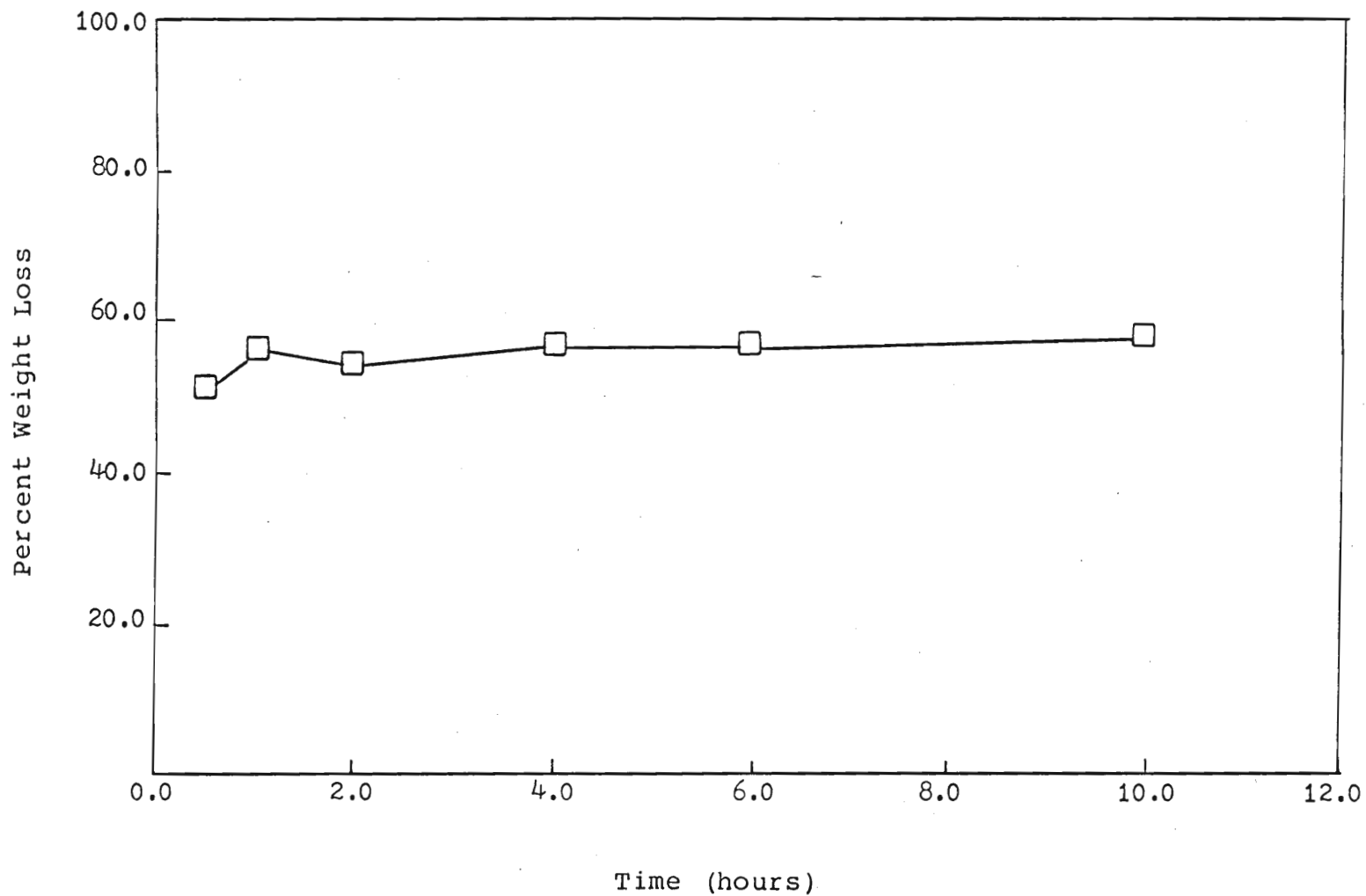


Figure 16. Weight loss during reaction at 1450°C.

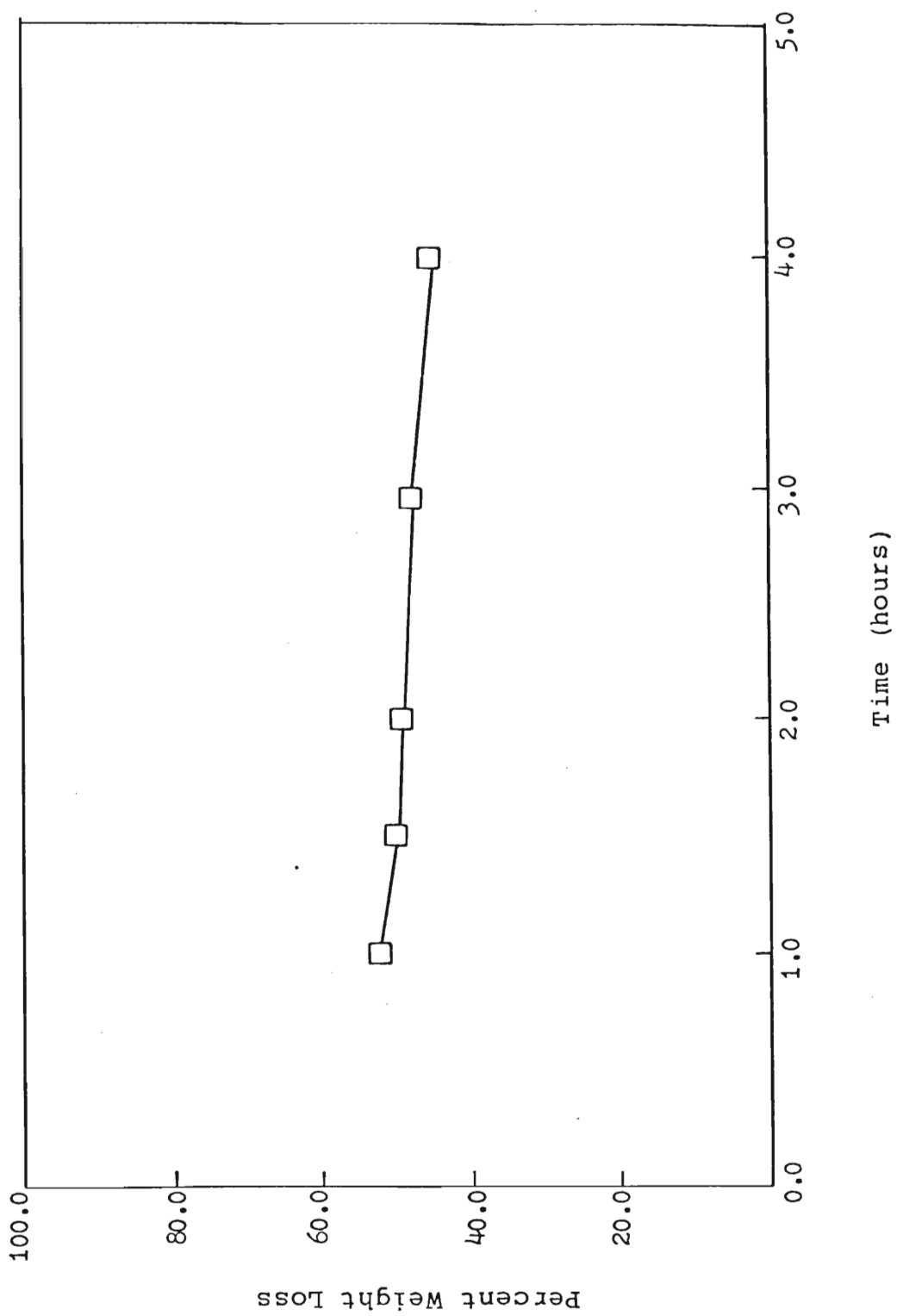


Figure 17. Weight loss during reaction at 1500°C.

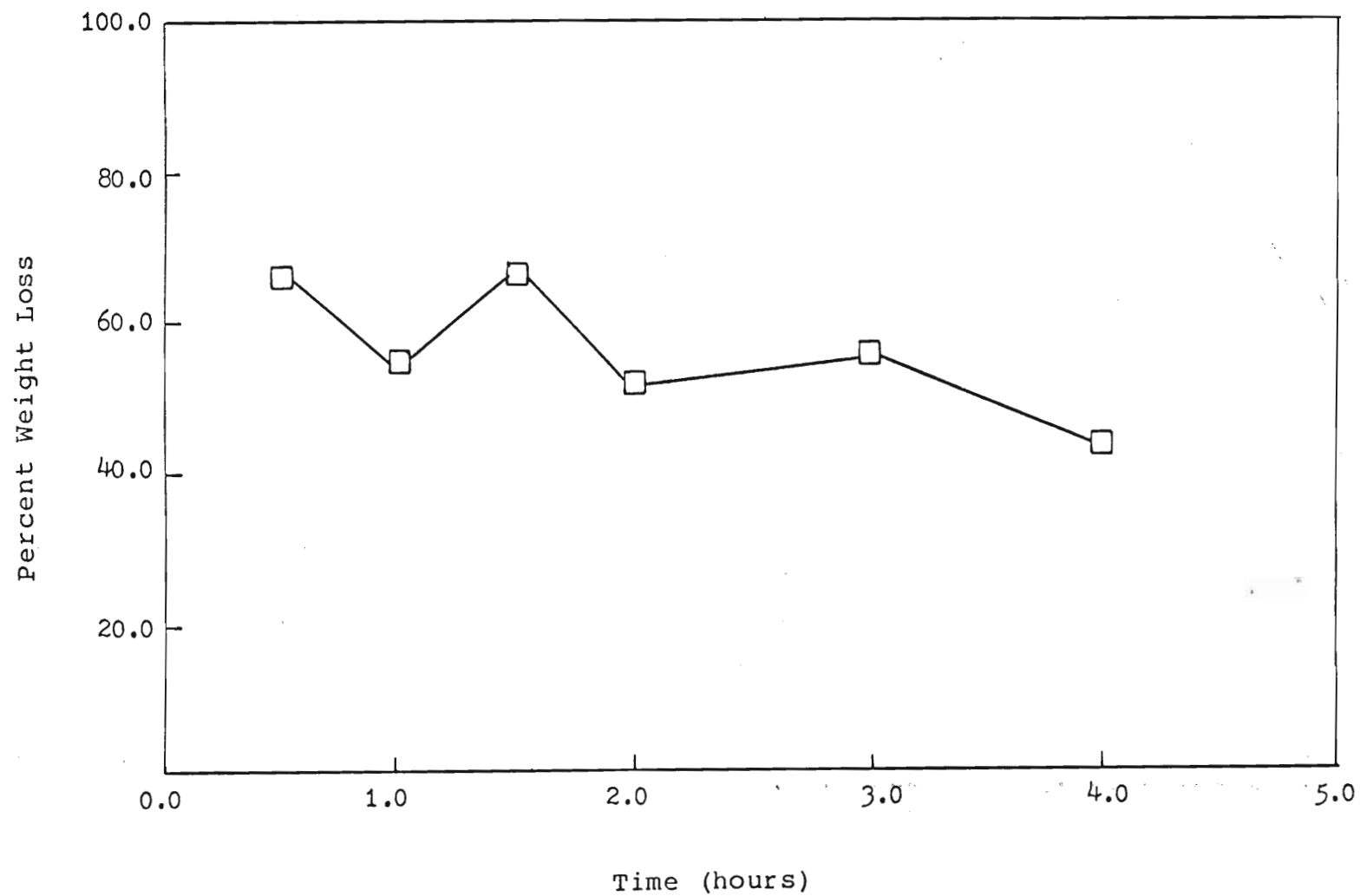
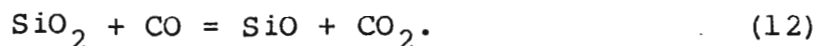


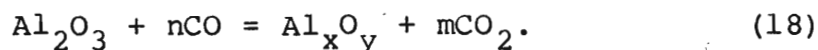
Figure 18. Weight loss during reaction at 1550°C.

Effects of Mixing

In the proposed mechanism for the carbothermal reduction of silica the rate controlling steps are a chain reaction:



A similar reaction is proposed for the reduction of alumina:



In both cases, carbon monoxide and carbon dioxide gases must travel between the surfaces of silica, alumina, and carbon particles. For a rapid reaction, the gases must be able to transport back and forth quickly. Thorough mixing of the carbon black with the waste material will reduce the distances between the particles and may enhance the reaction rate. If the carbon is not well mixed, then CO_2 and CO gases would have to diffuse over much larger distances. Consequently, the local partial pressure of carbon dioxide would rise, driving the overall reaction into an unfavorable range thermodynamically.

If the reactions proceed through gaseous intermediates as proposed, then intimate mixing of the carbon and waste material should give the best results. In waste material, carbon is uniformly dispersed naturally. But care must be taken to thoroughly mix the added carbon black.

To confirm these assumptions, two samples were prepared with different degrees of mixing. The first sample was arranged with alternative layers of coal waste and carbon black. The second was vigorously shaken for twenty minutes in a plastic container. Both were reacted for two hours at 1500°C. Table VI shows the results. The better mixed sample shows a greater amount of aluminum nitride and silicon nitride formed. This corresponds with a higher reaction rate. When the carbon and waste material are separated by layers, the reaction rate is slow. Although this information does not eliminate other possible reaction mechanisms (i.e., true solid-solid contact) it is consistent with the proposed mechanism of a solid-solid reaction proceeding through gaseous intermediates as explained above.

Surface Area Effect

For gas-solid reactions, it is generally true that the overall reaction rate depends on the surface area of the reactants. A large surface area maximizes the sites available for gaseous reactions to occur and thereby increases the reaction rate. By the proposed mechanism, the surface area available from the solid reactants is fully involved in the rate of reaction.

To test this assumption, experiments were performed varying the particle size of the coal wastes material. The carbon black was maintained at -200 mesh. Four

different size fractions of wastes were used: -200, 100 x 200, 65 x 100, and -65 mesh. Table VII lists the results. As the particle size increases, the formation of aluminum nitride and silicon nitride decreases. The reaction rate decreases with increasing particle size. This is consistent with the proposed mechanism.

Effect of Temperature

Thermodynamic calculations of the reactions involved show them to be endothermic. Since heat is required for the reaction to proceed, raising the temperature should increase the rates of reaction.

Experiments were run as low as 1300°C. At this temperature, no aluminum nitride formed, but silicon carbide and silicon nitride were detected. When the temperature was increased to 1350°C, aluminum nitride formed. This temperature is somewhat lower than other investigators claim is necessary for this reaction. Perhaps the amorphous nature of the aluminum silicates in coal wastes makes the formation of aluminum nitride more favorable. Normally the free energy values available for solids are for materials that correspond as closely as possible to the formulas given. Minerals are characteristically "impure" and may differ structurally from the chemical compound. If so, the effective free energy of formation would be less than the standard value, and the equilibrium temperature would in turn be lower.

TABLE VI. Effect of Mixing

Sample	Relative Percent of Products*			Percent Conversion†		
	AlN	SiC	Si ₃ N ₄	AlN	SiC	Si ₃ N ₄
Layers	18.2	63.8	18.0	54.7	74.2	24.3
Mixed	33.2	16.9	49.3	99.7	19.7	66.6

TABLE VII. Effect of Particle Size

Mesh	Relative Percent of Products*			Percent Conversion†		
	AlN	SiC	Si ₃ N ₄	AlN	SiC	Si ₃ N ₄
-200	30.7	23.6	45.7	92.2	27.4	61.8
100x200	24.3	23.2	52.6	73.0	27.0	71.1
65x100	21.7	30.1	48.2	65.2	35.0	64.9
+65	21.4	36.9	41.7	64.3	42.9	65.4

* Impurities excluded to make total of AlN + SiC + Si₃N₄ = 100%.

† Percent of original amount in coal waste converted to product.

As indicated in Table VIII, increasing temperature enhances the formation of aluminum nitride to a point. However, if the temperature is too high, or the reaction time too long, the formation of aluminum nitride drops off. From the data, it appears that the optimal temperature range is approximately 1450-1500°C for 1½ to 3 hours. At these conditions, roughly 95% of the alumina originally present in the coal waste is converted to aluminum nitride.

In an article reviewing the Serpek process,¹⁰ it was noted that overheating causes the material to fuse together, thus destroying porosity and causing nitrification to cease. A more recent patent¹¹ states that in the alumina-nitrogen-carbon system, overheating of the reactants involves volatilizations which may cause sintering, thus impairing the quality of the end product.

It has been found that high temperatures promote the formation of carbides.¹⁰ In practice, it has been found⁴ that the production of aluminum nitride falls off rapidly at temperatures greater than 1700°C, possibly because aluminum carbide becomes the stable phase, as seen in Figure 4. Kohlmeyer and Lundquist⁵¹ found carbon and alumina to form aluminum carbide at temperatures as low as 1560°C.

Because of the complexity of the system, other compounds besides carbides could be forming, causing decreased production of aluminum nitride. For example,

TABLE VIII. Effect of Temperature

Time (hours)	Temperature (°C)	Relative Percent of Products*			Percent Conversion†		
		AlN	SiC	Si ₃ N ₄	AlN	SiC	Si ₃ N ₄
1	1500	15.3	52.6	32.1	45.9	51.2	43.4
	1550	18.7	58.4	22.9	56.1	67.9	30.9
	1600	29.6	22.5	47.9	88.9	26.2	64.8
2	1350	27.4	44.9	27.7	82.3	52.2	37.4
	1450	32.7	46.8	20.5	98.2	54.4	27.7
	1500	30.5	19.1	50.4	91.6	22.2	68.1
	1550	29.2	26.8	44.0	87.7	31.2	59.5
3	1400	21.0	31.4	47.5	63.0	36.5	64.3
	1500	30.1	13.0	56.1	90.4	15.1	76.0
	1550	24.0	17.8	58.2	72.0	20.7	78.6
4	1400	27.5	31.2	41.3	92.6	36.3	55.8
	1450	30.1	35.3	34.6	90.4	41.0	46.8
	1500	27.5	14.2	58.2	82.9	16.5	78.6
	1550	21.8	10.3	67.9	65.5	12.0	86.8
6	1350	25.7	11.2	63.1	77.2	13.0	85.3
	1400	24.7	27.4	47.9	74.2	31.9	64.7
	1450	30.8	44.0	25.2	92.5	51.2	34.1
10	1350	26.5	9.3	64.2	79.6	10.8	86.8
	1450	30.9	22.8	46.3	92.8	26.5	62.6

* Impurities excluded to make total of AlN + SiC + Si₃N₄ = 100%.

† Percent of original amount in coal waste converted to product.

according to Pechiney,⁵² the formation of aluminum cyanide by reaction 19 increases with temperatures greater than 1700°C.



Aluminum oxy-carbide and other sub-oxides are other possible products of reaction. The formation of any of these products would explain the decrease in aluminum nitride formation observed in this study.

Effect of Pelletizing

According to Szekely, et al.,⁵ in conducting studies of gas-solid reactions it is usually advisable to form the reactants into single solid pellets. Fine powders may be used, but care should be taken to avoid losing particles in the moving gas stream. Pelletizing also has the advantage of better heat transfer and diffusion of gases.

Several of the experiments in this study were completed using pelletized reactants, formed in a hydraulic press with a suitable die.

Figures 19 and 20 show the effect of pelletizing versus nonpelletizing at 1450°C and 1500°C. For the lower temperature, pelletizing enhances the reaction. At 1500°C, pelletizing the sample caused the end product to partially sinter. The longer the pellet was reacted, the more difficult it became to remove, analyze and leach.

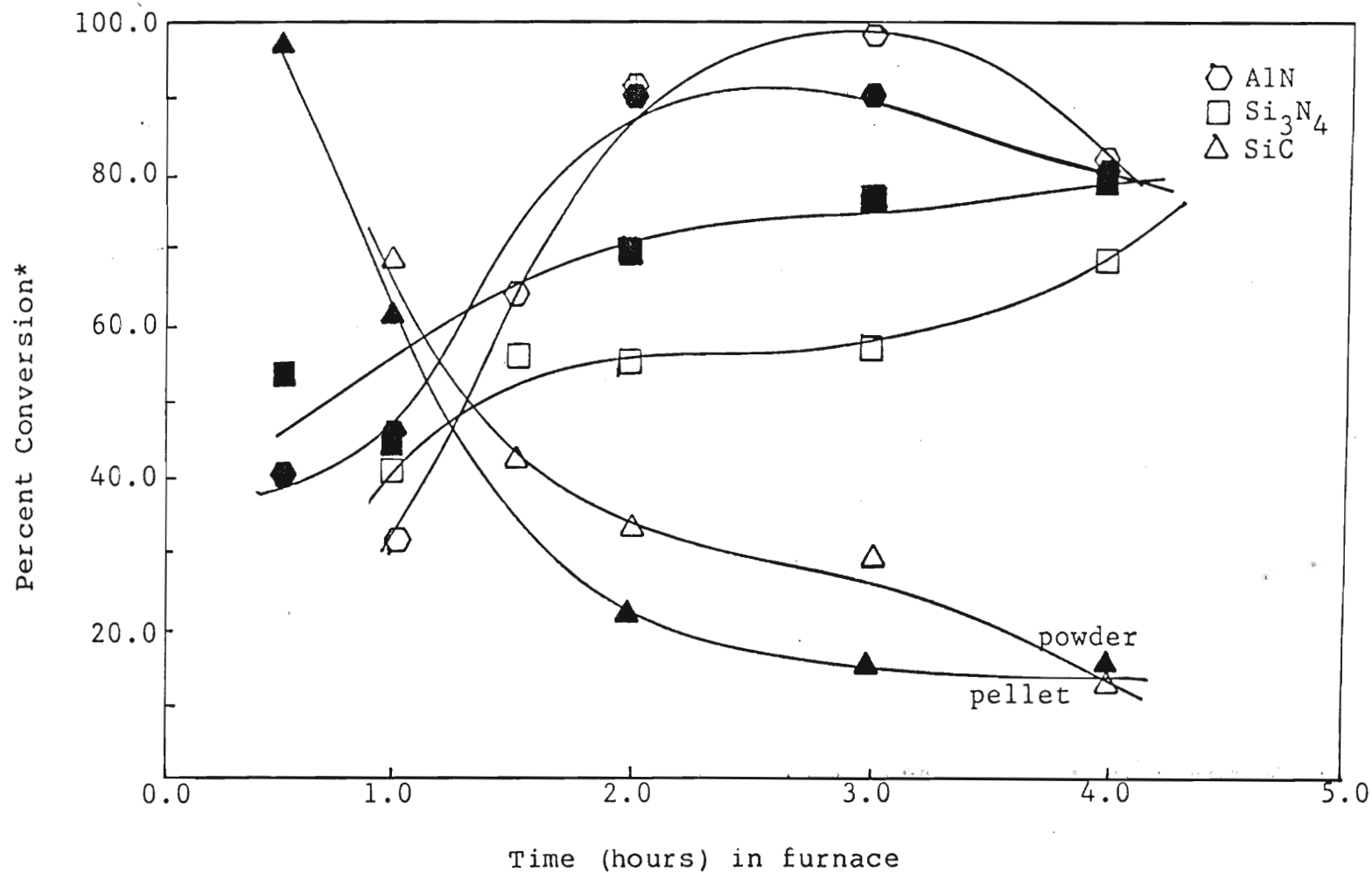


Figure 19. Effect of pelletizing at 1500°C.

*Percent of original amount in coal waste converted to product.

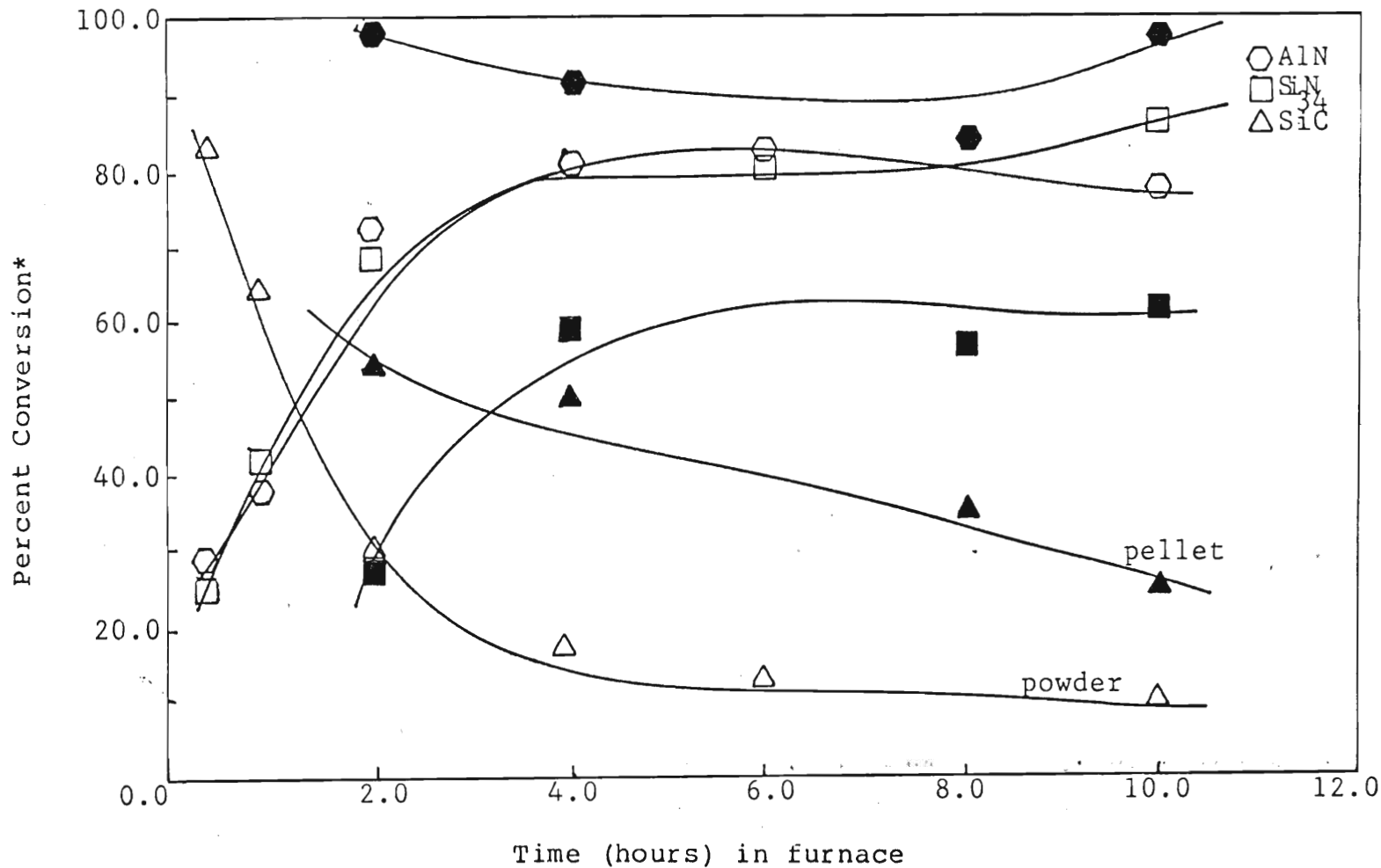


Figure 20. Effect of pelletizing at 1450°C.

*Percent of original amount in coal waste converted to product.

Sintering occurs when a porous compact increases in density when held at a high temperature. Sintering limits access by the reactant gas, thus markedly reducing the overall rate of reaction. Similar occurrences have been found for the reduction of nickel oxide with hydrogen.⁵³

Effect of Nitrogen Flow Rate

The rate of nitrogen gas flow was varied holding other conditions constant to examine the effect on the final products. Table IX lists the results of four such comparisons. As seen, the rate of flow appears to have only a slight effect.

Mah,²⁸ in producing silicon nitride from silica, found that the reaction rate is essentially independent of the total gas flow. As long as nitrogen gas is flowing, any carbon monoxide produced in the reaction can be carried away.

However, lack of nitrogen brings about partial sintering of the charge which makes completion of the nitriding operation impossible.¹¹ Therefore, nitrogen must be constantly flowing.

Leaching

As previously stated, the success of this process rests on the ability to leach the aluminum nitride formed by reaction 1 to obtain alumina and ammonia. Several leaching experiments were performed on the reaction

TABLE IX. Effect of Nitrogen Flow Rate

Condition	Rate (lit/min)	Relative Percent of Products*			Percent Conversion†		
		AlN	SiC	Si ₃ N ₄	AlN	SiC	Si ₃ N ₄
1500°C 1 hour	0.75	10.7	59.2	30.1	32.1	59.9	40.7
	1.75	9.7	55.0	35.3	29.1	64.0	47.7
1500°C 2 hours	0.75	33.1	20.0	46.9	99.4	23.3	63.4
	1.75	31.2	25.2	43.6	93.7	29.3	58.9
1500°C 3 hours	0.95	32.6	28.1	39.3	97.9	32.6	53.1
	1.95	33.1	24.1	42.4	99.4	28.0	57.3
1550°C 1 hour	0.95	26.9	27.7	45.4	80.8	32.2	61.4
	1.95	23.8	22.6	53.6	72.5	26.3	72.4

* Impurities excluded to make total of AlN + SiC + Si₃N₄ = 100%.

† Percent of original amount in coal waste converted to product.

products produced after two hours in the furnace at 1500°C to obtain the optimal leaching conditions.

For greatest efficiency, the optimal time of the leach is important. Figure 21 shows the recovery versus time using a one molar concentration of sodium hydroxide at boiling temperature. Beyond two hours of leaching, no significant increase in recovery is obtained. Recovery is a measure of alumina in the leach solution (determined by atomic absorption spectroscopy) as compared with the original amount of alumina known to be present in the coal waste.

Figure 22 summarizes the effect of different caustic concentrations when leaching for two hours at the boiling temperature. As seen, a concentration of approximately one molar gives the best results in the amount of aluminum nitride decomposed. When the caustic concentration is increased, more silicon and iron compounds are leached into solution, while the recovery of aluminum decreases. It could be that increasing the caustic concentration causes the formation of some insoluble aluminum compound. The Handbook of Chemistry and Physics³³ lists several alumina-silica-sodium compounds which are insoluble in alkaline solutions. These include: $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, $3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Other combinations are also possible.

Silica and iron are impurities in the system and are detrimental to the recovery of alumina. Therefore,

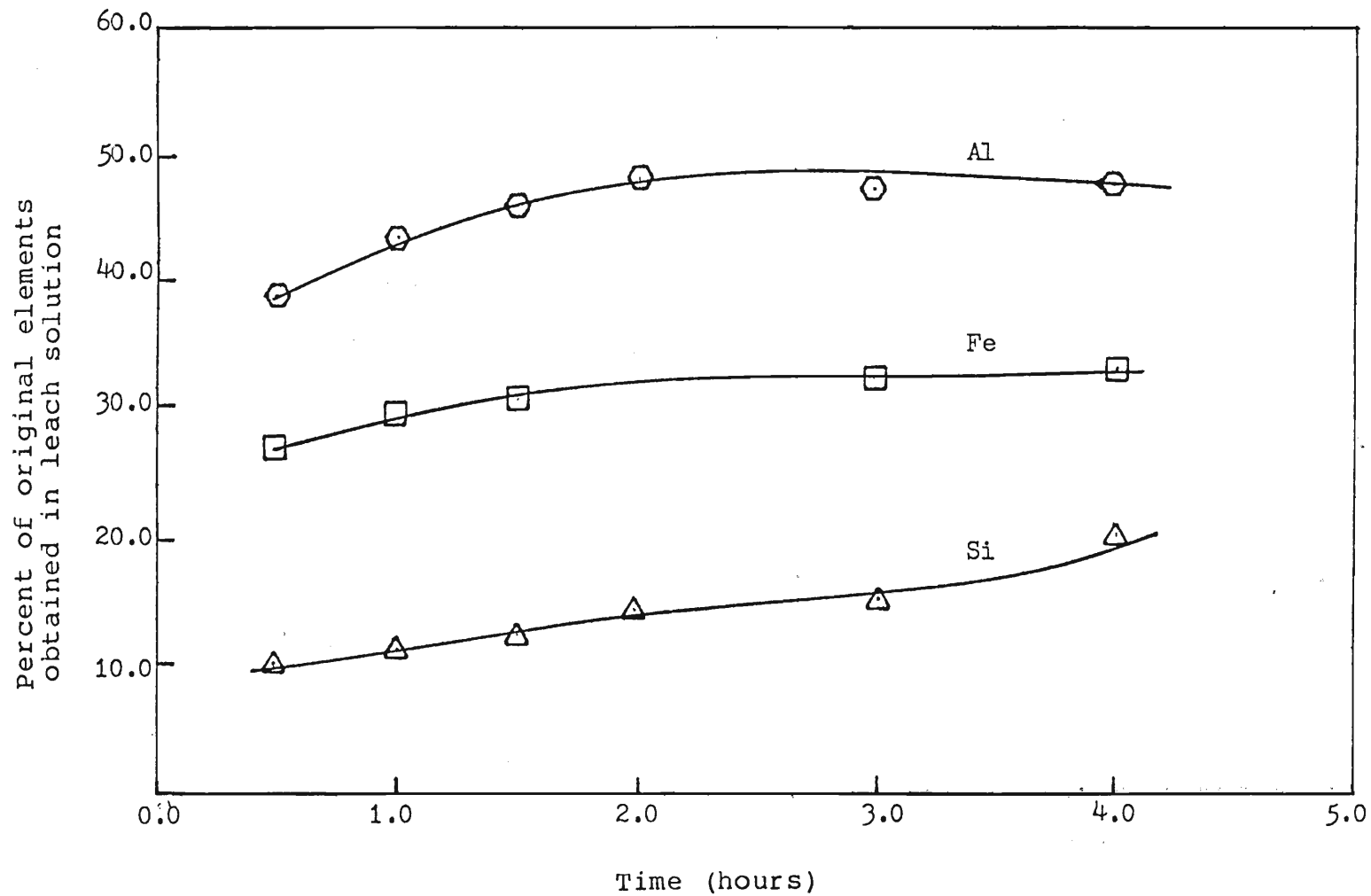


Figure 21. Effect of leach time on the dissolution of reaction products.
1 M NaOH, boiling temperature.

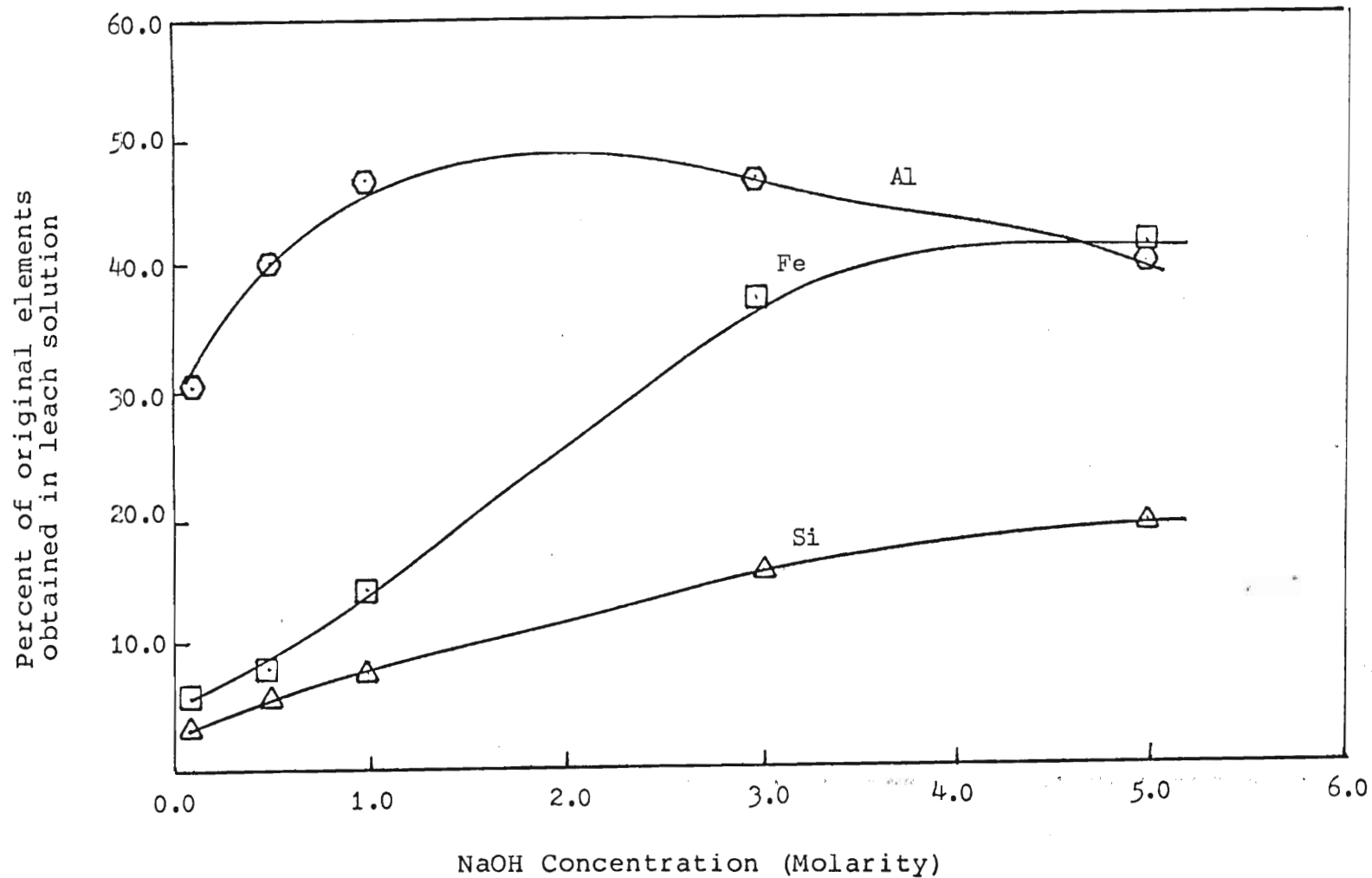


Figure 22. Effect of NaOH leach concentration on the dissolution of reaction products. 2 hours, boiling temperature.

the remaining experiments were done using a one molar concentration of sodium hydroxide.

The effect of the leachant temperature is clearly shown in Figure 23. These experiments were completed using a one molar caustic concentration and leaching for two hours. The higher the temperature, the better the recovery of alumina. The best results are obtained when the solution is boiling.

All further leaching experiments were performed using these optimal conditions. The results are shown in Figures 24-26. As seen, the recovery of aluminum nitride proceeds through a maximum. This appears to confirm the assumption made previously that aluminum nitride formation by reaction 1 decreases with increasing reaction time in the furnace. As seen in Figures 24-26, beyond 1½ to 2 hours in the furnace the recovery of alumina by leaching decreases. At these periods of time, the aluminum nitride being produced is not readily leached.

Even the maximum recovery of alumina under optimal conditions of 1500°C for 1½ to 2 hours is less (about 60%) than expected. It could be concluded that either reaction 1 is not going to completion, or the aluminum nitride formed is not readily leached. In such a complex system, a combination of these is possible.

To investigate the solubility of aluminum nitride, a relatively pure sample was obtained from Chem-Tech

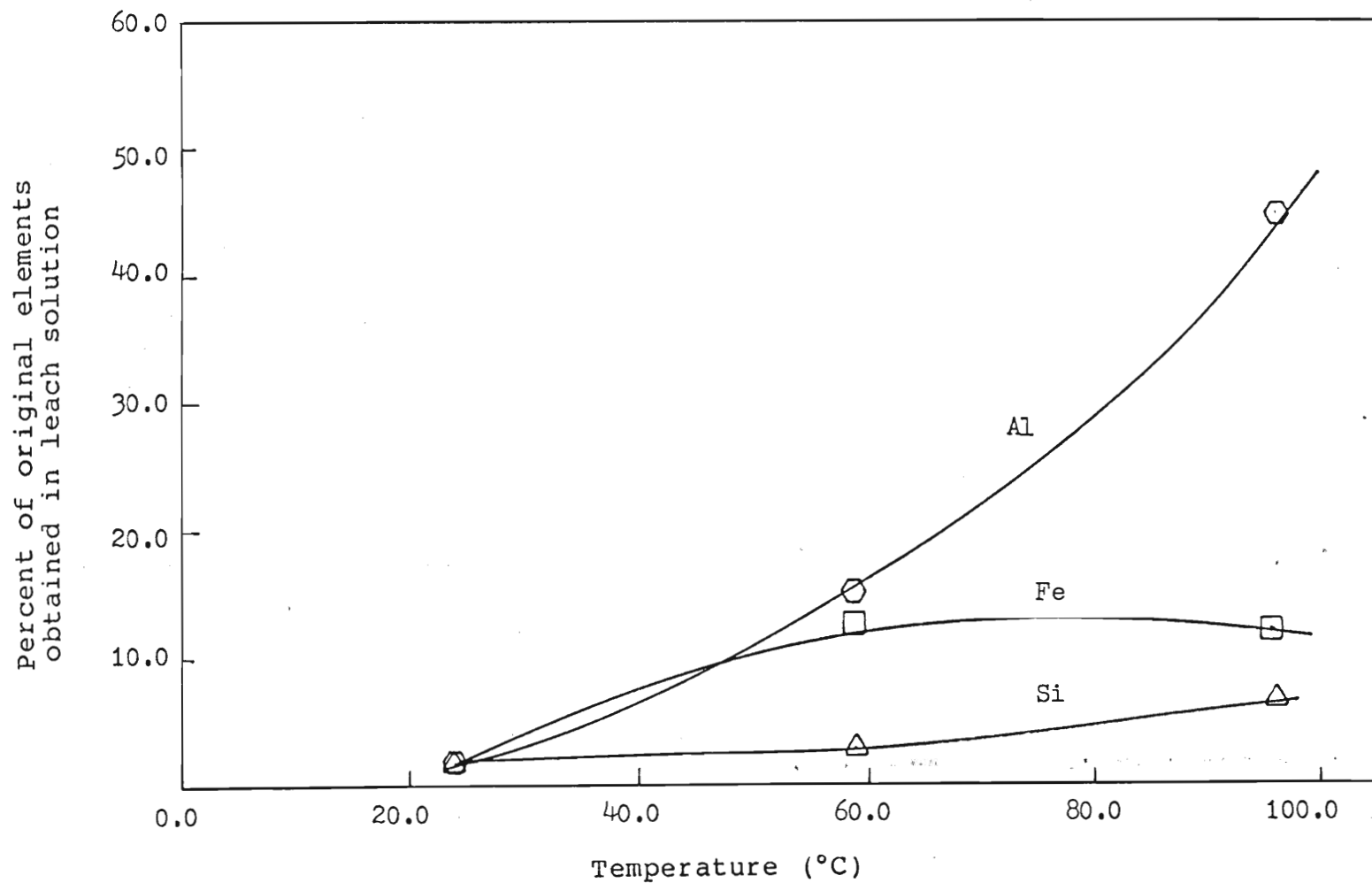


Figure 23. Effect of leachant temperature on the dissolution of reaction products.
1 M NaOH, 2 hours.

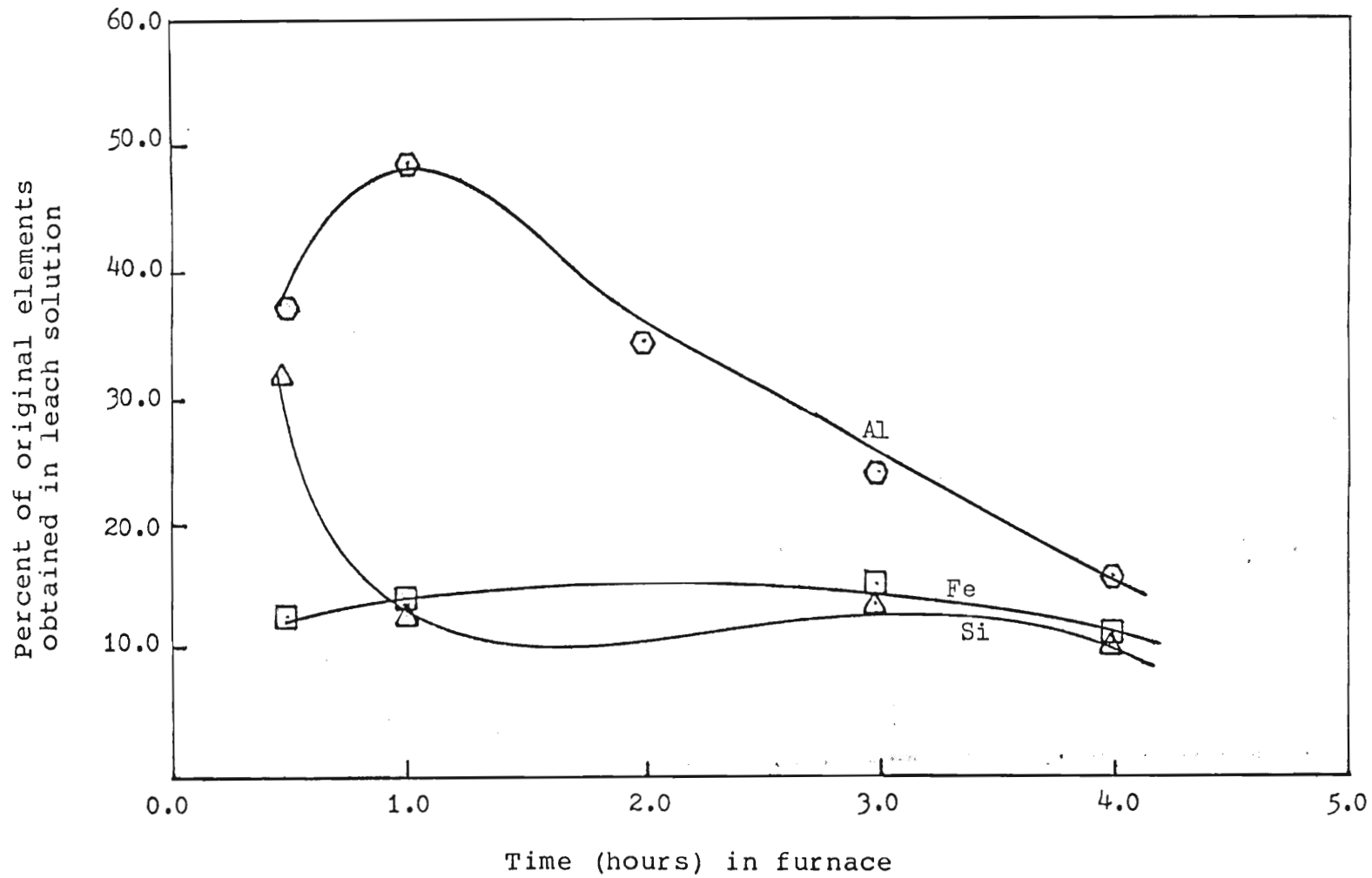


Figure 24. Leaching of products of reaction obtained at 1500°C. Leaching conditions: 1 M NaOH, boiling temperature.

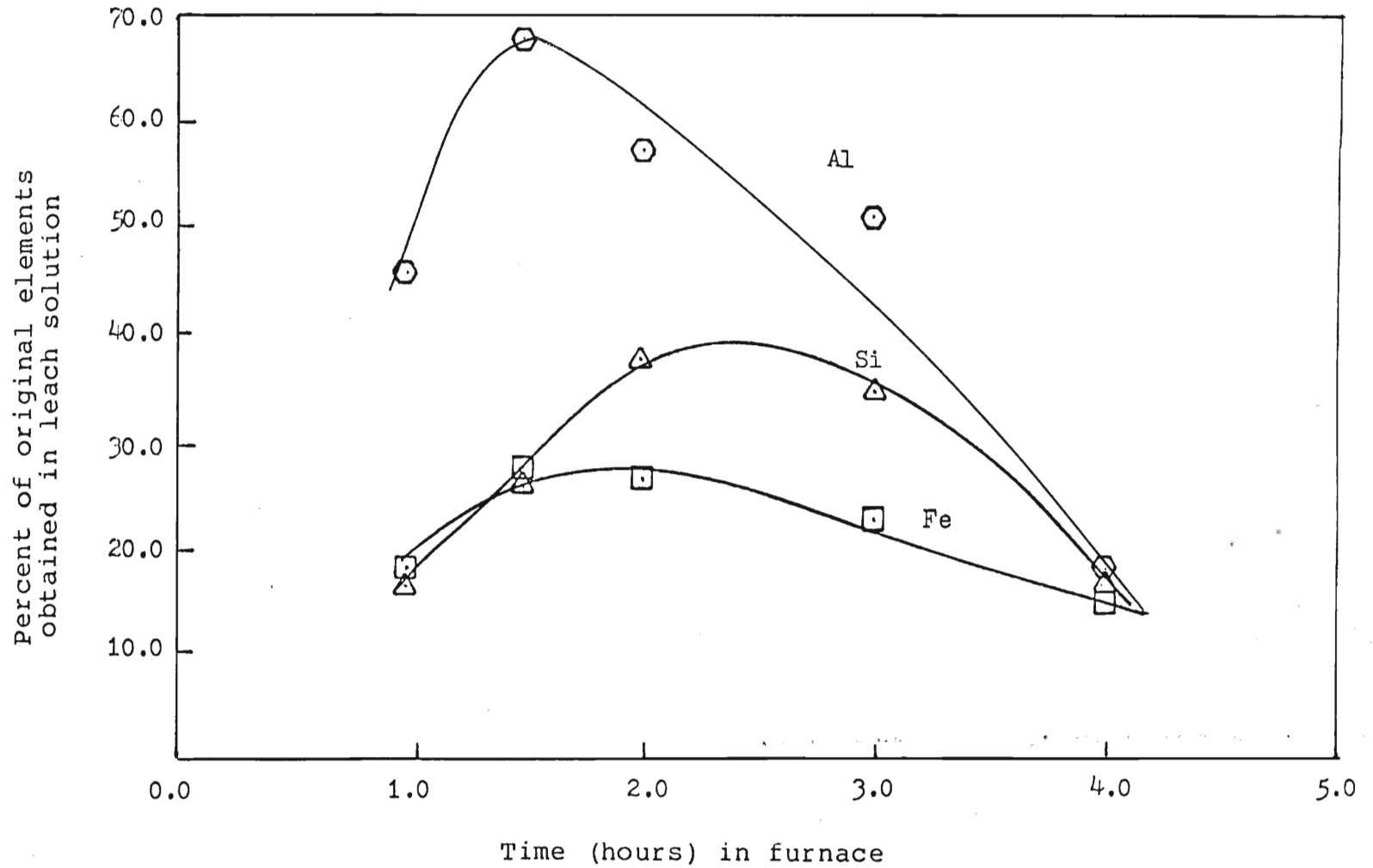


Figure 25. Leaching of products of reaction obtained at 1500°C.
 Leaching conditions: 2 hours, 1 M. NaOH, boiling temperature.

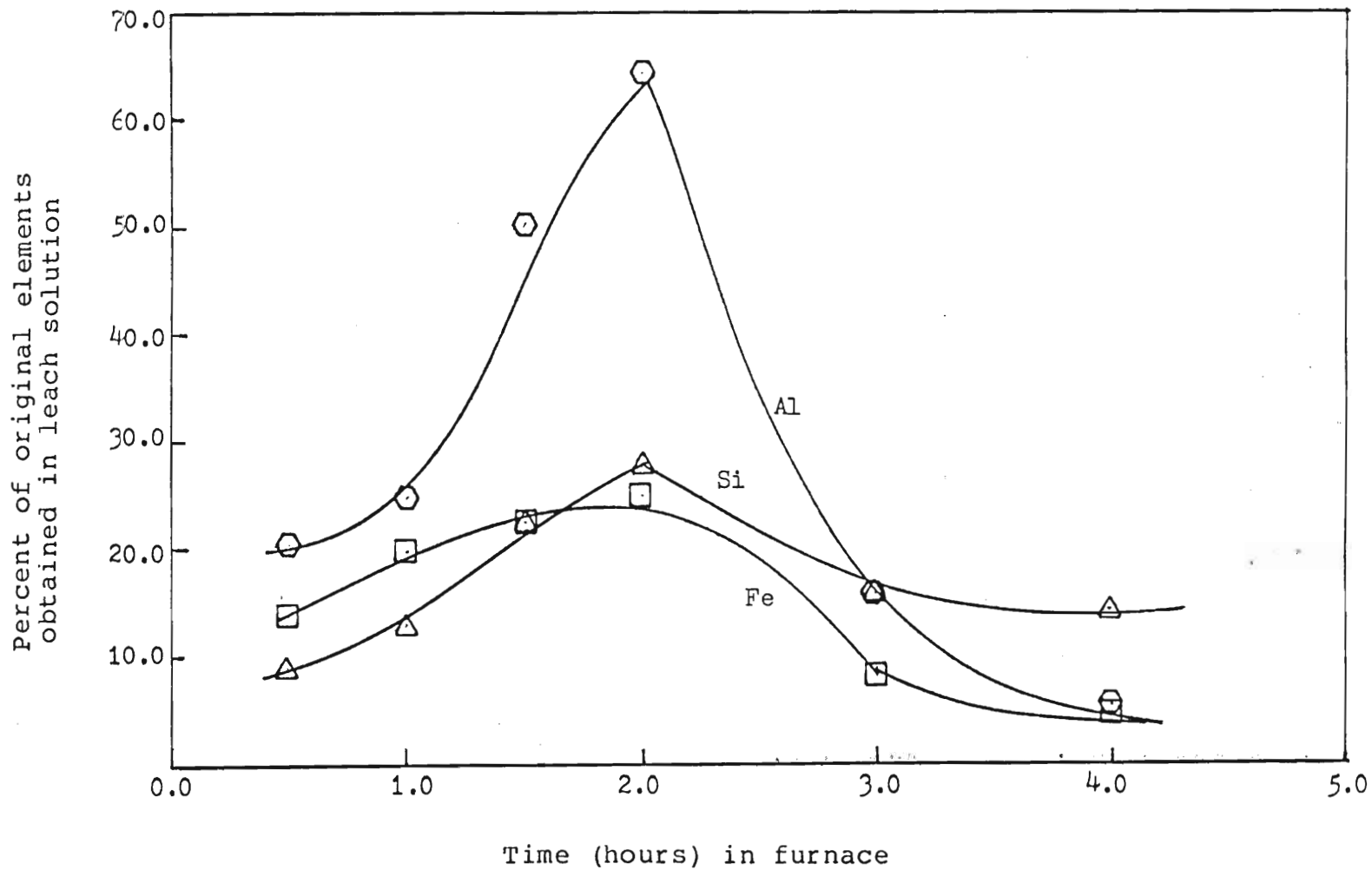


Figure 26. Leaching of products of reaction obtained at 1550°C.
 Leaching conditions: 2 hours, 1 M NaOH, boiling temperature.

Laboratories. When leached at optimal conditions, 99% of the aluminum nitride decomposed. This demonstrates that aluminum nitride dissolves easily in caustic solutions. However, it should be noted that the aluminum nitride produced by Chem-Tech is formed by heating powdered aluminum mixed with 1% sodium fluoride (which catalyzes the reaction at a temperature of 700°C,) in a current of nitrogen, a common practice in industry.¹² This is a much lower temperature than used in this study.

In the 1920s, Alcoa⁴ industries performed extensive leaching experiments on aluminum nitride produced by reaction 1. Because of the refractory behavior of the nitride, many difficulties were encountered. Studies showed that the crystalline variety of aluminum nitride formed at these high temperatures was much more difficult to decompose than anticipated.

In 1956, Kohn, et al.,⁵⁴ incidentally obtained small crystals of aluminum nitride while working at high temperatures on another project. Analysis showed that the crystals were relatively inert. A few years later, Long and Foster⁵⁵ produced high purity aluminum nitride by striking a d.c. arc between two high-purity aluminum electrodes in a nitrogen atmosphere. An unexpected finding was the extreme chemical inertness of the aluminum nitride formed at these very high temperatures.

These and other findings led Taylor and Lenie³⁰ to conclude that aluminum nitride prepared at high tempera-

tures is relatively inert. They produced crystals by two different methods: first, by heating aluminum nitride to induce crystal growth by recrystallization; second, by heating aluminum metal powder in a nitrogen atmosphere to sufficiently high temperatures to vaporize aluminum and form crystals by a vapor-phase reaction. It was observed that short, extremely fine filaments of aluminum nitride formed in the range 1450-1750°C. The higher the temperature, the more well defined the crystals. It appears that the degree of crystallinity and the degree of inertness are related.

In this study, some of the aluminum nitride from Chem-Tech was heated at 1500°C for 2 hours under a nitrogen atmosphere. Leaching under optimal conditions, only 85% of the alumina was recovered, verifying that crystalline aluminum nitride formed at high temperatures is more inert and difficult to leach.

It was also pointed out previously that high temperatures of reaction appear to cause sintering of the end product. Sintering reduces the surface area. Thus, it would take more effort to leach sintered aluminum nitride. All of these possibilities (sintering, crystallization, and the formation of other aluminum compounds besides aluminum nitride) would help explain the low recovery of alumina in the leaching process.

Precipitation

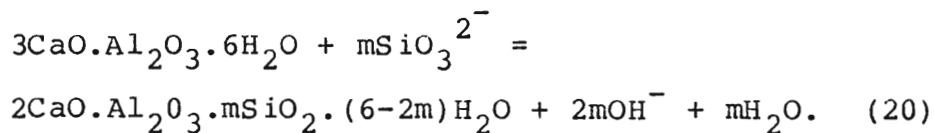
Once aluminum nitride is digested, a relatively pure form of aluminum hydroxide must be precipitated to obtain alumina. Several compounds were used to try to precipitate alumina. Hydrochloric acid, sulfuric acid, and carbon dioxide gas were used to lower the pH of the solution and aid in precipitation of alumina. However, because of the similar behaviors of aluminum and silicon, precipitating alumina simultaneously precipitated silica.

$\text{Al}(\text{OH})_3$, Al_2SO_4 , and Al_2O_3 were added as seed crystals to cause alumina to drop out of solution. Satisfactory results were not obtained.

It was concluded that iron and silica impurities must be removed before alumina can be precipitated. Removal of iron proved to be relatively easy because it drops out of solution before silica or alumina. In fact, if the solution sits for several days, the iron precipitates on its own.

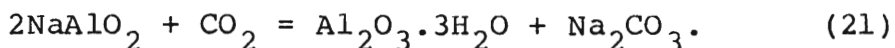
Silica is more difficult to remove. The traditional Bayer method of desilication proved ineffective in this study. Alcoa⁴ also found that for the aluminum nitride process, silica went into solution and could not be precipitated as a conventional desilication product. The researchers concluded that a separate and expensive desilication process would be necessary for a good recovery of alumina.

However, since that time more work has been done on desilicating sodium aluminate solutions. It has been proposed⁵⁴ that increasing the solution temperature aids in precipitating sodium aluminosilicate. This, however, was of little help in this study. A method proposed by Noworyta³⁶ gave more promising results. The pH of the solution was adjusted to 12.5 with the aid of hydrochloric acid. Next, the temperature was raised to 96°C. A given amount of a 10 gpl solution of calcium hydroxide was added and the entire solution was left to desilicate for one hour. Noworyta believes desilication occurs by the following reaction:



After heating, the solution was filtered and analyzed for alumina and silica. The results are shown in Figure 27. At a certain point, all of the silica is removed as calcium aluminosilicate with most of the alumina remaining in solution. Approximately 10% of the alumina is lost to the calcium aluminosilicate. If too much calcium hydroxide is added, alumina can be totally precipitated out of solution. Care must be taken to add the ideal amount of desilicant.

With iron and silica removed, aluminum hydroxide was precipitated by bubbling carbon dioxide gas through the alumina rich solution according to reaction 21.



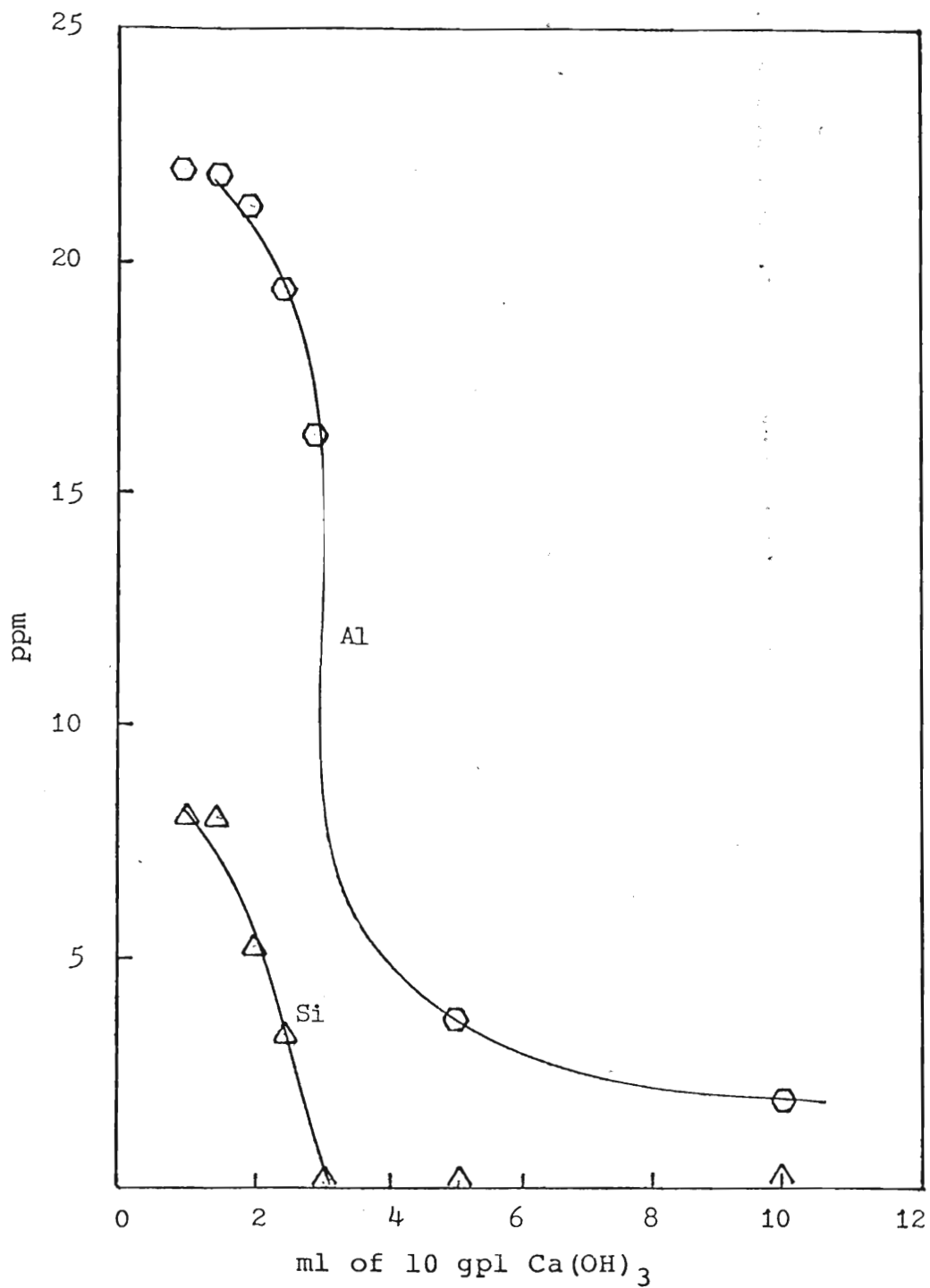
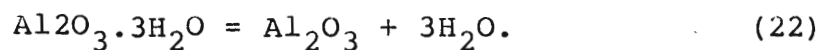


Figure 27. Desilication of sodium aluminate solution.

This precipitate was washed with warm water to dissolve any precipitated salts, and calcined in a platinum crucible at a temperature of 1200°C to remove the waters of hydration.



X-ray diffraction analysis showed alumina to be the final product. Any aluminum hydroxide not precipitated can be recycled and allowed to precipitate again.

CONCLUSIONS

A process to obtain alumina from coal waste has been investigated in this study. It consists of three basic stages, each of which was investigated to obtain optimal operating conditions for the greatest yield of alumina.

Stage I

Carbothermal Reduction of Alumina in Coal Waste Under a Nitrogen Atmosphere to Produce Aluminum Nitride

The effect of several parameters was determined. By quantitative x-ray diffraction analysis, it was determined that in the temperature range of 1450-1500°C, for the time span of 1½ to 3 hours, up to 98% of the alumina originally present is converted to aluminum nitride. At higher temperatures (greater than 1550°C) for the same length of time, the conversion decreases to below 80%. It was postulated that at these higher temperatures other aluminum compounds besides aluminum nitride are formed, thus decreasing the yield of aluminum nitride. A temperature of at least 1350°C is needed for the reduction to occur.

It was also observed that long reaction times (greater than 4 hours) have a detrimental effect on the conversion

to aluminum nitride, dropping the conversion to as low as 50%. It is believed that under these conditions, sintering of the product occurs.

Decreasing the particle size and increasing the degree of mixing increases the reaction rate and aids in the formation of aluminum nitride. The better the sample is mixed and the smaller the particle size of the waste material, the higher the reaction rate.

Pelletizing and increasing the nitrogen flow rate appear to have little effect on the reaction rate, although pelletizing seemed to aid in the sintering of the end product.

One of the advantages of this process is that the silica in the coal waste is reduced to silicon carbide, a valuable by-product of the ceramics industry. It was shown that this silicon carbide can act as a reducing agent on the remaining silica to form SiO gas and subsequently silicon nitride.

Stage II

Leaching of Aluminum Nitride to Obtain Aluminum Hydroxide

The products of reaction obtained at 1450° and 1500°C for two hours of reaction were leached to determine the optimal conditions for this stage. It was determined that a leach time of 2 hours at boiling temperature in a one molar sodium hydroxide solution gives the best results. Under these conditions, approximately 70%

of the alumina originally present is obtained in the leach solution.

This is lower than expected. A literature survey showed that aluminum nitride formed at high temperatures is crystalline in nature, and therefore more difficult to leach.

Leaching the products of reaction obtained at various lengths of time showed the recovery of alumina to proceed through a maximum after approximately 2 hours time in the furnace. This verifies the conclusion in Stage I that increasing reaction time in the furnace decreases the formation of aluminum nitride.

Stage III

Desilication and Precipitation of Sodium Aluminate Solutions

It was found that calcium hydroxide acts to desilicate the leach solution. If the right amount of a 10 gpl solution of calcium hydroxide is added to the sodium aluminate solution, all of the silica will be precipitated while only 10% of the alumina is lost to the precipitate.

Once desilicated, bubbling carbon dioxide gas through the solution precipitates aluminum hydroxide, which can be calcined at 1200°C to obtain reaction grade alumina.

The process flowsheet shown in Figure 28 gives the yields of alumina at the intermediate stages when optimal operating conditions have been maintained.

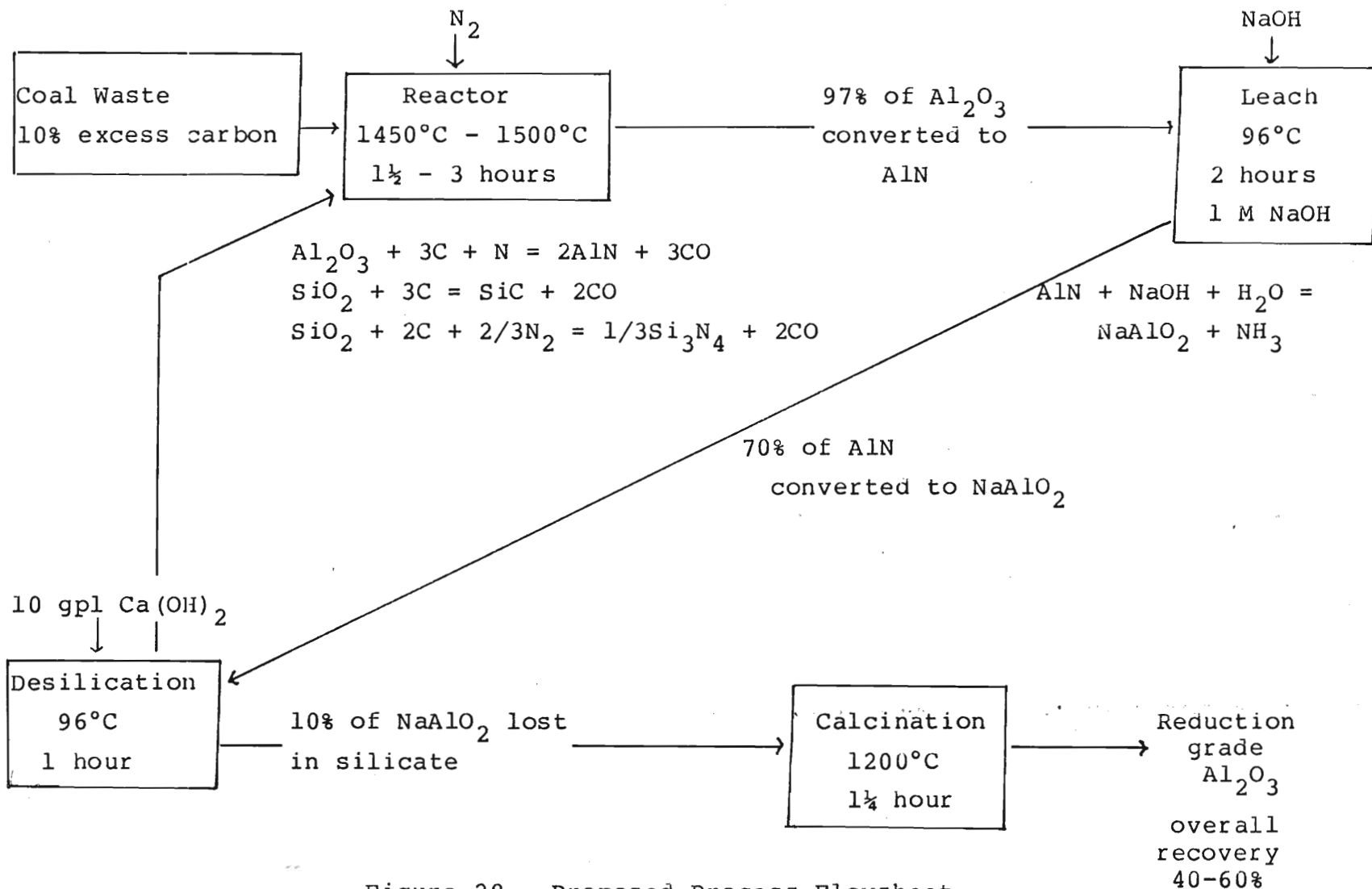


Figure 28. Proposed Process Flowsheet.

If each stage is operated at peak conditions, then the overall conversion of alumina from the coal waste is about 60%.

RECOMMENDATIONS FOR FURTHER STUDY

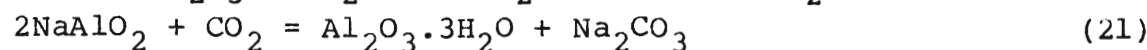
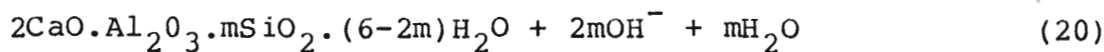
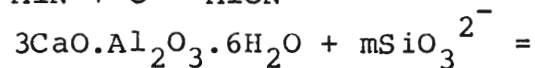
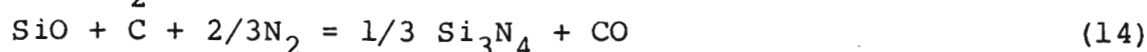
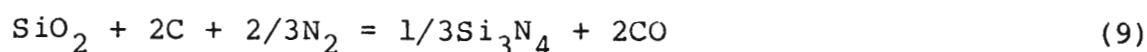
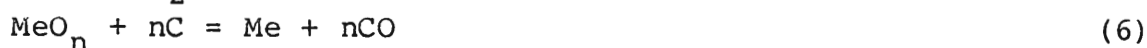
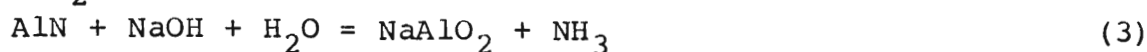
The major purpose of this study was to investigate the possibility of obtaining alumina by carbothermal reduction of coal waste. Although several parameters were investigated, it was not the goal of this research to perform detailed investigations on each stage of the process. But, through the work done in the study, an overall view of the process was obtained.

The conversion of alumina to aluminum nitride can be relatively complete, as are the desilication and calcination steps. It appears that the greatest loss in recovery occurs in the leaching process. Only up to 70% of the aluminum nitride formed is leached. Therefore, it is recommended that this step be more thoroughly investigated to find ways to increase the recovery. Because of the refractory behavior of alumina nitride formed at high temperatures, perhaps high pressure and high temperature leach solutions should be experimented with to solve this problem.

Once this major problem is overcome, more time could be spent in improving the other stages of the process.

APPENDIX

TABLE OF EQUATIONS



REFERENCES

1. K.B. Bengtson, "A Technological Comparison of Six Processes for the Production of Reduction-Grade Alumina from Non-Bauxite Raw Materials," TMS Paper Selection, LM-79-14.
2. O. Serpek, U.S. Patent 867 615, 1907. U.S. Patent 987 408, 1911.
3. I. Cutler, Patent Pending.
4. P.T. Stroup, "Carbothermic Smelting of Alumina," Transactions of The Metallurgical Society of AIME, April 1965, 230, 365.
5. J. Szekely, J. Evans, and H.Y. Sohn, Gas-Solid Reactions, Academic Press, New York, 1974.
6. T. Rosenqvist, Principles of Extractive Metallurgy, McGraw-Hill Book Comp., New York, 1974.
7. D. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd ed., U.S. Dept. of Commerce, 1970.
8. T. Willson, British Patent 21 755, 1895.
9. W. Fraenkal and J. Silbermann, "Uber die Bildung von Aluminiumnitride Aus Tonerde, Kohle und Stickstoff," Zeitschrift fur Electrochemie, 1913, 516, 107.
10. J. Edwards, F. Frary, and Z. Jeffries, The Aluminum Industry, McGraw-Hill Book Co., New York, 1930.
11. J. Clair, U.S. Patent 3 032 398, 1962.
12. L.A. Kost, N. Novikove, L. Sin'kova, and M. Shpirt, "The Possibility of Obtaining Nitride-Containing Materials from Coal Wastes," Khimiya Tverdogo Topliva, 1977, 11(5), 33-36.
13. _____, Japanese Patent 48-22919, Cl. 15M1 (ColB 21/06)
14. B. Bechtold, "Carbothermal Reduction of Kaolin Caly and Resulting Silicon Carbide Formation," Ph.D. Thesis, U. of Utah, 1978.

15. W. Knippenbert, "Growth Phenomena in Silicon Carbide," Phillips Research Reports, 1963, 18, 161-274.
16. J. Lee, "Carbide and Nitride Ceramics by Carbothermal Reduction of Silica," Ph.D. Dissertation, U. of Utah, 1976.
17. J. Blumenthal, M. Santy, and E. Burns, "Kinetic Studies of High Temperature Carbon-Silica Reactions in Charred Silica-Reinforced Phenolic Resins," AIAA Journal, 1966, 4(6), 1053-7.
18. J. Lee and I. Cutler, "Formation of Silicon Carbide from Rice Hulls," Bulletin American Ceramic Society, 1975, 54(2), 195-8.
19. N. Sharma, "Silica in Rice Hulls and Its Conversion to SiC," M.S. Thesis, U. of Illinois, 1976.
20. N. Klinger, E. Strauss, K. Komarek, "Reactions between Silica and Graphite," Journal American Ceramic Society, 1966, 49(7), 369-75.
21. K. Grjotheim and B. Welch, "Impact of Alternative Processes for Alumina Production," J. Metals, Sept. 1981, 26-32.
22. K. Repenko, R. Efimenkp, and A. Gul'ko, "Collection of Scientific Papers of UANIO," Metallurgizdat, 1962, 6.
23. A. Lejus, Bulletin Soc. Chim. France, 1962, 2123.
24. Engineering Properties of Selected Ceramic Materials, Columbus: American Ceramic Society Publications, 1966.
25. J. Clauss, Engineer's Guide to High Temperature Materials, Addison Wesley Pub. Com., Mass., 1969.
26. J. Collins and R. Gerby, J. Metals, 1955, 7, 612.
27. ___ Mehner, German Patent 88,999, 1896.
28. T. Jah, "Feasibility of the Formation of Silicon Nitride from Rice Hulls," M.S. Thesis, U. of Utah, 1972.
29. D. Hoggard, "Chemical and Mineralogical Effects of Impurities on the Formation and Sinterability of SIALON," M.S. Thesis, U. of Utah, 1978.

30. K. Taylor and C. Lenie, "Some Properties of Aluminum Nitride," Journal of the Electrochemical Society, April. 1960, 107(4), 308-14.
31. F. Snell and C. Hilton, Ency. of Ind. Chem. Anal. Vol 5, Interscience Pub., New York, 1965.
32. Soc. Gen. Des Nitrures, German Patent 241 339, 1911.
33. R. Weast, Handbook of Chemistry and Physics, The Chem. Rubber Co., Cleveland, 1967.
34. A. Adamson, "Alumina Production: Prin. and Prac.," Jan. 1970, 239, 156-64.
35. K.J. Bayer, U.S. Patent 382 505, 1888.
36. A. Noworyta, "Removal of Silica from Aluminate Solutions," Hydromet., 1981, 7, 99-106.
37. H.L. LeChatelier, British Patent 957, 1859.
38. I. Cutler, Monthly Report Utah Engineering Exp. Station to the Amer. Met. Products Co.
39. J. Rakszawski, F. Rusinko, and P. Walker, Proceedings of the Fifth Conference on Carbon Vol. w, Pergamon Press, New York, 1962, 243.
40. P. Walker, M. Shelef, and R. Anderson, Chemistry and Physics of Carbon, Marcel Dekker Inc., New York, 1968, 287-383.
41. K. Portnoi, V. Gribkov, and B. Shchetanov, "Mech. of growth and Etching of Whisker Crystals of Aluminum Nitride," Kristallografiya, May 1973, 18, 599.
42. I. Kolthoff, and E. Sandell, Quantitative Chem. Analysis 4th Ed., The Macmillan Co., London, 1969, 658-660.
43. J. Yule and G. Swanson, "A Rapid Method for Decomposition and the Analysis of Silicates and Carbonates by Atomic Absorption Spectroscopy," Atomic Absorption Newsletter, Mar. 1969, 8(2).
44. Inorganic Index to the Powder Diffraction File, Joint Committee on Powder Diff. Standards, Phil., 1970.
45. G. Renlund, "Separation of Al_2O_3 from Clay by Carbo-thermal Reduction," M.S. Thesis, U. of Utah, 1981.

46. W. Kingery, H. Bowen, and D. Uhlmann, Intro. to Ceramics, Wiley-Interscience Pub., New York, 1975, 309.
47. D. Hoggard, "Minimization of Impurities in SIALON from Clay and Carbon," M.S. Thesis, U. of Utah, 1981.
48. D. Miller, "Silicon Monoxide Formation Via the Carbothermal Reduction of Silica," M.S. Thesis, U. of Utah, 1977.
49. W. Pultz and W. Hertl, "SiO₂ and SiC Reaction at Elevated Temperatures," Trans. Faraday Soc., 1966, 62, 2499.
50. R. Wright and H. Wolff, "Refractory Problems in Production of Hydrogen by Pyrolysis of Natural Gas," Journal American Ceramic Soc., 1948, 31(2), 31-8.
51. E. Kohlmeyer and S. Lundquist, Z. Anorg. Allg. Chem., 1949, 260, 208.
52. Pechiney Campahnie, U.S. Patent 3 032 398, 1962.
53. J. Szekely and J. Evans, Chem. Eng., Sci., 1971, 26, 1091.
54. J. Kohn, P. Cotter, and R. Potter, Am. Min., 1956, 41, 355.
55. G. Lang and L. Foster, "Aluminum Nitride, a Refractory for Alumina to 2000°C," J. of Am. Ceram. Society, Feb. 1959, 42(2).

