AN INVESTIGATION INTO THE EXTRACTION OF VALUE ADDED PRODUCTS FROM RED MUD

by

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ABSTRACT

The pyrochemical extraction of alumina from bauxite ore leaves behind an iron oxide rich, reddish, process waste called red mud. The intent of this thesis is to determine the feasibility of extracting the value added products of alumina, iron and titanium oxide from red mud generated from North Coast Jamaican bauxite as well as to determine the sequence of extraction.

Each value added product requires varying extraction techniques. Alumina extraction begins by sintering the red mud with sodium carbonate to form sodium aluminate, and then leaching and washing the mud to dissolve the aluminate. Recovering iron entails reducing the red mud with petroleum coke, magnetically separating the reduced iron from the red mud, evaluating the magnetic product and smelting, if necessary. The non-magnetic product from the separation is processed to recover titanium oxide by either carbo-chlorination or conversion from perovskite to rutile. Two sequences for alumina, iron and titanium oxide removal are employed during experimentation recognized as the modified simultaneous sintering and reduction sequence and the separate sintering and reduction sequence. The modified simultaneous sintering and reduction sequence consists of drying, simultaneously sintering and reducing, leaching, washing, magnetically separating, smelting and carbo-chlorinating or converting perovskite to rutile to recover all three value added products. The separate sintering and reduction sequence employs the same processing steps except that reduction occurs after washing instead of during sintering.

The success of extracting the value added products varies greatly due to the inherent material characteristics of the red mud. As much as 83% alumina recovery is

attained after processing is complete. Iron extraction is not successful due to the failure of magnetic separation. Because titanium extraction employs such reactive processes, it is contingent upon the separation of iron out of the existing red mud. Thus titanium extraction proves to be unsuccessful. The exposure of the reduced iron to leaching and washing in the modified simultaneous sintering and reduction sequence induces a passivating oxide layer to form on the iron, spoiling the effects of full reduction. Thus the separate sintering and reduction sequence is the only viable route.

Other results generated that provide additional insight into the behavior and characteristics of red mud are the following. Sodium content decreases by the process of washing. Cadmium is eliminated during reduction while zinc is not. Leaching the red mud does not take iron, titanium or calcium into solution. Radioactive elements such as uranium and thorium exist in the red mud at 2.0 and 0.85 PPM and increase with further processing to as high as 4.7 and 8.5 PPM respectively. The red mud, prior to processing, exhibits unusual magnetic characteristics possibly caused by either inherent particle size or aluminum solubility in iron. The reduced iron in the red mud converts back to an oxide after a period of time.

Due to the inability to extract two out of the three constituents from red mud, some alternative routes for utilization are suggested. These suggestions include selling the red mud after alumina extraction and iron reduction to a blast furnace operation to use as feed for iron making, smelting the red mud after reduction to recover pig iron and a titanium rich slag followed by extraction of titanium from the slag and finally using titanium enriched red mud as feed for ferro-titanium production.

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1
INTRODUCTION

The pyrochemical extraction of alumina from bauxite leaves behind a process waste called red mud. The intent of this thesis is to determine the possibility of extracting various value added products from red mud produced from North Coast Jamaican bauxite as well as to determine the sequence of extraction. Throughout history, the volume and toxicity of industrial wastes have invariably compromised the payoffs from ore processing. Today, the impediments imposed from these wastes have a more deleterious impact on our society due to the growth of population. This circumstance necessitates paralleled efforts in rationalizing innovative proposals to alleviate the waste disposal problem. The aluminum industry plays a significant role in waste disposal issues through the production of red mud at the front end of the aluminum production process. This study hopes to contribute to the development of utilization of red mud by examining the plausibility of extracting its various compounds and subsequently reducing the amount of waste produced. Presented below is a statement of the problem given, the objectives and scope of this thesis and an introduction into the methods employed.

1.1 STATEMENT OF THE PROBLEM

Red mud is a by-product of alkaline processing of bauxite to produce alumina. It is a conglomerate of about 12% aluminum oxide, 68% iron oxide, 7% titanium oxide, 6% calcium oxide, 3% silicon oxide and other trace elements as the balance. The high amounts of aluminum oxide, iron oxide and titanium oxide make red mud attractive for metal recovery. Aside from this potential use, red mud exhibits several debilitating effects from its existence. For every ton of alumina produced, 0.5-2 tons of red mud are also discarded residing in huge 50-70 acre ponds across the world (1, 2). The ponds cause several problems such as the inability to be revegetated, potential threat to the local water supply, consumption of valuable farm land and high cost in maintenance. Because of this, the aluminum industry has taken an active interest in the eradication of this waste product through metal recovery.

1.2 OBJECTIVES AND SCOPE OF THE THESIS

The objective of this study is to investigate the possibility of utilizing red mud through the extraction of alumina, iron and titanium oxide as well as to determine the sequence of extraction. During investigation other objectives have come into play. These objectives include identifying important intrinsic characteristics of the red mud and recommending some potentially commercial applications for the products resulting from prior processing. The scope of this thesis entails a review of several references encompassing a wide spectrum of knowledge pertaining to red mud including past documentation about extraction, a theoretical analysis describing the methods implemented for extraction, results from experiments performed, discussion of these results and suggestions for further exploitation of the subsequent product. The following section provides a more detailed introduction into this study.

1.3 RED MUD PROCESSING

Red mud, also known as spent bauxite, in the past was identified as a waste product subject only to disposal. However, today, increasing problems with waste storage combined with more sophisticated technology and composition of red mud makes it a candidate for exploitation. Efficiently removing alumina, iron and titanium oxide from the mud while simultaneously reducing the amount of waste generated could prove to be a profitable venture for the aluminum industry.

The removal of alumina, iron and titanium oxide from red mud can be approached in a number of different ways. The composition of bauxite varies widely around the world and requires different conditions in the Bayer process for successful alumina extraction. After processing, these different bauxites result in varying red mud compositions. The red mud used in this research is a by-product of processing North Coast Jamaican bauxite. Investigators such as the U.S. Bureau of Mines have examined the extraction of these three constituents from Jamaican red mud (3). An approach very closely related to this research is presented here. The extraction of alumina entails combining the mud with sodium carbonate at high temperatures to form sodium aluminate, known as sintering. The sodium aluminate is then dissolved in caustic solution and washed to recover the alumina. The extraction of iron begins by fully reducing the iron oxide to produce a ferromagnetic iron. This step is followed by a magnetic separation of the iron from the remaining red mud constituents. If it is determined that the recovery of iron is low, the magnetic product is smelted to produce pig iron. The extraction of titanium oxide can be performed a number of different ways. One method utilizes carbo-chlorination of the titanium oxide if it is in the form of rutile. The red mud is exposed to chlorine and carbon at high temperatures to produce unpolluted titanium tetrachloride and carbon dioxide. The titanium tetra-chloride is then either utilized in various applications or further prepared to produce pure titanium metal through the Kroll process. If the titanium oxide is in the form of perovskite, another method suggests converting the perovskite to rutile via sulfation to produce a material suitable for commercial use. Titanium oxide extraction does promote other major reactions to occur and thus should only be performed after the other constituents are removed. This last statement suggests the sequence of removal of the value added products is a vital issue for success in extraction. Two sequences are thoroughly investigated known as the modified simultaneous sintering and reduction sequence and the separate sintering and reduction sequence. The modified simultaneous sintering and reduction sequence dries the red mud and simultaneously sinters and reduces it. The mud is then leached and washed to remove alumina and magnetically separated. The magnetic product is evaluated for iron content and smelted, if necessary, to produce pig iron. The non-magnetic product is processed to recover titanium oxide. The separate sintering and reduction sequence dries the red mud, sinters it, then leaches and washes to remove the alumina. Afterwards, the mud is reduced and then magnetically separated and smelted, if necessary, to recover iron. The remaining non-magnetic portion of the separation is processed to recover titanium oxide. It should be noted that the removal of alumina, iron and titanium oxide leaves behind a material very similar in composition to Portland cement, providing an avenue for complete utilization of red mud.

The extraction processes mentioned above demonstrate potentiality using well-established technology. The processes succeed in both obtaining usable products from the red mud while concurrently reducing the amount of waste produced. However, it should be noted that red mud, a composite of minerals originally contained in the ore bauxite and then exposed to the Bayer process does not need to abide by the normal behavior of uncontaminated compounds. The red mud will most likely and with no surprise behave with some degree of unpredictability.

2
BACKGROUND AND LITERATURE REVIEW

A background regarding the origin of red mud is provided to help understand its unique behavior. A literature review is prepared to establish a rational foundation for the actions performed in this thesis.

2.1 BACKGROUND

The origin of red mud is associated with the production of alumina, by alkaline extraction from bauxite ore. Bauxite, an ore rich in aluminum hydroxides, is mined from the earth. The ore is taken to a Bayer processing plant where alumina is produced along with red mud as a waste product. Alumina is primarily used for the production of aluminum metal where it undergoes fused salt electrolysis depositing aluminum metal on the cathode (4). Meanwhile, the red mud is transported to ponds where solids are allowed to settle out and spent liquor is recycled back into the Bayer process. Below is a more detailed account describing the origin of red mud beginning with the mining of bauxite.

Bauxite, the primary ore used to produce alumina, is actually a mineral known as laterite. Laterite is a mineral created from the longtime weathering of dolerite and granite. When laterite contains over 27% aluminum oxides it is known as bauxite (5). Bauxite consists of three different aluminum hydroxides; gibbsite, boehmite and diaspore. These three hydroxides differ in several different ways including crystal structure and specific gravity. However, most importantly, they differ in temperature of rapid dehydration and solubility in NaOH. Gibbsite is the first to dehydrate at 150°C, while boehmite and diaspore dehydrate at 350°C and 450°C respectively. The solubility of gibbsite in a 100g/l of NaOH solution is 128g/l Al_2O_3 while boehmite's solubility is 54g/l Al_2O_3 and diaspore is considered insoluble in some cases (6). Each bauxite is unique in composition. North Coast Jamaican bauxite, the mined material processed at Kaiser Gramercy via a high temperature/pressure Bayer process producing the red mud analyzed in this thesis, is comprised of the compounds represented in Table 2.1, as dried and analyzed at the Colorado School of Mines.

Table 2.1 Composition of Dried North Coast Jamaican Bauxite

Compound	%	Compound	%
Al_2O_3	56.4	TiO_2	4.3
SiO_2	0.7	CaO	1.2
Fe_2O_3	35.1	P, S, Cr, Mn, Zn, Cd	2.3

On average, bauxite contains 45% available alumina and 1.5% reactive silica (7). Jamaican bauxite consists primarily of gibbsite with small amounts of boehmite. Bauxite is mainly found in areas such as Jamaica, Surinam, Ghana, Sierra Leone, Australia, Russia and Hungary (6). It is primarily mined at open cut mines (5). After being crushed, the ore is shipped over to the plant for processing.

The Bayer process is the process of extracting alumina from bauxite. The crushed bauxite is digested using a powerful solution of high temperature sodium hydroxide. A multitude of constituents in the bauxite remain insoluble during this digestion. The insoluble material is what is known as red mud. Through decantation and filtration, the red mud is separated and placed in ponds. Meanwhile, the alumina, because of its inherent amphoteric characteristics, behaves like an acid in the strongly alkaline sodium hydroxide solution and forms soluble sodium aluminate. The solution of sodium aluminate grows supersaturated by cooling and is seeded with aluminum hydroxide crystals to precipitate out the hydrated alumina. The hydrated alumina is separated from the spent liquor, washed and calcined to alumina. The spent liquor is recycled back into the process (2). During digestion, other constituents are supplemented for added efficiency to the process. One such constituent is calcium oxide. The calcium oxide helps to tie up the reactive silica so as to prevent the silica from reacting with the alumina to form insoluble aluminosilicates. Otherwise the aluminosilicates precipitate out in the red mud creating substantial alumina as well as sodium hydroxide losses. It is also used to control P_2O_5 content and TiO_2 interference by converting the TiO_2 to perovskite ($CaTiO_3$). In addition, the calcium oxide improves yield by weakening the aluminous goethite lattice and improves mud settling characteristics by converting iron goethite to hematite. The calcium oxide also helps to react the Na_2CO_3 formed during CO_2(g) absorption back into sodium hydroxide (6).

The red mud, after being filtered, thickened and washed is ready to be disposed. The mud is transferred to huge 50-70 acre ponds. Here, the mud settles out by gravity and the supernatant liquor is recycled back into the Bayer process. The red mud consists of the following oxides as dried and determined at the Colorado School of Mines.

Table 2.2 Composition of Dried Red Mud Produced from North Coast Jamaican Bauxite

Compound	%	Compound	%
Fe_2O_3	67.7	CaO	6.6
Al_2O_3	11.7	SiO_2	2.5
TiO_2	7.1	Na, P, S, Cr, Mn, Zn, Cd	4.4

Both the environment as well as industry are adversely affected by red mud. Due to its composition, the red mud is an attractive material for metal recovery. Using the above red mud composition as an example for calculations, if the alumina industry produces 40 million tons of red mud a year (1), the industry can potentially recover 27 million tons of Fe_2O_3, 2.8 million tons of TiO_2 and 4.7 million tons of Al_2O_3 if such metal retrieval processes are effective. Red mud poses an economical incentive for potential metal recovery.

2.2 LITERATURE REVIEW

A literature review is prepared to provide a logical basis for the work completed in this research effort. The review describes the various uses for red mud suggested by investigators. It also entails the results of metal recovery reported from previous research.

2.2.1 VARIOUS APPLICATIONS FOR RED MUD

The interest in reducing or eliminating red mud has grown substantially. As a result, several innovative solutions have been thought of to utilize the waste. Two solutions entail employing the red mud as a soil product or utilizing the red mud waste as an ingredient in industrial processes. A third solution suggests recovering value added products from the mud. A diagram of these various uses is given in Figure 2.1.

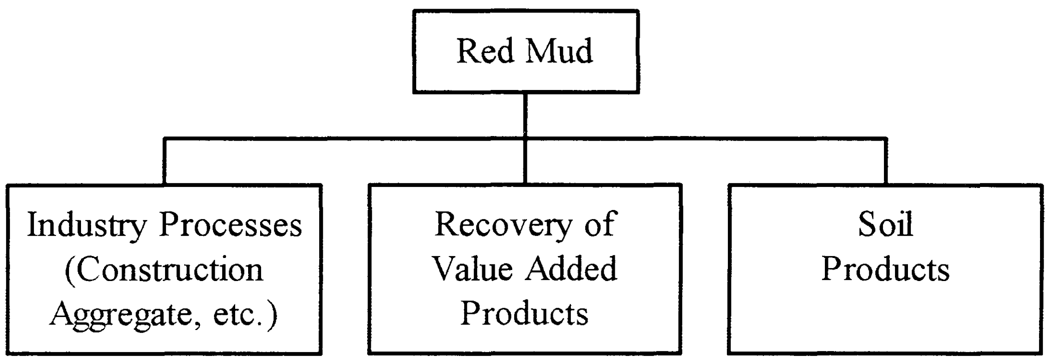

Figure 2.1 Diagram of the Various Uses for Red Mud

Below are examples of employing the red mud as a soil product or utilizing the red mud in industrial processes. This section is followed by various methods investigated in the extraction of value added products from red mud. Much of the research presented here is selected from a paper by L. Piga, F. Pochetti and L. Stoppa (1).

Reduction or utilization of red mud waste can be sought by processing on site. Dewatering and stacking reduce the red mud volume while revegetation utilizes the mud as a soil. By in situ evaporation, red mud is dewatered to 37% solids at a depth of 1.5m (1, 8). Improved dewatering is accomplished by vacuum or high pressure filtration yielding 47% solids (1, 9). This method reduces the volume of the red mud to a limited degree. Stacking methods, such as the production of thin layers of mud allowing for dehydration before the next layer is applied, even further reduce the red mud volume (1, 10). Revegetation is a natural solution implemented in several mine recovery projects. However, red mud is a more difficult material to revegetate because of its high salinity and alkalinity as well as its content of hostile constituents. A study to determine if red mud ponds are able to naturally revegetate concludes that even though grasses grow and remain for a couple of years and other plant species attempt to propagate on the red mud, the overall trend suggests that fewer species become commonplace as time passes (11). More recently, one study indicates that an addition of gypsum to the red mud would provide an adequate soil for the plants to grow and propagate (12). These solutions for red mud deal with on site disposal and are feasible possibilities if no other solutions are implemented.

Several other solutions exist involving the complete elimination of the red mud. Some researchers suggest using the red mud to make bricks. The resulting material, consisting of 90% red mud, exhibits light weight, low density characteristics (1, 13, 14, 15, 16). More than 50% red mud can be employed as an ingredient in tile production (1, 17). Red mud can also be used as a filler in rubber, or in thermohardening resins in flooring. This latter process uses up to 75% of the red mud (1, 18, 19). Others attempt to adopt it as a flocculant for treating wastewater. Similar to this, red mud can be used to remove toxic metals such as nickel ions (20). These two methods only utilize a small amount of red mud (1). These solutions use the mud as an ingredient in industrial processes. However, Piga, Pochetti and Stoppa report the conclusions from Chandler who suggests the following (1).

> ....despite the intensive research to find uses for red mud, its storage in dedicated areas continues because the building industry, the only one that could really effectively use these residues, utilizes cheaper raw materials.

> One reason other materials are cheaper is that brick or tile plants would have to be close to the alumina plant to ensure competitive costs.

Thus, research continues in the economical utilization of red mud.

2.2.2 REVIEW OF EXTRACTION POSSIBILITY

Substantial effort has been expended to recover metals from red mud. Several papers have been written and conveniently summarized again by Piga, Pochetti and Stoppa. These papers present various means of extracting iron, aluminum and/or titanium from red mud relevant to this thesis. Some of these papers are discussed below.

Considerable work has been completed on the independent beneficiation of iron, aluminum and titanium. The extraction of iron, the main constituent in red mud, is the focus of several papers. One investigator suggests separating the red mud (in slurry form) using high intensity magnetic separation. The resulting magnetic product can be used as an ingredient for iron making or as a pigment for pottery making. The non-magnetic portion can be applied in building materials or supplemented back into the Bayer process. Recovery of the iron is low (1, 21). Another investigator reduces the iron with chlorocarbons before magnetic separation and uses the resulting magnetic portion as feed for iron making (1, 22). A team of researchers known as McDowell Wellman Engineering Co. at Dwight-Lloyd research center has developed a process to convert the mud into steel. The research suggests drying the red mud, blending with lime and ground coal and feeding the mixture into a machine which agglomerates it into ½ in. diameter balls. After, the balls are prereduced at high temperatures in a circular grate. The balls are then fed into a submerged-arc electric furnace for smelting and transported to a BOF where the high quality steel is produced. The final product yields about 98-99% iron (23). Another process entails mixing the red mud with $Fe_2(SO_4)_3$. This solution removes the sodium from the mud leaving behind material eligible for iron making (1, 24). Simultaneous recovery of aluminum and sodium is performed by mixing the red mud with a solution of caustic soda and lime at 300°C at pressures of 4-9MPa. This solution is supplemented into the Bayer process for increased alumina recovery (1, 25). One approach utilizes the amphoteric characteristics of aluminum by extracting it via treatment with sulfuric acid. It also attempts to extract the aluminum through biological leaching using sewage sludge bacteria (26). Another process that emphasizes titanium recovery, converts the red mud into sodium-aluminum fluoride compounds. The red mud is mixed with HCl and hydrofluoric acid to obtain silicic acid which is then separated out. Evaporation leaves behind a material close to that of cryolite. The remaining material is mixed with the residual liquor which dissolves the iron and aluminum. The titanium rich solid remaining can be further processed via chlorination (1, 27).

Synchronous recovery of aluminum, iron and titanium is investigated by a number of researchers. One method utilizes chlorination combined with fractional distillation to extract iron and titanium from red mud. The red mud can be leached prior to this to retrieve aluminum (1, 28). The U.S. Bureau of Mines has performed a more extensive investigation into the extraction possibility of red mud. Briefly, red mud, carbon, lime and sodium carbonate are mixed, dried, ground and then simultaneously sintered and reduced at various times and temperatures. The mixture is then ground and leached with water at 65°C for 1 hour. After leaching, the blend is washed and magnetically separated in a Davis tube leaving both a magnetic and non-magnetic compound. The non-magnetic portion is either discarded or acid-treated to produce titanium oxide while the magnetic portion is inserted into an induction furnace for smelting. Favorable conditions for the recovery of iron and alumina from the simultaneous sintering and reduction tests include 1.5 hours at 900°C with a Na_2CO_3 to Al_2O_3 ratio of 1.45, a ratio of CaO to TiO_2 of 1.75 and a carbon addition slightly excess of stoichiometry. These conditions produce an alumina recovery of approximately 87% and an iron recovery of 78% based on initial starting composition. The results from the induction furnace experiment indicate that iron recovery reaches 95.5% of the magnetic portion before heating to 1480°C suggesting almost full reduction. The principal components after smelting include alpha iron, austenite and $CaTiO_3$. This paper offers a feasible route for the extraction of iron and alumina. However, because of its low grade even after several processing steps, titanium oxide proves not to be an option for extraction (3).

These experiments provide a basis for further investigation. Part of this thesis is a confirmation and extension of the results presented in the U.S. Bureau of Mines article (3) by means of attempting to reproduce and further some of these experiments and explain the data as well as determine the optimum sequence for extraction based upon the knowledge gathered.

3
THEORETICAL CONSIDERATIONS

Before any attempt at extraction is commenced, careful consideration is made into the nature and sequence of extraction. Below is a detailed analysis of the means of extraction of alumina, iron, titanium oxide and other compounds of interest. This analysis is followed by a summary of the sequences of extraction that are implemented.

3.1 EXTRACTION PROCESSES

The goal of extraction is to selectively remove the constituent of interest while avoiding the removal of other constituents and minimizing interference with any subsequent extractions all the while satisfying the issues of cost and feasibility. The limits dispatched from interested parties, equipment available as well as materials accessible and allowable for use should be considered. More importantly, the production of waste should be minimized so as not to defeat the purpose for this research. A thermodynamic analysis on the proposed methods of extraction is presented. All of the thermodynamic values and calculations are provided by the software package HSC manufactured by Outokumpu Research Oy.

3.1.1 EXTRACTION OF ALUMINA

Alumina continues to be a significant constituent in red mud even after being exposed to pressure extraction operations in the Bayer process. After the Bayer process, the alumina present in the mud constitutes several different forms. Some of these forms, such as boehmite, are suitable for direct leaching while other forms, such as Bayer sodalite, are not. Because each of these forms may or may not be accepting to one type of extraction process over another, the most appropriate method for extraction is to first convert these various forms into one product and then leach that product from the red mud. A more detailed account of this procedure is presented below.

The removal of alumina from red mud includes converting the alumina into sodium aluminate and then leaching the aluminate out of the mud. First, a sintering step is performed which includes reacting sodium carbonate with alumina at high temperatures to produce sodium aluminate. Sodium carbonate is an abundant, inexpensive material suitable as a reactant. The reaction, assuming the general form of alumina, is as follows.

$$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2(g) \qquad [3.1]$$

This reaction proceeds at temperatures greater than 662°C. Recommended sinter temperatures are 850°C and above (3). After sintering is accomplished, the next step is to remove the sodium aluminate. This step is accomplished by leaching. The U.S. Bureau of Mines suggests leaching the sintered product in water (3). However, Kaiser Aluminum recommends using a weak sodium hydroxide solution for leaching. The hydroxide acts as a stabilizer, keeping the aluminate in solution even at room temperature. The concentration of this solution is 5g/l NaOH and the recommended ratio of alumina to caustic (Na_2O) in the leach solution is 0.6 including sodium from the sinter process. The temperature and time recommended by Kaiser Aluminum is 65°C for 1.5 hours, sustaining constant agitation. The reaction for this process is as follows.

$$NaAlO_2(s) = NaAlO_2(aq) \quad [3.2]$$

The equilibrium constant for the reaction at 65°C is $2.13*10^3$, a value signifying the reaction proceeds to the right. A simple wash with distilled water is implemented to further enhance recovery and participate in sodium recovery discussed subsequently. During sintering, other constituents such as TiO_2, SiO_2 and Fe_2O_3 all theoretically react with sodium carbonate to a varying degree. It is not known what products may form. These possible side reactions (particularly with SiO_2) can potentially consume the sodium carbonate so as to decrease its activity and ability to react with alumina. To account for this potential sodium carbonate loss, excess sodium carbonate is supplemented to the sinter mix. Also, after sintering, some products may form that might be soluble in the sodium hydroxide solution consequently decreasing alumina solubility. Thus, a measurement of the quantity of various constituents in the post-leach liquor is taken to determine if this is indeed the case.

3.1.2 EXTRACTION OF IRON

After being filtered out of the Bayer process, iron oxide is considered to be the principal constituent contained within red mud. The forms of iron oxide in the red mud are known to be hematite, maghemite (metastable form of hematite) and goethite. For this analysis the main form of iron oxide is assumed to be hematite because between 350°C and 390°C the goethite readily forms hematite via loss of its OH groups (29). The extraction of iron oxide from the red mud can be handled in a variety of ways. However, considering the equipment and material available as well as cost incurred and research performed, a pyrometallurgical approach is recommended. This approach entails converting the iron oxide into iron. The iron, now a ferromagnetic is easily separated from the remaining red mud constituents via magnetic separation. If the percent iron recovery in the magnetic product is sufficient, the iron product is ready for sale. However, if recovery is not complete, the iron undergoes final separation via smelting. The product is then sold as pig iron.

Theory proposes that iron oxide is converted into iron in a reducing atmosphere. A proposed direct reduction is the reaction of choice. However, direct reduction can only take place exclusively if once carbon monoxide is formed, it is immediately flushed away. It is dubious if indirect reduction can be completely prevented (30). Thus, both direct and indirect reduction occur. Some of the carbon reacts to form the following, noting the approximate temperatures at which the product is stable.

$$C + O_2(g) = CO_2(g) \quad \text{below } 700°C \qquad [3.3]$$

$$C + \tfrac{1}{2}\, O_2(g) = CO(g) \quad \text{above } 700°C \qquad [3.4]$$

The carbon dioxide in equation 3.3 reacts with more carbon to form carbon monoxide above 700°C.

$$CO_2(g) + C = 2CO(g) \qquad [3.5]$$

The principal reactants for iron reduction are carbon and carbon monoxide. The partially direct/indirect reactions are as follows.

$$Fe_2O_3 + CO(g) = 2FeO + CO_2(g) \qquad \text{indirect} \qquad [3.6]$$

$$2FeO + C = 2Fe + CO_2(g) \qquad \text{direct} \qquad [3.7]$$

$$CO_2(g) + C = 2CO(g) \qquad [3.8]$$

By combining these three equations, a final direct/indirect reaction is reached which is used for stoichiometric calculations.

$$Fe_2O_3 + 2C = 2Fe + CO(g) + CO_2(g) \qquad [3.9]$$

This reaction is stable at 622°C. Suggested reduction temperatures are 850°C or above (3). The mechanisms behind these reactions are as follows. Carbon reacts with oxygen to form carbon dioxide. As temperature increases, carbon dioxide reacts with carbon to form carbon monoxide and carbon and oxygen also react to form carbon monoxide. The carbon monoxide reacts with hematite to form magnetite which reacts to form wüstite. The wüstite can now, being the outer most layer on the iron oxide particle and most susceptible to contact with carbon, be directly reduced to form iron. To aid in maintaining a reducing atmosphere, the red mud mixture is coated with a layer of CaO. As mentioned previously, the interference of other elements with the reduction process should be avoided. Using carbon as the reductant, the following information about the reduction of other oxides contained in the red mud is determined. Manganese, chromium, silicon, zinc titanium and sodium oxides do not participate in reduction until at least 1100°C. Aluminum and calcium oxides are unable to be reduced with carbon at sensible temperatures. Cadmium and phosphorus oxides are theoretically reduced below 1000°C. Consequently, the only real uncertainty lies with the last two oxides mentioned. Fortunately, these oxides do not exist in large amounts and should not significantly detract from carbon activity. The iron product is predicted to be ferrite, a ferromagnetic material susceptible to magnetic separation. Therefore, after a reduction is successfully completed a magnetic separation is performed. The magnetic product should consist primarily of iron. The iron product is now evaluated for recovery by comparing its composition to direct reduced iron (DRI). If comparable, the iron is a competitive material for steel making. The composition of DRI is given in Table 3.1.

Table 3.1 Composition of Direct Reduced Iron (DRI)

Product	Weight %
Total Iron	85.50
SiO_2	2.90
Al_2O_3	1.10
CaO + MgO	0.04
Others	9.96
TiO_2	0.50

If iron recovery is not comparable with DRI then smelting is the path chosen. Identification of the constituents within the magnetic sample is made, after which smelting takes place above 1450°C adding appropriate amounts of carbon and CaO to create a reducing atmosphere and basic slag. After cooling, the iron is sold as pig iron. Pig iron consists of 3-4.5% carbon, 0.15-2.5% manganese, up to 0.2% sulfur, 0.025-2.5% phosphorus and 0.5-4% silicon, iron being the balance (31).

3.1.3 EXTRACTION OF TITANIUM OXIDE

Red mud contains some titanium oxide that could serve as a value added product if extracted economically. The form of titanium oxide is anatase, originating in the bauxite ore, and/or perovskite(3,32). Perovskite is formed during the Bayer process through the addition of calcium oxide. These different forms of titanium oxide call for different methods of extraction. These methods employ reactive species. Thus it is recommended and assumed that both alumina and iron are removed prior to titanium oxide extraction. In both instances, it is not known what the residual compounds in the red mud after iron and alumina extraction will do to the success or failure of titanium oxide extraction.

If titanium oxide is in the form of anatase, carbo-chlorination is implemented. This method reacts titanium oxide with carbon and chlorine gas at approximately 900°C to form titanium tetrachloride and carbon dioxide gas (33). The reaction is presented below.

$$TiO_2(s) + C(s) + 2Cl_2(g) = TiCl_4 + CO_2(g) \qquad [3.10]$$

The titanium tetrachloride is then fed into a Kroll processing facility to produce pure titanium metal. The reaction is as follows.

$$TiCl_4(g) + 2Mg = Ti(s) + 2MgCl_2 \qquad [3.11]$$

This reaction takes place between 950°C and 1150°C (33). Because calcium can react with chlorine gas forming calcium chloride, perovskite is not able to be carbo-chlorinated.

If the form of titanium oxide is decidedly perovskite, the U.S. Bureau of Mines suggests converting the perovskite to rutile. Briefly, this entails the following. The red mud undergoes sulfation to convert the perovskite and other elements to strong acid insoluble sulfates. The reaction is presented below.

$$CaTiO_3 + 3H_2SO_4 = CaSO_4 + Ti(SO_4)_2 + 3H_2O \quad [3.12]$$

Next, the residue is leached with water to separate the insoluble $CaSO_4$ and unreacted perovskite. The pregnant solution is mixed with sulfuric acid again to precipitate out $TiOSO_4{:}H_2O$. Subsequently, the precipitate is dissolved in solution in preparation for hydrolysis. The solution is seeded and heated to precipitate out TiO_2. The pigment is washed and bleached to produce high purity TiO_2 applicable for commercial use (34).

3.1.4 EXTRACTION OF OTHER ELEMENTS

The mechanisms for removal of sodium, zinc and cadmium through the physicochemical processes already mentioned are as follows.

Sodium removal from red mud is achieved through washing performed during alumina extraction. The washing step is designed to primarily lower the sodium in the sintered and leached product since sodium interferes with subsequent processing. However, as sodium is removed, alumina is also recovered. Sources of sodium include residuals from the Bayer process, and sintering and leaching from red mud processing. Sodium removal is as follows.

$$NaAlO_2(s) = NaAlO_2(aq) \quad [3.13a]$$

$$Na_2O + H_2O = 2NaOH(aq) \quad [3.13b]$$

These reactions proceed at room temperature, but a washing temperature of 100°C is recommended.

The origins of zinc and cadmium stem back to the bauxite ore. Both of these constituents are assumed to be in oxide form and can be reduced with carbon. The zinc oxide is reduced with carbon which is thermodynamically stable at 1194°C.

$$2ZnO + C = 2Zn + CO_2(g) \qquad [3.14]$$

The zinc metal is vaporized. This reaction is stable at an even lower temperature of 906°C.

$$Zn(s) = Zn(g) \qquad [3.15]$$

Similar reactions are observed for cadmium oxide. Reduction with carbon is thermodynamically possible around 346°C. Vaporization is favorable at 766°C. The reactions are as follows.

$$2CdO + C = 2Cd + CO_2(g) \qquad [3.16]$$

$$Cd = Cd(g) \qquad [3.17]$$

These two constituents can be reduced with carbon and vaporized if the conditions are appropriate.

3.2 SEQUENCE OF EXTRACTION

Planning the sequence of extraction is a vital step in processing the red mud. If done properly, the right sequence can provide optimum, economical extraction of each constituent with minimal interaction between processes and low waste production. Several aspects are examined in choosing the correct path for extraction. These aspects begin to shape the sequence and only then will experiments proceed.

Two separate sequences, known as the simultaneous sintering and reduction sequence and the separate sintering and reduction sequence, are adopted in this thesis for the removal of alumina, iron and titanium oxide. The simultaneous sintering and reduction sequence encompasses the following. The red mud is first dried and simultaneously sintered and reduced. The product is then magnetically separated. The magnetic sample is evaluated for iron recovery. If the iron content is not adequate, the magnetic sample is smelted to recover pig iron and slag which is discarded. The non-magnetic sample is leached and washed to recover alumina. The residue from leaching is processed to recover titanium oxide. The waste from this process is then discarded in an appropriate manner. This sequence is summarized in Figure 3.1. The advantage of this process is the energy savings acquired by combining the sinter and reduction steps. The disadvantage is that the sintered and reduced product depend on magnetic separation to continue processing. Previous articles suggest that magnetic separation is not an entirely successful process (3,35). Thus, the simultaneous sintering and reduction sequence is modified to account for unsuccessful magnetic separation. Again, the red mud is dried and simultaneously sintered and reduced. The sintered and reduced material is then leached and washed to recover alumina. The residue left from leaching is either magnetically separated and processed for iron and titanium oxide recovery if such a step is possible or processed further. Further processing techniques depend on the resulting product and thus are discussed subsequent to experimental investigation. The modified simultaneous sintering and reduction sequence is seen in Figure 3.2. The advantages of this sequence include the same energy savings aforementioned, but also the sintered and reduced product do not depend on the success of magnetic separation to continue processing. Also, further processing is applicable if magnetic separation does not succeed. The disadvantage is the sintered and reduced product is exposed to the leaching process, possibly implementing an interaction between alumina and iron extraction. The separate sintering and reduction sequence entails the following. The sequence begins with drying and sintering the red mud. The red mud is leached and washed to recover alumina. After which the mud is reduced and magnetically separated or further processed. Upon magnetic separation, the magnetic product is evaluated for its iron and either smelted or left as is for commercial use. The non-magnetic product is processed to recover titanium oxide and the residue from this step is discarded. This sequence is presented in Figure 3.3. The advantages of this process include no initial dependence on magnetic separation. Also, the reduced product is not subject to leaching and washing. If magnetic separation is not successful, the product can be processed further. The disadvantage is the excess energy evoked upon separation of the sinter and reduction steps.

Both the modified simultaneous and the separate sintering and reduction sequences provide for optimum extraction of each element, minimum interaction between processes and low waste production. If alumina, iron and titanium oxide are successfully extracted, approximately 86.5% of the red mud is utilized not including the elimination of other constituents or the excess additions of reactants. The wastes from the modified simultaneous and separate sintering and reduction sequences fall into two categories including the slag from smelting and the residue left behind after titanium oxide extraction. These materials, now rich in calcium and silicon oxide, are comparable to Portland cement and can be processed to be used as such. This avenue completely utilizes the entire waste product known as red mud. Also note that "further processing" paths may consume the entire red mud product.

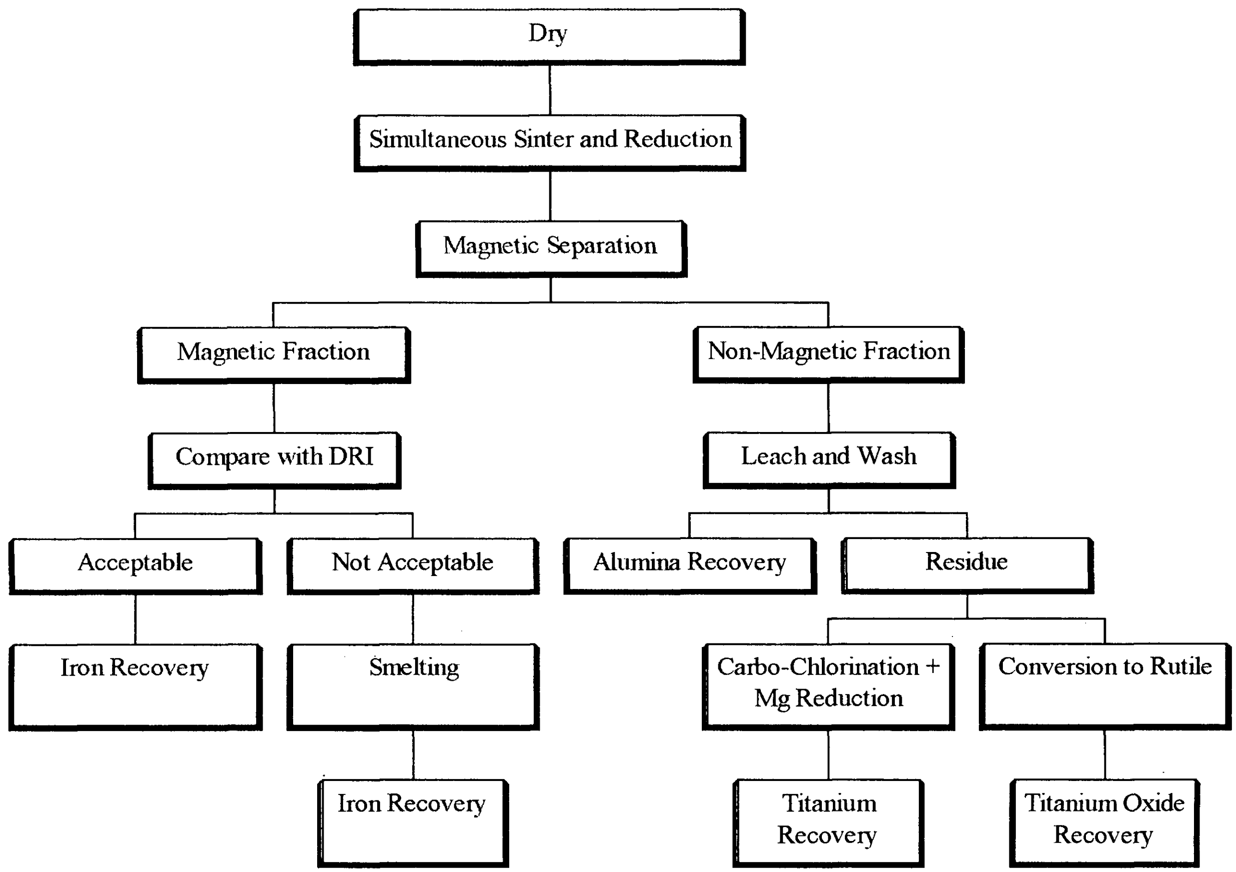

Figure 3.1 Diagram of the Simultaneous Sintering and Reduction Sequence Used to Extract Alumina, Iron and Titanium Oxide from Red Mud

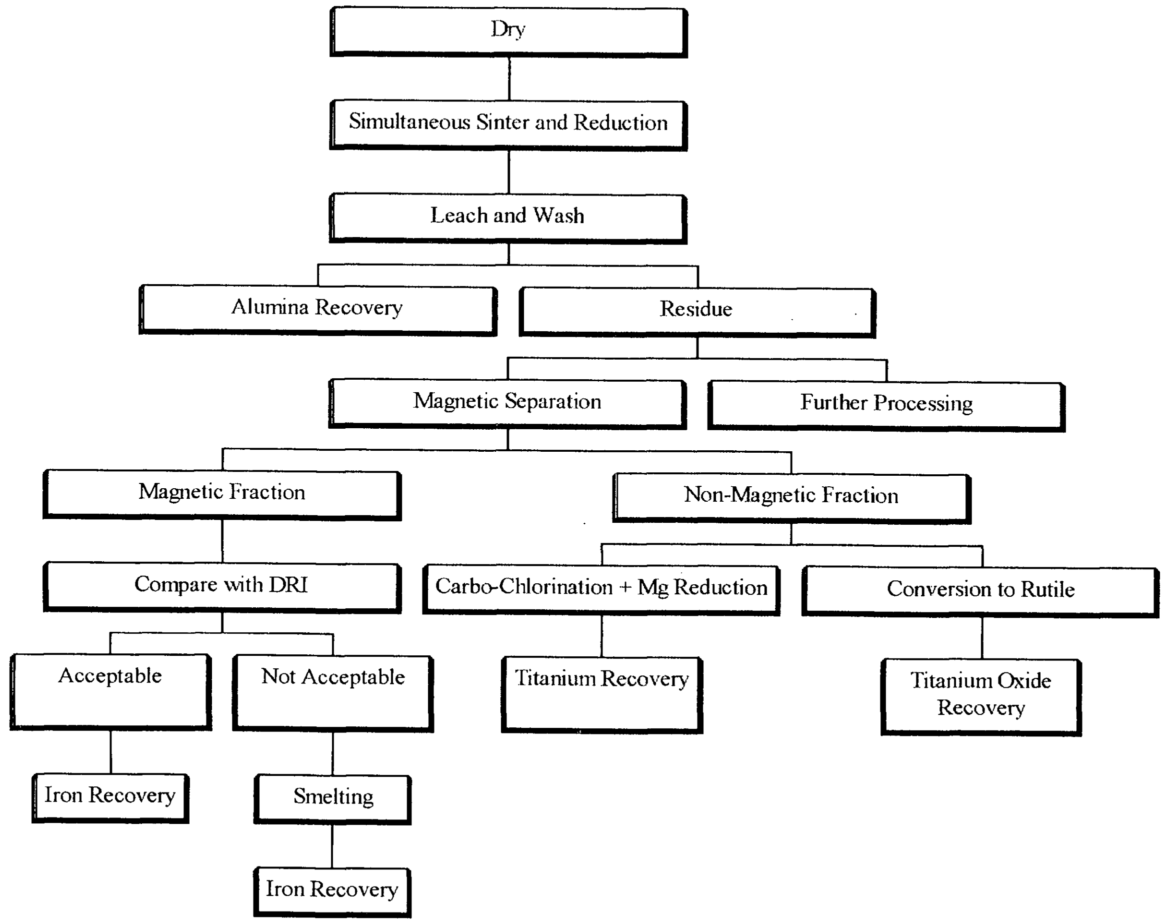

Figure 3.2 Diagram of the Modified Simultaneous Sintering and Reduction Sequence Used to Extract Alumina, Iron and Titanium Oxide from Red Mud

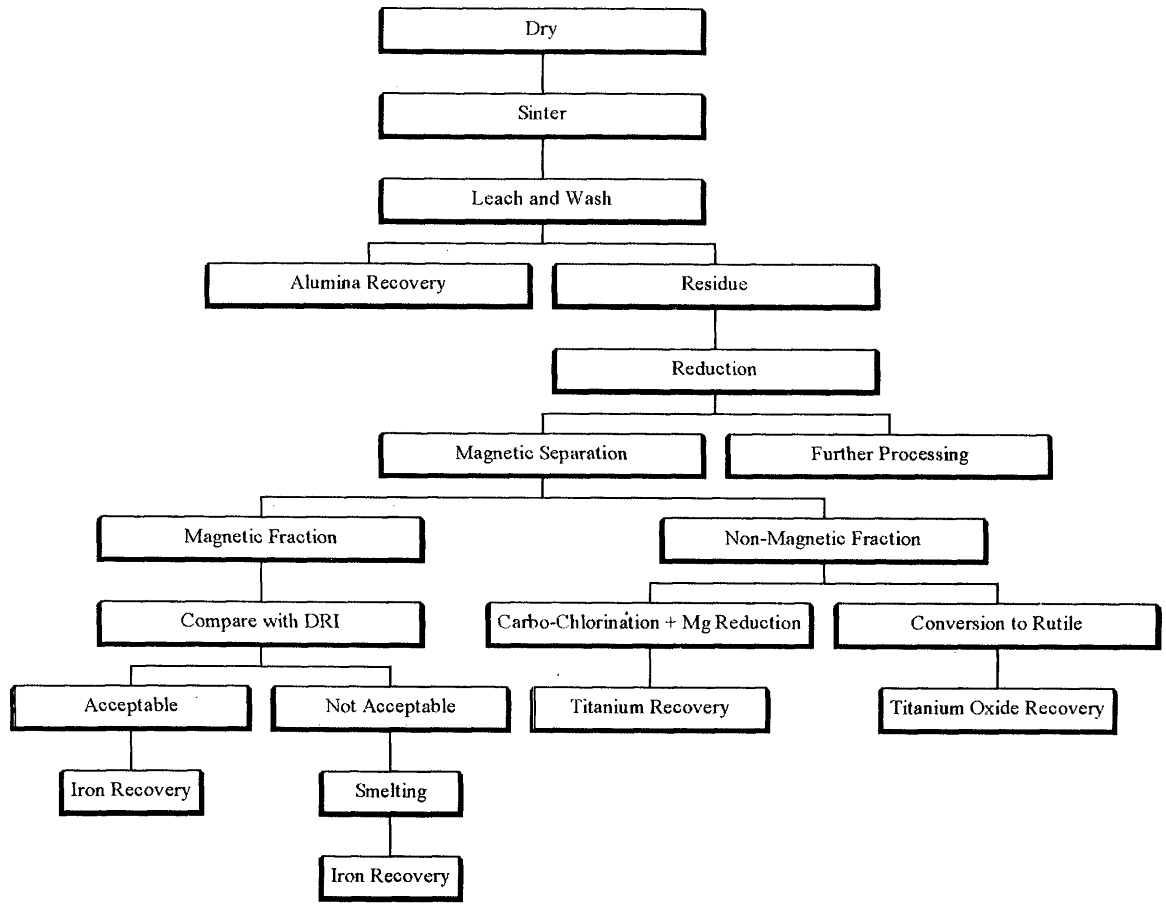

Figure 3.3 Diagram of the Separate Sintering and Reduction Sequence Used to Extract Alumina, Iron and Titanium Oxide from Red Mud

4
EXPERIMENTAL STUDIES

Several different experimental systems and procedures are necessary to extract the value added products from the red mud. Smelting, carbo-chlorination and conversion of perovskite to rutile are not performed in this thesis and therefore not described. These are proven commercial techniques except for the conversion of perovskite to rutile. The remaining experiments that are performed include drying, sintering, reducing, leaching, washing and magnetic separation. To evaluate the product from each experiment several different material characterization techniques are employed. Below is a brief description of the purpose of each experiment, equipment used, procedure followed and the results obtained. This description is followed by a list of equipment used for material characterization and the purpose each serves in analysis.

4.1 DRYING

The intent of a drying operation is to eliminate the moisture and some of the volatiles from the red mud. This procedure aids in subsequent handling of the red mud for further processing. All drying experiments are performed in a Model 56724 1700°C Crucible Furnace manufactured by Lindberg/Blue M (a General Signal Company). The furnace uses a type B thermocouple. A sample is weighed to a tenth of a gram, put into a MgO crucible, heated at 2°C/min up to 400°C for one to two hours maintaining a N_2

atmosphere at a 2-3 cubic feet per hour (CFH) flow rate (to protect the molybdenum disilicide heating coils) and then cooled at 2°/min. The red mud is then weighed. After drying, the red mud is ground and filtered to -70 mesh (212μm) to provide for improved contact between constituents in subsequent reactions.

4.2 SINTERING

The purpose of sintering is to react the sodium carbonate with alumina to form sodium aluminate. The equipment used is the Lindberg furnace mentioned above. The alumina content is determined using energy dispersive x-ray (EDX) analysis discussed subsequently. Using the predetermined alumina content combined with reaction 3.1 the amount of sodium carbonate is calculated. Depending on the experiment, the amount of sodium carbonate varies from stoichiometry to a maximum of 100% excess. Before insertion into the furnace, the red mud is ground using a Black & Decker coffee mill and filtered through -70 mesh sieve. The red mud is mixed with the appropriate amount of sodium carbonate which is also filtered through -70 mesh sieve for one to two minutes in a sealed plastic container. A measurement to a tenth of a gram is taken and the mixture is placed into an MgO crucible which is inserted into the furnace. The sample is heated at 2°C/min to the specified temperature for a length of time all the while maintaining an N_2 atmosphere with a flow rate of 4 CFH. The temperature of sintering ranges from 850°C to 1100°C. The time of sintering is 2 hours in all experiments. The sample is cooled at 2°/min and is again weighed and observations made.

4.3 REDUCTION

The goal of this process is to reduce the iron oxides to iron. Once again, the Lindberg furnace is used for these experiments. The amount of iron oxide contained in the red mud is determined using EDX analysis. Carbon content is calculated using the iron oxide content and the direct/indirect reaction, 3.9. Depending on the experiment performed, the amount of carbon ranges from 100% excess of stoichiometry to 300% excess. The form of carbon used for all of these experiments is petroleum coke. The red mud and coke are measured out and ground with a Black & Decker coffee mill and sieved to -70 mesh. The two constituents are vigorously mixed for one to two minutes in a sealed plastic container. The mixture is then placed in a MgO crucible. Depending on the experiment, a CaO powder layer is placed on top of the mixture after which a ceramic lid is situated on top of the crucible. The crucible is placed into the furnace and heated at 2°C/min up to the required temperature at which point it is held for a period of time and then cooled. A N_2 atmosphere is continuously run through the furnace at a flow rate of 3-4 CFH. The temperature of reduction ranges from 900°C to 1100°C and the time of reduction is 2 to 4 hours. Afterwards, the sample is cooled down at 2°/min and weighed. Observations are subsequently made.

4.4 SIMULTANEOUS SINTER AND REDUCTION

Certain experiments combine sintering and reduction depending on the sequence imposed. The red mud is combined with sodium carbonate and coke and mixed following the same procedures stated above. A few alterations may be imposed to the heating cycle for the combined process. Results are gathered including weight loss and observations.

4.5 LEACHING

The objective of leaching is to dissolve the sodium aluminate product into solution. The alumina can then be recovered by recycling the leachant back into the Bayer process or directly seeding to precipitate out the alumina. Prior to leaching a solution of sodium hydroxide is prepared using NaOH crystals and distilled water. The concentration of the solution is 5g/l NaOH (0.125M). The amount of alumina combined with Figure 4.1 on the following page specifies the amount of leaching solution required per kilogram of sintered and reduced red mud. This figure calculates the amount of caustic required for leaching by first determining the amount of sodium oxide contained in the mud from sintering (sodium carbonate) and subtracting that off the amount of caustic required based on alumina content. Using a set alumina to caustic ratio (A/C ratio) and concentration of leaching solution, the ratio of caustic to red mud product is attained. From that value, the amount of caustic required is calculated. A set A/C ratio of 0.6 is used for all experiments. Excess caustic ranging from 0-100% is used depending on the experiment. The caustic solution is heated on a hot plate and temperature is measured. Upon reaching 65°C the red mud is added to the solution. Throughout the experiment, the mixture is stirred with a mechanical stirrer containing a stainless steel impeller. A light is used to observe and correct for (by increasing the speed of the impeller) mud settling on the bottom of the beaker. The mixture is continuously stirred for 1.5 hours. Upon completion, the mud is filtered through a #3 filter separating the filtrate from the residue. The residue is collected, dried using the hot plate and weighed.

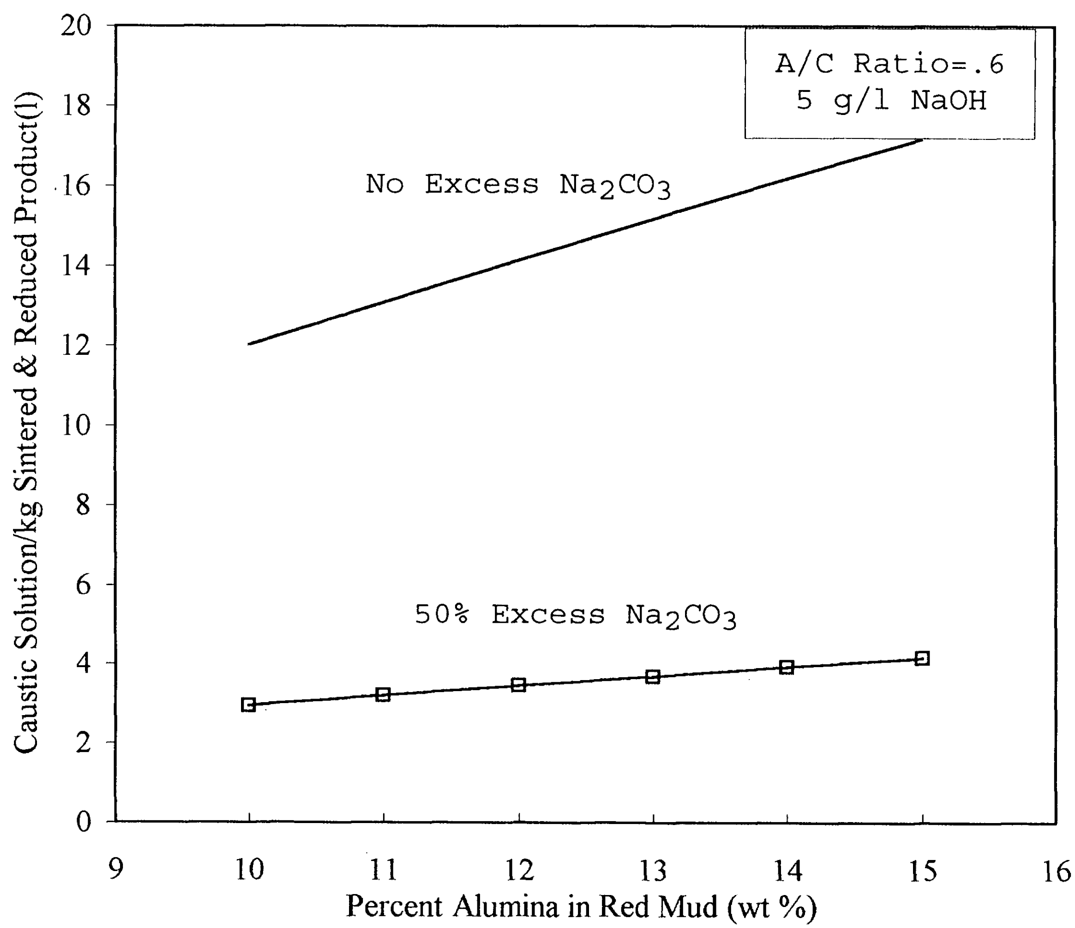

Figure 4.1 Requirement of Caustic Solution for Leaching Experiments Performed in the Extraction of Alumina from Red Mud

4.6 WASHING

After leaching, residual amounts of sodium remain in the red mud residue. A wash is performed to increase the alumina recovery as well as dissolve the sodium compounds. A sample of red mud is measured. Distilled water is placed into a beaker and heated to the set temperature. The temperature range for the experiments performed varies between 25 and 100°C. Depending on the experiment, a specified amount of red mud is added after the required temperature is reached. The ratio of red mud to distilled water varies between 2 and 50g/l. The mixture is stirred for a given amount of time making sure the red mud does not settle to the bottom. The time of washing varies between 5 and 30 minutes. The mud is then filtered through a number three filter. The residue is dried with the hot plate and weighed.

4.7 MAGNETIC SEPARATION

A magnetic separation is performed on the red mud to exclusively separate the iron from the remaining constituents. Two types of processes are imposed including wet and dry magnetic separation. For wet magnetic separation, the red mud is placed in distilled water. A magnet of a strength of at least 750 Gauss is put into a plastic bottle which is then inserted into the water. The magnetic material collects onto the plastic bottle and is removed from the water and placed in another beaker of distilled water. The magnet is removed from the plastic bottle after which the magnetic material drops to the bottom of the beaker. Both the magnetic and non-magnetic materials are dried. Dry magnetic separation is similar to wet separation, the only difference being the media is replaced with air. Weight measurements of both the magnetic and non-magnetic constituents are recorded. Material characterization is performed via EDX.

4.8 INSTRUMENTS USED FOR MATERIAL CHARACTERIZATION AND OTHER ANALYSIS

Material characterization is an essential part of data analysis. It is the act of defining each constituent and its amount or defining a certain constituent and its various phases. Various characterization steps are performed on twelve major components in the red mud including the following.

Table 4.1 List of Elements Analyzed During the Investigation into the Extraction of Alumina, Iron and Titanium Oxide from Red Mud

Element	Element
Sodium	Calcium
Aluminum	Titanium
Sulfur	Chromium
Phosphorus	Iron
Silicon	Cadmium
Zinc	Manganese

Much of material characterization is performed on the Scanning Electron Microscope (SEM) using the Energy Dispersive X-Ray (EDX) system for the actual characterization. Other material identification is performed on a Mössbauer instrument. XRD is also implemented for specific samples. Instruments used for other analysis include a thermo-gravimetric and differential thermal analyzer. This instrument is used primarily for inquiries into reduction.

4.8.1 EDX ANALYSIS

The EDX analysis identifies the elements mentioned above by measuring the characteristic x-rays emanating from the sample. The SEM used in conjunction with material characterization is a JEOL JXA-840 Scanning Microanalyzer. The EDX system is produced by Tracor Northern. Using a quantitative analysis known as ZAF, the weight percents of each element are calculated. The SEM is not capable of detecting elements below sodium. Indeed, even the weight percent of sodium is not a precise figure. Oxygen, an important constituent in the red mud, is not accounted for. Thus, using assumed oxide states, the weight percents of the compounds in the red mud are recalculated. This analysis is performed at various stages of processing. The assumed oxide states are based on the original analysis of the mud and imposed processing.

4.8.2 MÖSSBAUER SPECTROSCOPY

Mössbauer spectroscopy is a technique that provides vital information about iron processing. This information encompasses identification of various iron bearing constituents and the relative fraction of these constituents. The mechanisms of Mössbauer spectroscopy briefly entail the following. The Mössbauer effect is described as a recoilless absorption of gamma ray photons and re-emission of those photons. Specific nuclei in the sample move to and from excited energy states when exposed to a low energy gamma ray consisting of a range of photon frequencies including the exact frequency to excite the nuclei (to obtain a range of frequencies in the gamma ray, the source is accelerated back and forth causing a Doppler shift). As a consequence, those nuclei that absorbed the specific photons will re-emit the photons in a random direction depleting that photon frequency. The photons passing through the sample are detected as a function of the source velocity. At characteristic frequencies a decrease in detected photons occurs. All the frequencies are then accounted for and those which are depleted describe the resulting compounds contained within the sample. Each compound has its own characteristic absorption behavior due to the different chemical, magnetic and crystallographic state of iron atoms. By comparison to known compounds, this technique identifies the constituents in the red mud. More information on this subject is provided by Leopold May (36). Sample preparation includes pressing 5 milligrams of red mud ground to -270 mesh and 5 grams of powdered sugar into a flat pill. The analysis is performed in all stages of red mud processing. Certain compounds contained within the red mud and detected by the Mössbauer are presented in Table 4.2 along with a brief description of what they represent.

Table 4.2 Iron Compounds Detected in Red Mud During Mössbauer Characterization Before and After Processing

Compound	Description
Fe_2O_3	hematite, also described as magnetic Fe_2O_3; a canted anti-ferromagnetic which displays a very weak magnetic signal
Fe_3O_4	magnetite, magnetic
FeO	wüstite, non-magnetic
Fe	iron usually in the form of ferrite, ferromagnetic
Fe/Fe_3O_4	not able to decipher between Fe and Fe_3O_4
non-magnetic	iron constituent that displays non-magnetic characteristics; could be austenite
magnetic oxide	Fe_3O_4 or Fe_2O_3
Fe^{2+}	Iron depleted of two electrons; could be combined with other red mud constituents such as silicon; displays magnetic and non-magnetic characteristics

4.8.3 XRD ANALYSIS

Few samples are examined by XRD. Qualitative XRD serves to be of little or no use due to the ambiguousness of the XRD pattern. Quantitative XRD does prove to be of some importance in identifying various mineral constituents such as boehmite, hematite, goethite, etc. in the starting red mud composition. The results from this analysis have already been presented in the previous section.

4.8.4 TGA/DTA

Thermo-gravimetric analysis and differential thermal analysis (TGA/DTA) are used to observe weight loss and enthalpy behavior during reduction. The Netzsch simultaneous thermal analysis instrument (STA) 409C is employed to acquire TGA and DTA data. The TGA measures the change in mass of a sample during the heating cycle while the DTA simultaneously measures enthalpy. This instrument provides useful information about the reactions that occur upon heating the red mud to the specified reduction temperature. The red mud is measured out and mixed with the appropriate amount of carbon. Two tests are performed varying only the amount of carbon from 100% up to 200% excess of stoichiometry. The sample weight is approximately 45 milligrams. The machine is calibrated with a pure alumina sample exposed to the same heating cycle, after which the red mud carbon mixture is placed in the crucible and heated. The heating cycle consists of heating the sample at 20°/min from room temperature up to 1050°C and holding for five hours in an inert atmosphere of argon. During this time the instrument takes weight and enthalpy measurements and the data is plotted and subsequently evaluated.

5
EXPERIMENTAL RESULTS AND DISCUSSION

This section presents results gathered from the experiments performed on the extraction of alumina, iron and titanium oxide followed by a discussion of the optimum sequence for removal, other results gathered and options for furthering processing.

5.1 EXTRACTION OF ALUMINA, IRON AND TITANIUM OXIDE

The purpose of this thesis is to determine if the extraction of value added products is a feasible route for red mud exploitation. The theoretical considerations provide a means for extracting each constituent. However, this analysis does not fully determine the feasibility of this route. By evaluating the influences of the active variables involved in the extraction processes, the prospect of this route can be more completely resolved. The experiments on the extraction of alumina, iron and titanium oxide from red mud produced from North Coast Jamaican bauxite are performed consecutively following either the modified simultaneous or the separate sintering and reduction sequence. However, the results from these experiments are viewed individually allowing for examination and some optimization of each extraction process. Because of this approach, the results from these extraction processes do not always correspond with one another.

5.1.1 EXTRACTION OF ALUMINA

Alumina extraction is dependent on three processes including sintering, leaching and washing. Sintering transforms the alumina into sodium aluminate (Equation 3.1), leaching dissolves the aluminate into solution and washing dissolves the residual sodium aluminate. The success of these three steps ensures alumina extraction. Below is a discussion of the variables within each procedure, the results obtained from the experiments performed and some rationale for the data accumulated.

The variables within sintering, leaching and washing strongly influence the outcome of alumina extraction. Sintering depends on several factors including temperature, amount of sodium carbonate and sequence of removal. Temperature can increase the tendency of the reaction to occur by increasing its change in free energy. Amount of sodium carbonate can influence the amount of sodium aluminate formation. If the amount of sodium carbonate is not adequate, some of the available alumina is left unreacted. Sequence can influence the reactants added or the products formed during sintering which can affect the leaching process. Successful leaching depends on a number of variables. However, most of these variables remain constant. For example, concentration of sodium hydroxide solution, time for leaching, temperature of leaching and A/C ratio all remain constant. One factor that is altered is the volume of leach liquor supplemented to the leaching solution. This variable is altered because at higher volumes of leach liquor more sodium aluminate dissolution may occur. One other variable that affects leaching is the amount of calcium oxide added to the sinter (the modified simultaneous sintering and reduction sequence). Too much calcium oxide can potentially detract from sodium aluminate dissolution. Washing the residual sodium aluminate from the red mud is important step in improving alumina recovery. The washing conditions are kept constant at 100°C for 15 minutes using a ratio of 10g/l of red mud to distilled water, continuously stirred.

In the information that follows are results obtained from the experiments performed. A summarized table of significant results is presented in Appendix A. To focus on some of the key characteristics observed during experimentation, this table is divided into smaller tables presented below. To begin, experiments one, two and three demonstrate the effects of temperature on alumina extraction, all other conditions remaining the same, such as excess soda, time of sintering, etc.

Table 5.1 Influence of Temperature During Sintering on the Extraction of Alumina from Red Mud

	Sintering			Leaching			Washing
Exp.	Temp.	Excess Soda	Sequence	A/C Ratio	Excess Caustic	Recovery Al_2O_3	Recovery Al_2O_3
#	°C	%	sim./sep.	-	%	%	%
1	850	50	sep.	0.6	100	66.7	76.8
2	950	50	sep.	0.6	100	67.4	81.5
3	1050	50	sep.	0.6	100	69.6	83.1

*sim. = modified simultaneous sintering and reduction sequence
sep. = separate sintering and reduction sequence

Alumina extraction increases as temperature increases. At 850°C sodium aluminate does form, but not all of the alumina available for reaction is converted. At 1050°C more of the alumina available for reaction is reacted and extraction is increased. Temperature influences the results by increasing the driving force of the reaction. This result corresponds to the U.S. Bureau of Mines article (3). Alumina recovery subsequent to washing demonstrates the true extent of sodium aluminate formation. Experiments two and four illustrate the consequence of excess sodium carbonate, maintaining similar experimental conditions.

Table 5.2 Influence of the Amount of Sodium Carbonate During Sintering on the Extraction of Alumina from Red Mud

	Sintering			Leaching			Washing
Exp.	Temp.	Excess Soda	Sequence	A/C Ratio	Excess Caustic	Recovery Al_2O_3	Recovery Al_2O_3
#	°C	%	sim./sep.	-	%	%	%
4	950	0	sep.	0.6	100	62.7	66.2
2	950	50	sep.	0.6	100	67.4	81.5

*sim. = modified simultaneous sintering and reduction sequence
sep. = separate sintering and reduction sequence

As excess sodium carbonate is increased alumina extraction improves. Additional sodium carbonate, increases the opportunity for contact between red mud and sodium carbonate particles during sintering. This increased contact promotes more individual reactions to occur. It is not known what additional excess sodium carbonate will do to furthering alumina extraction, but it is assumed increasing sodium carbonate is only beneficial up to a point beyond which leaching is inhibited due to low amounts of liquor required for sodium aluminate dissolution. The U.S. Bureau of Mines also finds that increasing sodium carbonate improves alumina recovery (3). Experiments two and five demonstrate the effects of sequence on alumina extraction. Note that calcium oxide is not added to the mixture in the modified simultaneous sintering and reduction sequence. All other experimental conditions remain the same.

Table 5.3 Influence of the Modified Simultaneous Sintering and Reduction Sequence vs. the Separate Sintering and Reduction Sequence on the Extraction of Alumina from Red Mud

	Sintering			Leaching			Washing
Exp.	Temp.	Excess Soda	Sequence	A/C Ratio	Excess Caustic	Recovery Al_2O_3	Recovery Al_2O_3
#	°C	%	sim./sep.	-	%	%	%
5	950	50	sim.	0.6	100	66.9	75.3
2	950	50	sep.	0.6	100	67.4	81.5

*sim. = modified simultaneous sintering and reduction sequence
sep. = separate sintering and reduction sequence

The recovery of alumina fairs slightly better in the separate sintering and reduction sequence as oppose to the modified simultaneous sintering and reduction sequence. Possibly the carbon added in the modified simultaneous sintering and reduction sequence decreases the opportunity for contact between sodium carbonate and alumina. Experiments three and six compare the effects of excess caustic during leaching on alumina recovery, all other conditions being the same.

Table 5.4 Influence of Excess Caustic During Leaching on the Extraction of Alumina from Red Mud

	Sintering			Leaching			Washing
Exp.	Temp.	Excess Soda	Sequence	A/C Ratio	Excess Caustic	Recovery Al_2O_3	Recovery Al_2O_3
#	°C	%	sim./sep.	-	%	%	%
6	1050	50	sep.	0.6	0	59.9	76.0
3	1050	50	sep.	0.6	100	69.6	83.1

*sim. = modified simultaneous sintering and reduction sequence
sep. = separate sintering and reduction sequence

As excess caustic increases, alumina recovery also increases. The excess caustic provides more volume for the dissolution of the sodium aluminate. Because not all of the sodium aluminate is dissolved during leaching in experiment six, the washing conditions mentioned previously are not appropriate for complete dissolution of the remaining sodium aluminate. The alumina recovery from experiments five and seven differ greatly from each other. The conditions in both experiments are the same except for sinter temperature, excess caustic and calcium oxide addition (30g).

Table 5.5 Influence of a Calcium Oxide Addition on the Extraction of Alumina from Red Mud

	Sintering			Leaching			Washing
Exp.	Temp.	Excess Soda	Sequence	A/C Ratio	Excess Caustic	Recovery Al_2O_3	Recovery Al_2O_3
#	°C	%	sim./sep.	-	%	%	%
7	1050	50	sim.	0.6	150	32.5	48.7
5	950	50	sim.	0.6	100	66.9	75.3

*sim. = modified simultaneous sintering and reduction sequence
sep. = separate sintering and reduction sequence

Even though the conditions in experiment seven promote better alumina extraction, the experiment is subject to lower recovery because of the large presence of calcium oxide originating in the sintering and reduction process (the modified simultaneous sintering and reduction sequence). Too much calcium oxide interferes with leaching by reacting with dissolved alumina to form hindering insoluble products such as tricalcium aluminate hexahydrate ($Ca_3Al_2(OH)_{12}$). This substance is known to form when excess amounts of calcium oxide are added to hydroxide solution containing alumina (32). A decrease in alumina recovery through the excess addition of calcium oxide is also observed by the U.S. Bureau of Mines reporting a decline in alumina recovery after 4% addition of calcium oxide (3). Throughout all of the experiments, the observation of complete alumina extraction does not arise. This observation is possibly due to the availability of the alumina to react with the sodium carbonate and the kinetic limitations of the reaction. Some of alumina is not in a form that allows for sintering to occur. The results obtained in the experiments above do appear to be similar to what the U.S. Bureau of Mines has reported (3). However, the article does receive much higher alumina recovery from sinter and leaching. It is noted that the procedures indicated in the article grind the mixture of sintered and reduced product to -325 mesh before leaching while the current experiments grind the mixture to only -70 mesh. Increasing the surface area of the mixture should provide better results. However, even the finer particle size does not result in 100% alumina extraction.

Alumina recovery is dependent on a number of variables, most of which are altered to determine their effects on extraction. From the results it is concluded that **alumina extraction is a feasible process and its oxide can be successfully recovered to as much as 83% by the separate sintering and reduction sequence when sintering is conducted at 1050°C using 50% excess sodium carbonate and leaching is performed using 100% excess caustic followed by a wash**. A final thermodynamic analysis is performed on red mud during sintering using 50% excess sodium carbonate presented in Appendix B. This analysis describes the equilibrium products formed at various temperatures. The red mud now contains about 2% alumina and other oxides and elements such as iron, titanium, silicon, calcium, sodium, sulfur, phosphorus, manganese, chromium, zinc and cadmium.

5.1.2 EXTRACTION OF IRON

Recovering iron from the red mud is a complex process. A number of approaches can be sought and successfully achieved if performed properly. In this thesis, an approach involving three to four successive processes is chosen to recover iron. These processes include reducing the iron oxide to iron, magnetically separating the iron out of the red mud, evaluating the iron product for commercial use and smelting (if necessary) to recover iron as a value added product. Each of these steps depends on a number of variables, significantly altering the individual end products. All of these steps are covered in the both the modified simultaneous and separate sintering and reduction sequences, but in differing order. Below is a discussion of each of the steps taken for iron recovery in both sequences. Within each step is a brief analysis of the influential variables, the results produced from experiments performed and some explanation for these results.

5.1.2.1 REDUCTION

Several variables play a significant role in the reduction of iron oxide. These variables include carbon content, temperature, time, calcium oxide layer and sequence. Each of these variables performs differing roles either in completing reduction or aiding it. For example, the carbon content of the red mud mixture and temperature of reduction have to be sufficient to achieve full reduction. The time should be adequate to allow for equilibrium to be reached. Other variables also affect reduction including calcium oxide layer and simultaneous sintering. Maintaining a calcium oxide layer helps to trap the carbon monoxide formed in the reaction providing a protective, less oxidizing environment. Sequence can affect the products formed during reduction.

The following experiments attempt to determine the significance of each variable so as to achieve a successfully reduced product. Appendix C presents the results gathered from six experiments performed following either the modified simultaneous or separate sintering and reduction sequence. This table is divided into smaller tables presented below to aid in understanding the effects of different variables. Note that the content of the atmosphere during reduction is not carefully controlled. $N_2(g)$ is flushed through the furnace throughout the reduction and a lid is placed on top of the crucible to minimize oxidizing environments. However, because of this minimal control of the atmosphere, it is difficult to determine the exact conditions the red mud is exposed to. It should be noted that the source of carbon is petroleum coke which is not the best reductant for iron oxide since it lacks volatile matters and moisture. The two measurements taken to determine whether reduction has taken place as well as the extent of reduction, are weight loss calculations and Mössbauer analysis. Weight loss comprises of the actual weight loss observed during the experiment, the theoretical weight loss based on stoichiometric calculations (Equation 3.9) and the difference between these two measurements. A negative value indicates an excess weight loss occurs in the actual experiment compared with the theoretical weight loss while a positive value indicates an insufficient weight loss occurs in the actual experiment. Mössbauer analysis determines the phases of the iron after reduction. Discussed below are the results produced from changing these variables. To begin, experiments one and two describe the effect of temperature on reduction. Both samples are reduced in two hours, contain a calcium oxide layer and 300% excess carbon and follow the modified simultaneous sintering and reduction sequence.

Table 5.6 Influence of Temperature on the Extent of Reduction of Iron Oxide Contained in Red Mud Reduced in 2 Hours Using 300% Excess Carbon and a Calcium Oxide Layer Following the Modified Simultaneous Sintering and Reduction Sequence

	Reduction	Weight Loss Analysis			Mössbauer Analysis				
Exp.	Temp.	Lost	Th. Loss	Difference	Fe	FeO	Fe_3O_4	Fe_2O_3	other
#	C	%	%	%	%	%	%	%	%
1	900	17.6	22.6	5	32	54	6	0	8 Fe/Fe_3O_4
2	1050	26.5	22.6	-3.9	93	4	-	-	3 Fe^{2+}

In experiments one and two, as temperature increases, reduction also increases as seen by the weight loss and products detected by the Mössbauer. Different temperatures prefer different oxide states. Figure 5.1 demonstrates the thermodynamic equilibrium compositions of products formed at various temperatures starting with one mole of iron oxide (Fe_2O_3) and six moles of carbon (200% excess carbon). The calculation and plot are created by HSC software. Higher temperatures promote a more reduced form of iron. In this figure, even at 800°C some iron oxide is in equilibrium with iron. Using this diagram combined with results from experiments performed, it is concluded that to achieve almost full reduction, temperatures around 1050°C should be used. The occurrence of excess weight loss in experiment two is not exactly known but it could be from the loss of excess carbon upon atmospheric oxidation or the reduction and/or evaporation of cadmium and phosphorus oxides. Experiments two and three demonstrate the influence of time after 2 hours reduction. Both samples are reduced at 1050°C, contain 300% excess carbon and a calcium oxide layer and follow the modified simultaneous sintering and reduction sequence.

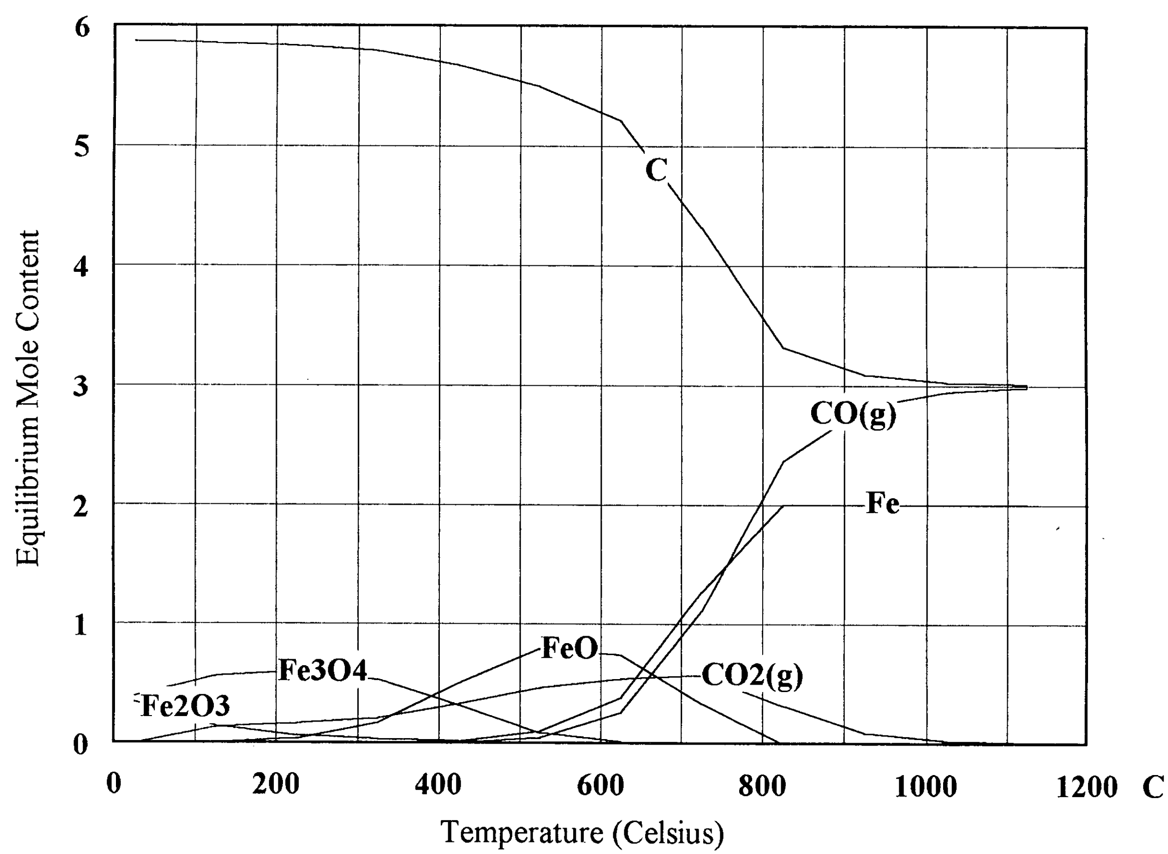

Figure 5.1 Effect of Temperature on the Equilibrium Iron Products Formed During Reduction of Fe2O3 Using 200% Excess Carbon

Table 5.7 Influence of Time on the Extent of Reduction of Iron Oxide Contained in Red Mud Reduced at 1050°C Using 300% Excess Carbon and a Calcium Oxide Layer Following the Modified Simultaneous Sintering and Reduction Sequence

	Reduction	Weight Loss Analysis			Mössbauer Analysis				
Exp.	Time	Lost	Th. Loss	Difference	Fe	FeO	Fe_3O_4	Fe_2O_3	other
#	hours	%	%	%	%	%	%	%	%
2	2	26.5	22.6	-3.9	93	4	-	-	3 Fe^{2+}
3	4	26.4	22.6	-3.8	92	5	-	-	3 Fe^{2+}

Time does not have a significant effect on reduction after two hours regarding the similarities in the weight loss and Mössbauer analysis. A period of time is required for reduction to occur after which further reduction does not occur. Experiments four and five illustrate the effects of calcium oxide layer on reduction. Both samples are reduced at 1050°C for two hours, contain 200% excess carbon and follow the separate sintering and reduction sequence.

Table 5.8 Influence of a Calcium Oxide Layer on the Extent of Reduction of Iron Oxide Contained in Red Mud Reduced at 1050°C for 2 Hours Using 200% Excess Carbon Following the Separate Sintering and Reduction Sequence

	Reduction	Weight Loss Analysis			Mössbauer Analysis				
Exp.	CaO top	Lost	Th. Loss	Difference	Fe	FeO	Fe_3O_4	Fe_2O_3	other
#	yes/no	%	%	%	%	%	%	%	%
4	yes	25.6	24.1	-1.5	96	3	-	-	1 non-mag
5	no	25.2	24.1	-1.1	88	-	8	3	1 non-mag

A layer of calcium oxide does increase the amount of reduction in the iron as seen by the Mössbauer results and weight loss differences. As mentioned above, the calcium oxide layer promotes a more reducing environment by trapping the carbon monoxide evolved during reduction. Experiments four and six describe the influence of carbon content on reduction. Both samples are reduced at 1050°C for two hours, contain a calcium oxide layer and follow the separate sintering and reduction sequence.

Table 5.9 Influence of Carbon Content on the Extent of Reduction of Iron Oxide Contained in Red Mud Reduced at 1050°C for 2 Hours Containing a Calcium Oxide Layer Following the Separate Sintering and Reduction Sequence

	Reduction	Weight Loss Analysis			Mössbauer Analysis				
Exp.	Carbon	Lost	Th. Loss	Difference	Fe	FeO	Fe_3O_4	Fe_2O_3	other
#	% excess	%	%	%	%	%	%	%	%
6	100	27.4	26.2	-1.2	81	-	13	4	2 non-mag
4	200	25.6	24.1	-1.5	96	3	-	-	1 non-mag

As carbon content increases from 100% excess to 200% excess, almost complete reduction is observed via the Mössbauer results. The effects of carbon content are further examined by performing TGA/DTA. Two samples from the separate sintering and reduction sequence are heated up to 1050°C at 20°/min and held for five hours in an argon atmosphere. The only variable altered in these experiments is carbon content. Figure 5.2 represents 100% excess carbon and Figure 5.3 represents 200% excess carbon. A large drop in weight occurs at 630°C for 100% excess carbon and at 930°C for 200% excess carbon. Weight loss over the whole temperature cycle is 21.7% and 33.6% for 100% and 200% excess carbon respectively. Stoichiometrically, weight loss should be 26.1% for 100% excess carbon and 24.0% for 200% excess carbon. In the 100% excess carbon sample, a sudden drop in weight occurs at 630°C and an associated DTA peak. During reduction, this temperature promotes products such as Fe_3O_4. In the 200% excess carbon sample, weight loss occurs at 930°C and an associated DTA peak. This temperature promotes products such as Fe and FeO. As carbon content increases, the temperature at which measurable reactions (reduction) occur increases, promoting a more reduced form of iron. The proportion of indirect to direct reduction of iron oxide is a function of temperature and activity of carbon (37). 200% excess carbon is sufficient to achieve almost full reduction at 1050°C. Experiments two and four compare the modified simultaneous sintering and reduction sequence to the separate sintering and reduction sequence. Both samples are reduced at 1050°C for two hours using a calcium oxide layer. Experiment two uses 300% excess carbon while experiment four uses 200% excess carbon. It is concluded that after 200% excess carbon, excess carbon does not have a substantial effect on the reaction outcome.

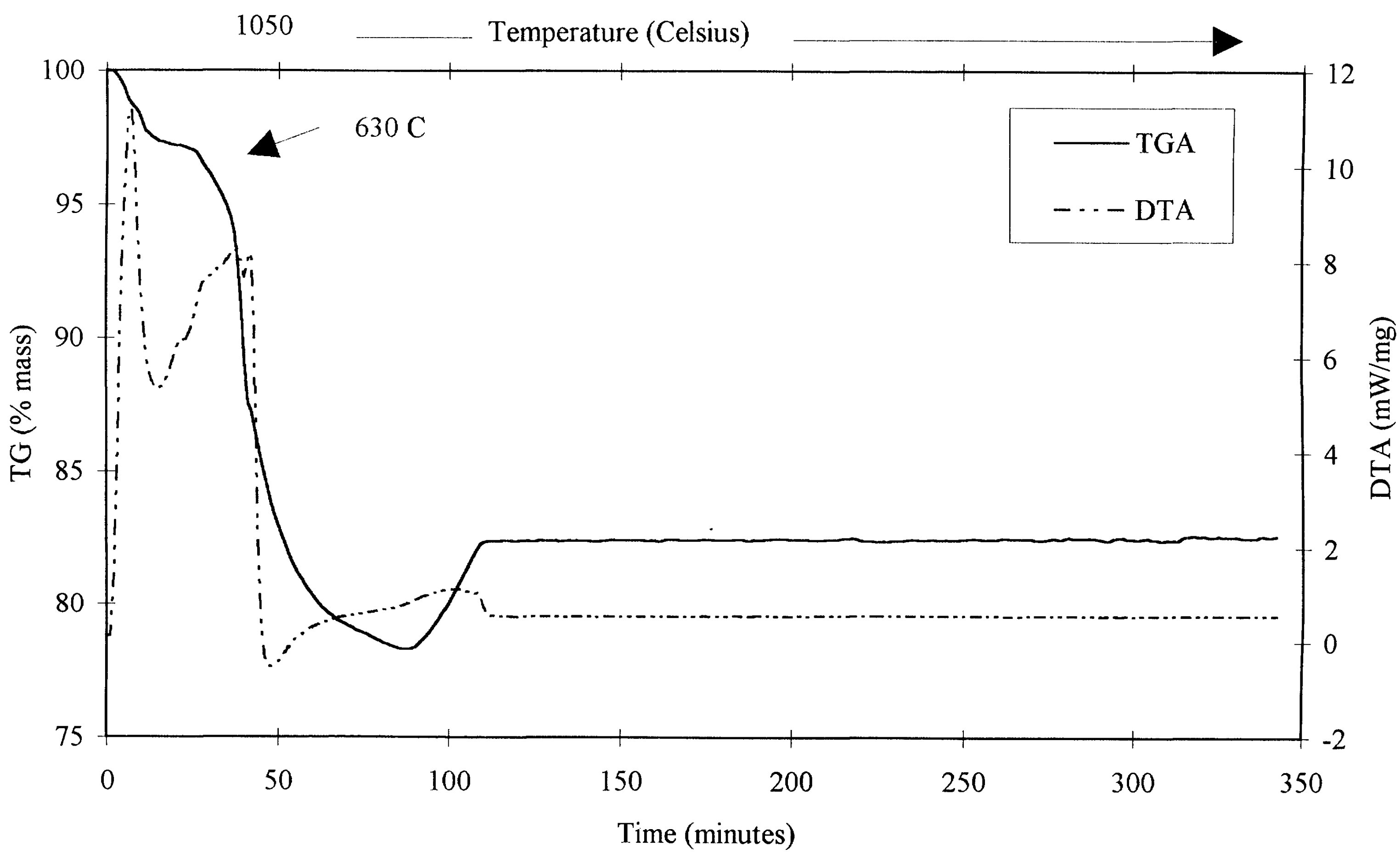

Figure 5.2 A TGA and DTA Analysis of a Reduction Experiment Performed on Red Mud Using 100% Excess Carbon

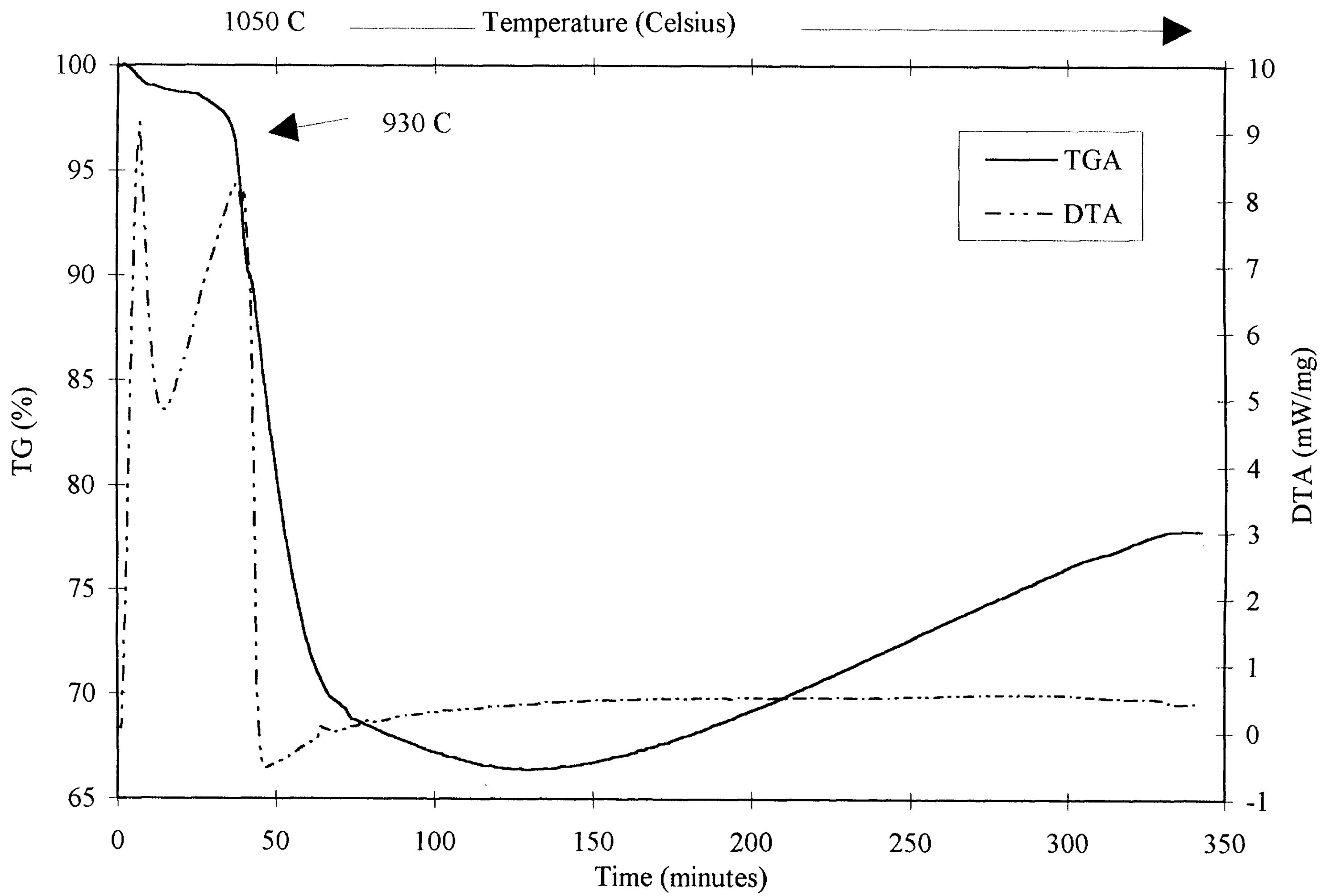

Figure 5.3 A TGA and DTA Analysis of a Reduction Experiment Performed on Red Mud Using 200% Excess Carbon

.Table 5.10 Influence of Sequence on the Extent of Reduction of Iron Oxide Contained in Red Mud Reduced at 1050°C for 2 Hours Using at Least 200% Excess Carbon and a Calcium Oxide Layer

	Reduction	Weight Loss Analysis			Mössbauer Analysis				
Exp.	Sequence	Lost	Th. Loss	Difference	Fe	FeO	Fe_3O_4	Fe_2O_3	other
#	sim./sep.	%	%	%	%	%	%	%	%
2	sim.	26.5	22.6	-3.9	93	4	-	-	3 Fe^{2+}
4	sep.	25.6	24.1	-1.5	96	3	-	-	1 non-mag

*sim. = modified simultaneous sintering and reduction sequence
sep. = separate sintering and reduction sequence

Simultaneously sintering the red mud while reducing it does have a minor effect on the extent of reduction. Different experiments are performed in this research as oppose to the U.S. Bureau of Mines research. Therefore no comparison of the results gathered are made. From the study performed, **at least 90% reduction of iron oxide is attained by reducing the red mud at 1050°C for two hours containing 200% excess carbon content and a calcium oxide layer, following either the modified simultaneous or separate sintering and reduction sequence**. A final thermodynamic analysis is performed on red mud during reduction using 200% excess carbon presented in Appendix D. This analysis describes the equilibrium products formed at various temperatures. The resulting product from the above analysis contains as high as 40% iron depending on the quantity of calcium oxide supplemented to the mixture.

5.1.2.2 MAGNETIC SEPARATION

A magnetic separation is performed to separate the reduced iron out of the remaining red mud. The only variable altered during magnetic separation is the process of wet verses dry magnetic separation.

Several tests are performed attempting to separate the non-magnetic from the magnetic portion of the red mud. The reduced red mud contains iron combined with titanium, aluminum, calcium, silicon oxides and residuals of sulfur, zinc, manganese, sodium, chromium and phosphorus. Figure 5.4 displays the results acquired from a typical wet or dry magnetic separation. Optimum results would display 100% iron in the magnetic product and the remaining constituents in the non-magnetic product. From Figure 5.4, it is concluded that magnetic separation is not possible. However, some interesting observations are as follows. Iron, calcium, titanium and aluminum segregate to the magnetic product while sulfur, manganese and sodium segregate to the non-magnetic product. Iron also distributes to the non-magnetic portion of the red mud. All other constituents appear to be about equally divided. Speculations into these observations are as follows. Iron, calcium and titanium appear to be intimately mixed with each other in all magnetic separations. It has been suggested that titanium is combined with iron in the bauxite ore. Calcium oxide is supplemented to the Bayer process to perform a number of tasks, but can react with titanium oxide to form perovskite. This perovskite can attach itself to the iron. Thus, both calcium and titanium are carried with the iron during magnetic separation. Perovskite is also noted in the U.S. Bureau of Mines article (3). Aluminum and iron are known to be combined in the bauxite ore (38). This combination can carry over to the red mud interfering with magnetic separation and leaching. Possibly during reduction, the manganese and sulfur react with the help of carbon to form manganese sulfide, a non-magnetic compound. The presence of iron in the non-magnetic product could be due to residual FeO remaining from reduction. The U.S. Bureau of

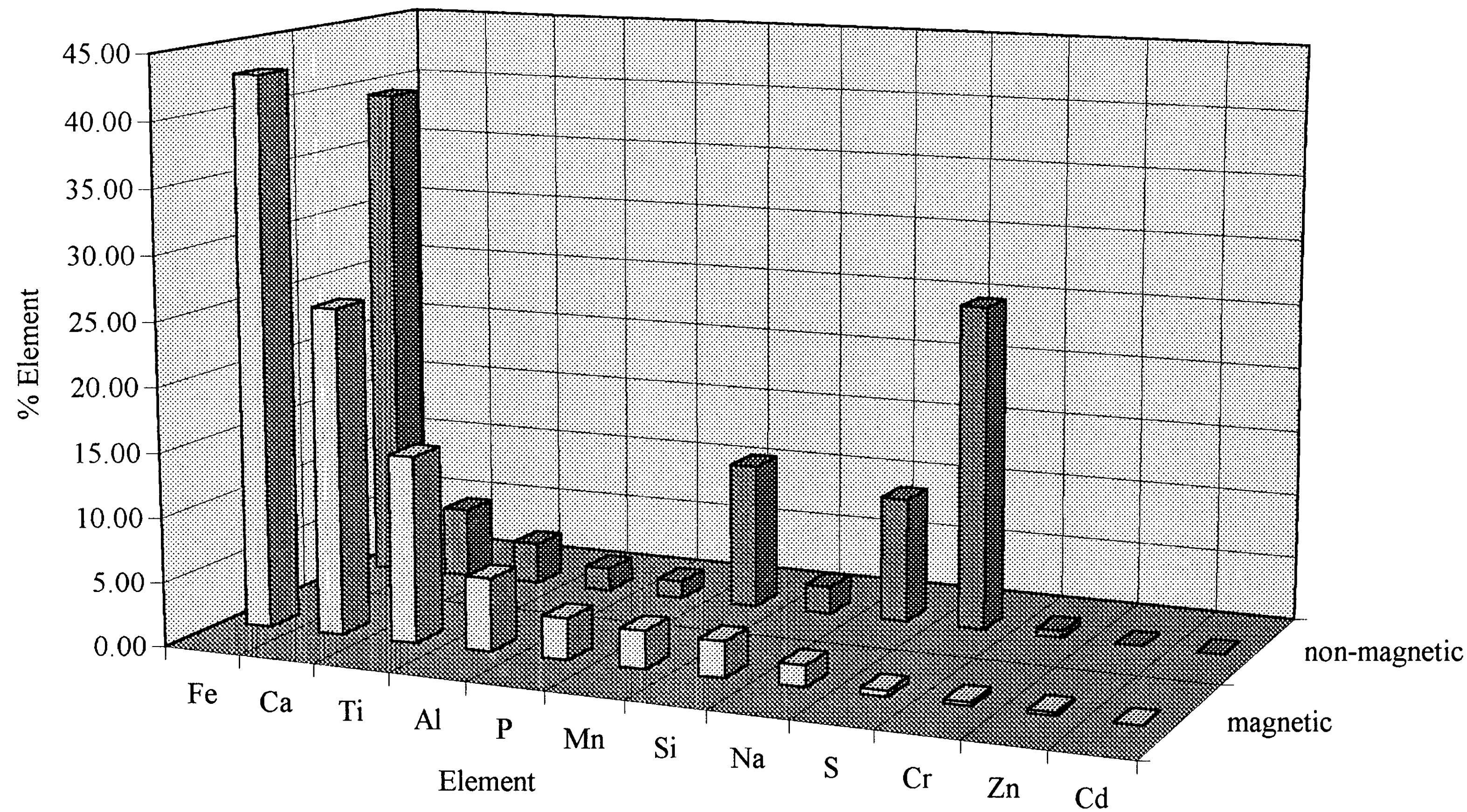

Figure 5.4 Results from a Typical Wet or Dry Magnetic Separation Performed on Reduced Red Mud

Mines performs several wet magnetic separation batch tests using a Davis tube. However, the iron content in the magnetic product from these experiments only reaches a maximum of 71.9% without ball milling (3). Magnetic separation is not a successful procedure as is readily apparent. This outcome has a severe impact on what is to come.

5.1.2.3 EVALUATION OF IRON PRODUCT AND SMELTING

After magnetic separation, the next and final step in iron recovery is evaluation of the iron product. The red mud, after a failed magnetic separation, contains up to 40% reduced iron and oxides and elements of calcium, aluminum, sodium, titanium, manganese, silicon, phosphorous, sulfur, zinc and chromium. This product, not comparing even closely with direct reduced iron (see Table 3.1), is not suitable for sale. Smelting can be performed on the unseparated red mud. However, smelting is not experimentally investigated since the magnetic separation has failed. If performed, smelting should be successful, recovering pig iron in the molten phase. Smelting is now considered to be an option for further processing discussed subsequently.

Considering the research performed thus far, full iron recovery, via reduction, magnetic separation and smelting, is not a feasible course of action. Both the modified simultaneous and separate sintering and reduction sequences reach this same conclusion. The iron existing in the red mud in both sequences is at least 90% reduced and maintains to be a value added product. Other processing techniques can be employed to utilize this iron in an economically feasible manner. These techniques will be discussed in subsequent sections. The resulting product after alumina extraction and iron reduction contains up to 40% iron depending on the quantity of calcium oxide supplemented to the mixture, approximately 6% alumina, 15% titanium oxide and other oxides and elements such as silicon, phosphorus, sulfur, chromium, manganese and zinc.

5.1.3 EXTRACTION OF TITANIUM OXIDE

Titanium oxide extraction is performed on the non-magnetic product after magnetic separation in both the modified simultaneous and separate sintering and reduction sequences. It is understood that alumina extraction is a successful operation, while iron extraction is not due to the failure of magnetic separation. Because of this, the composition of the red mud produced from North Coast Jamaican bauxite contains ample amounts of reduced iron. Consequently, titanium oxide extraction would be performed on the unseparated, reduced red mud. However the iron content complicates titanium oxide removal discussed subsequently.

Metallurgical techniques such as carbo-chlorination and sulfation are suggested for the extraction of titanium oxide. Carbo-chlorination employs chlorine, a very reactive substance. During carbo-chlorination, chlorine reacts with several constituents besides titanium oxide, such as iron. Because of this reactivity, combined with the large presence of iron contained in the unseparated, reduced red mud, carbo-chlorination is not an adequate process for extraction of titanium oxide. Conversion of perovskite to rutile is also suggested for titanium oxide extraction. However, H_2SO_4 used in the sulfation step forms iron sulfates. Again, the unseparated, reduced red mud is not a practical material for this process.

Titanium is the ninth most plentiful element in the earth's crust. The U.S. titanium ore self-sufficiency has decreased thirty percent between the sixties and eighties not because of decreasing amounts of titanium reserves, but because of the increasing supply of low-cost concentrates from other countries. Substantial supplies of titanium ore are known to exist in off-grade deposits, but extracting the titanium from these deposits has proven to be uneconomical (39). The hydrometallurgical extraction processes mentioned above result in large volumes of reactants to account for the iron reactions as well as large volumes of waste from the iron product. Because less expensive ways exist currently to produce titanium and its oxide, titanium oxide extraction from the red mud is concluded not to be a feasible process.

5.2 SEQUENCE OF EXTRACTION

One of the most important aspects of this thesis is successfully determining the order of extraction of alumina, iron and titanium oxide. Throughout this thesis both the modified simultaneous and separate sintering and reduction sequences are employed. In both processes, drying, sintering, leaching, washing and reducing all maintain to be successful procedures. However, magnetic separation, smelting and titanium oxide extraction, including carbo-chlorination and perovskite conversion, are not successful processes. Both sequences are weighed carefully to determine which process is most beneficial to the extraction of value added products. Benefits stem from exhibiting minimal interference between extraction processes, maximizing the extent of extraction of each component and providing a product viable for further processing if magnetic separation is not successful.

Recall that the modified simultaneous sintering and reduction sequence is the process of drying, simultaneously sintering and reducing, leaching and washing to recover alumina and magnetically separating to recover iron and titanium oxide. Hindering products do not form during simultaneous sinter and reduction that might interfere with alumina extraction or iron oxide reduction. It is recognized that in this sequence the fully reduced iron is exposed to leaching and washing because of the failure of magnetic separation. At a pH of approximately 12 and a potential of 0 volts, the iron develops a passivation layer in the sodium hydroxide solution. It is suggested, when iron is exposed to caustic solutions, a film of ferrous hydroxide $Fe(OH)_2$ initially forms on the iron followed by oxidation to $Fe(OH)_3$ (40). Mössbauer results given in Table 5.11 present the forms of iron after simultaneous sintering and reduction and after leaching.

Table 5.11 Phases of Iron After Sintering and Reduction and After Sintering, Reduction and Leaching Performed in the Modified Simultaneous Sintering and Reduction Sequence

Sample Identification	Fe	Non-magnetic Fe^{2+}	Magnetic Oxide	Fe_3O_4
Sintered and Reduced	93	4	0	3
Sintered, Reduced and Leached	82	11	7	0

The iron increases in oxide by 4% and increases in non-magnetic Fe^{2+} by 7% after leaching. Even though the Mössbauer analysis is not performed after washing, it is assumed that washing at 100°C also promotes the re-oxidation of iron. To serve in reduction, a layer of calcium oxide is provided on top of the red mud. After reduction, the calcium oxide is combined with the sintered and reduced mix and exposed to leaching and washing. As noted earlier, the calcium oxide addition detracts from alumina extraction if it is in excess. The addition of calcium oxide to the leach solution is yet another shortcoming of the modified simultaneous sintering and reduction sequence. Finally, the carbon dioxide evolved from combined sintering and reduction (3.1 and 3.9) influences both reactions to proceed to the left decreasing the sequence efficiency. The modified simultaneous sintering and reduction sequence provides some benefits such as decreasing energy costs by combining sintering and reduction and allowing the red mud to be further processed if deemed necessary. However, this sequence exhibits significant interference between extraction processes which detracts from the benefits incurred.

The separate sintering and reduction sequence is the process of drying, sintering, leaching, washing, reducing and magnetically separating. The magnetic product is evaluated for iron and smelted, if required. The non-magnetic product is directly processed for titanium oxide removal. Both alumina extraction and iron reduction are successful in this sequence. The iron is not converted back to an oxide during leaching and calcium oxide does not interfere with alumina extraction because the reduction comes at the end of the sequence. Also, this sequence fairs slightly better in the recovery of alumina and reduction of iron as observed in the results above and allows for the option of further processing. However, the separate sintering and reduction sequence results in a much more costly procedure. This sequence exhibits several benefits, but does increase processing costs.

After considering both the modified simultaneous and separate sintering and reduction sequences very carefully, some conclusions are drawn. The iron oxidation in the modified simultaneous sintering and reduction sequence combined with the interference of calcium oxide is significant enough to warrant this process self defeating. The separate sintering and reduction sequence minimizes interference between extraction processes upon separation of sintering and reduction and increases alumina recovery and iron reduction, but does increase processing costs. Both allow for the option of further processing. Upon weighing the positive and negative attributes of both of these sequences, it is determined that the separate sintering and reduction sequence is the most beneficial or the least detrimental to the extraction of value added products and therefore is the sequence recommended.

5.3 ADDITIONAL RESULTS AND ANALYSIS

During the investigation into the extraction of alumina, iron and titanium oxide, several other findings are made. These findings include a material balance for the separate sintering and reduction sequence as well as introductory information about sodium removal, cadmium removal, zinc removal, influence of other sintered red mud constituents on leaching, content of residual radioactive material, red mud magnetic behavior and stability of reduced iron. This information will expand the understanding of red mud produced from North Coast Jamaican bauxite and begin to explain the obscure behavior observed in this material. Presented below are the results of these findings.

5.3.1 MATERIAL BALANCE

The separate sintering and reduction sequence is the optimum sequence for the extraction of alumina, iron and titanium oxide. A preliminary material balance is performed on the separate sintering and reduction sequence to obtain an estimate of the outcome of specific constituents and the weight loss and gain throughout the sequence. To begin, a sample of 20g of dried red mud is measured. The red mud is sintered at 950°C for 2 hours adding 3.1g of (50% excess) sodium carbonate. After sintering, the red mud weighs 20.2g. Leaching is performed at 65°C for 1.5 hours, using a 0.6 A/C ratio and 100% excess caustic. The material weighs 16.2g after leaching (excess weight loss is due to remains left on various containers and filters). Washing is performed at 100°C for fifteen minutes using a ratio of 10g/l of red mud to distilled water. After washing, the red mud weighs 13.9g (again, excess weight loss is due to remains left on various containers and filters). It should be noted that both of these aforementioned processes are inexact and thus weight loss does not correspond directly to recovery of value added products.

Reduction is performed at 1050°C for 2 hours, using 4.4g (200% excess) carbon and a 3.6g calcium oxide layer (removed for EDX analysis shown below). After the reduction, the sample weighs 16.8g with the calcium oxide layer and 13.2g without the calcium oxide layer. If smelting takes place, the iron is supplemented with more calcium oxide and carbon to create a reducing atmosphere. Both an iron product and a slag are produced and analyzed separately. The weight of the final product is unknown but may be theoretically approximated to 12.8g. The variation in the red mud weight percent composition throughout all of these processes is presented in Table 5.12. A diagram of the processes imposed combined with the weight loss or gain in each is presented in Appendix E.

5.3.2 SODIUM REMOVAL

In both the modified simultaneous and separate sintering and reduction sequences a wash is required to remove the residual sodium aluminate and other sodium compounds from the red mud. Sodium is in several different forms derived from bauxite ore, the Bayer process and prior red mud processing. Several washing experiments are performed to determine the influences on and optimum conditions for removal. However, the EDX is not able to precisely detect sodium. Thus absolute values of this constituent are not reported. Only resulting trends in sodium removal after altering specific variables are applicable. Variables include temperature, time and the ratio of red mud to water. These three variables all interact with each other. At higher ratios, higher temperatures and longer times are required for adequate sodium removal. Smaller ratios of red mud to water increase the volume available for sodium dissolution. Higher temperatures allow for more interaction to occur between particles, increasing solubility. Longer times allow for more complete dissolution. However, temperature and ratio are considered the most significant factors involved in completing dissolution. Sodium is able to be removed to

Table 5.12 Composition and Weight Loss or Gain of Red Mud After Various Extraction Processes Performed in the Separate Sintering and Reduction Sequence

Process	Fe_2O_3	FeO	Fe	Al_2O_3	TiO_2	CaO	SiO_2	Other	Wt.
dried 400°C 1hr.	67.7	-	-	11.7	7.1	6.6	2.5	4.4	100%
sintered 950°C 2hr. 50% xs. Soda	56.4	-	-	12.7	6.7	8	2.4	13.8	101%
leached 65°C 1.5hr. 100% xs caustic	66.0	-	-	5	8.1	11.1	2.5	7.3	81%
washed 100°C 15 min. 10g/l	69.3	-	-	2.8	8.4	12.5	1.9	5.1	70%
reduced 1050°C 2hr. 200% xs C; CaO layer	-	5.2	36.5	6.7	14.8	19.8	3.7	13.3	66%*
smelted 1650°C	-	19	>90	-	29	22	7.5	22.5	64%

* without CaO

below 1% by washing at 100°C for fifteen minutes using a ratio of 2g/l of red mud to distilled water.

5.3.3 CADMIUM REMOVAL

A very small amount of cadmium exists in the red mud, approximately 0.027%. Observations in the EDX indicate that after heating to 1050°C while reducing, the cadmium is completely eliminated. Note that heating to 950°C does decrease the cadmium content, but does not eliminate the cadmium completely.

5.3.4 ZINC REMOVAL

The initial content of zinc is on average 0.3%. However, the removal of zinc is not observed in the reduced product because reduction does not exceed 1100°C.

5.3.5 OTHER LEACHING RESULTS

During sintering, possible reactions between iron oxide and sodium carbonate, titanium oxide and sodium carbonate and/or silicon oxide and sodium carbonate may occur. After sintering, these products and various calcium constituents might be soluble in the sodium hydroxide solution, decreasing alumina solubility and recovery of iron and titanium oxide. To determine if these reactions are occurring and any dissolution is taking place, a measurement of the quantity of iron and titanium in the post-leach liquor is made. Aluminum and calcium content are also measured, but silicon content is not. The red mud is dried, simultaneously sintered and reduced (the modified simultaneous sintering and reduction sequence) at 950°C and 1100°C using 50% excess carbon, 50% excess sodium carbonate but no calcium oxide layer and leached using 21.8% excess caustic. The element analysis is performed by Accu-Labs Research Inc. The results are presented below.

Table 5.13 Dissolution of Aluminum, Iron, Titanium and Calcium During Leaching of Red Mud Using a Sodium Hydroxide Solution

Elements	Aluminum (mg/l)	Iron (mg/l)	Titanium (mg/l)	Calcium (mg/l)
Sample	23000	<1.0	<1.0	<10

The solubility of aluminum is high as expected. Fortunately, the solubility of iron, titanium and calcium all appear to be low confirming the fact that none of these elements are taken into solution.

5.3.6 RADIOACTIVE MATERIAL

Two radioactive elements, uranium and thorium, are known to exist at higher levels in red mud produced from Jamaican bauxite compared to other soils (41). Both are measured and detected in the dried, the sintered and the reduced red mud following the separate sintering and reduction sequence. The results are presented in Table 5.14.

Table 5.14 Content of Radioactive Elements Contained in Red Mud Produced from North Coast Jamaican Bauxite After Drying, Sintering and Reduction

Sample Identification	Uranium (ppm)	Thorium (ppm)
Dried Red Mud	2.0	.85
Sintered Red Mud	2.6	3.4
Reduced Red Mud	4.7	8.5

As the red mud is processed, the concentration of the radioactive elements increases. This behavior is due to the decrease in other elements in the mud such as oxygen and aluminum during processing. The radioactive elements are not removed during any stage of either the modified simultaneous or separate sintering and reduction sequence. This increase in radioactive elements is important if further processing of the reduced red mud is to continue. Careful track of the radioactive concentration should be taken to avoid potential problems.

5.3.7 MAGNETIC CHARACTERISTICS

The magnetic characteristics of red mud are obscure and not well understood. Some observations of the starting red mud iron composition are investigated. Suggestions are made attempting to explain the behavior surveyed in this material. These observations and suggestions will shed some light on the complications with magnetic separation. The dried red mud contains 74% magnetic Fe_2O_3 (canted anti-ferromagnetic) and 26% "other" magnetic Fe_2O_3. The appearance of the "other" magnetic Fe_2O_3 is possibly due to either particle size or aluminum solubility in iron. When the particle size of a normally magnetic material is less than 100 Å, it switches magnetic domains several times a second. As a consequence, the material behaves paramagnetically (a material containing randomly oriented magnetic dipoles). This behavior is known as superparamagnetism (36). The superparamagnetism may cause this "other" magnetic behavior to occur. Note that the superparamagnetic material does not exist in the reduced red mud. During reduction, the small iron particles that function in this manner have a chance to grow and rid themselves of this behavior. The 26% "other" magnetic Fe_2O_3 could also be due to existence of aluminum. Goethite or hematite can take aluminum into solution. When this occurs, the aluminum lowers the Nèel temperature (temperature at which the material changes from paramagnetic to anti-ferromagnetic) of the iron to below room temperature, producing a paramagnetic iron oxide (42, 43). Difficulty lies in ascertaining which of these two types of behavior are occurring. To decrease the influence of superparamagnetism, the temperature is lowered, setting up an internal magnetic field. However, as temperature is lowered, the temperature at which the aluminous iron changes from paramagnetic to canted anti-ferromagnetic may be reached, which also initiates an internal magnetic field. Therefore it is not known what this "other" magnetic behavior is due to.

5.3.8 STABILITY OF REDUCED IRON

The reduced iron in the red mud is not a stable phase in an atmosphere filled with oxygen. It has a tendency to revert back to its more stable oxide state. The reduced iron in the red mud from the modified simultaneous sintering and reduction sequence consists of small particles which exhibit this pyrophoric behavior presented in Table 5.15. The red mud is stored in a plastic container between measurements. Simultaneous sintering and reduction is conducted at 900°C for 3 hours using 100% excess carbon and sodium carbonate and a calcium oxide layer. Note that reduction is not complete due to inadequate reducing conditions.

Table 5.15 Oxidation of Reduced Red Mud After 75 Days of Storage in a Plastic Container

Sample Identification	Fe	FeO	Fe_3O_4	superparamagnetic Fe/Fe_3O_4
Sintered, Reduced, Leached	19	58	9	14
Same Product 75 Days Later	2	71	11	16

This pyrophoric behavior is also observed in the U.S. Bureau of Mines article (3).

5.4 VARIOUS USES FOR RED MUD CONCLUDED FROM THIS STUDY

The red mud contains between 11-40% fully reduced iron, 0.5-5% iron oxide (FeO), 0.7-15% titanium oxide, 20-74% calcium oxide, 5-6% alumina and 1-4% silicon oxide after prior processing, the balance being constituents in order of decreasing quantity: manganese, sulfur, phosphorus, sodium, chromium and zinc. The variation in content is due to the amount of calcium oxide coated on the red mud mixture prior to reduction. This product is not futile. The red mud does demonstrate economic viability and can be further utilized. Three possible routes for further utilization of the red mud after prior processing are presented below including blast furnace supplementation, smelting and ferro-titanium production.

5.4.1 BLAST FURNACE SUPPLEMENTATION

A potential application for alumina depleted and reduced red mud is to sell it to a blast furnace operation. This sale provides several benefits for the iron making industry as well as the alumina industry. A preliminary calculation is made upon adding 100kg of red mud to 1000kg of iron ore. The total charge to the blast furnace consists of red mud, iron ore, coke and lime. The compositions of the iron ore, coke, lime, red mud and final product are presented in Table 5.16.

Table 5.16 Composition of Iron Ore, Coke, Lime, Alumina Depleted and Reduced Red Mud and Final Product Required for Blast Furnace Calculations

Sample	Fe %	FeO %	Fe_2O_3 %	CaO %	MnO %	MgO %	Al_2O_3 %	TiO_2 %	C %	SiO_2 %
iron ore	-	-	92	1	1	1	3	-	-	2
coke	-	-	-	-	-	-	5	-	75	20
lime	-	-	-	95	-	-	2	-		3
red mud	37	5	-	20	-	-	6	15	-	4
final product	92	-	-	-	1 Mn	-	-	-	5	2 Si

Appendix F demonstrates the calculational path for the following results. Note that this calculation does not take into account residual constituents contained within the red mud including manganese, phosphorus, sulfur, sodium, chromium and zinc. The benefits procured from the red mud addition for the iron industry are as follows. The percent coke conserved from the red mud addition totals about 3% which is equivalent to 10 kg of coke per thousand kilograms of hot metal. The addition increases the slag amount by approximately 15%. However 5% of this slag is rich in TiO_2. The TiO_2 serves as a blast furnace hearth protector acting as an acidic component enhancing the silica rich refractory. The red mud also contains calcium oxide which if sufficient can improve blast furnace efficiency by lowering the amount of calcium oxide required to produce a specific basicity. Because the red mud is depleted of alumina, the slag melting point is not increased by this constituent. The uranium and thorium present in the red mud oxidize in the furnace and therefore report to the slag. The slag is separated from the steel and cooled where these deleterious constituents are consequently entrapped in a glassy matrix. This eliminates the concern for radioactive contamination of the steel. Special precautions should be taken if this plan is implemented. The red mud now in powder form ought to be added to the furnace at tuyere level to avoid choking the stack resulting in a hanging wall (37). The sodium in the red mud should be kept to a minimum. This is performed through extensive washing discussed previously. Sodium, a basic oxide, if present in the blast furnace can harm the acidic refractory. Due to its inherent pyrophoric behavior, the reduced red mud should be kept in a low oxidizing atmosphere prior to supplementation to avoid iron oxide formation. The principal benefit derived from this method for the alumina industry includes complete elimination of the red mud and the associated problems with it. As a whole, if the sale of the pre-treated red mud less the cost to prepare the mud for the blast furnace results in a profit for the alumina industry, this method could prove to be a feasible route for utilization.

5.4.2 SMELTING

The option of smelting the alumina depleted, reduced red mud to produce pig iron is also a potentially viable application. The red mud containing up to 40% iron, 90% of which is completely reduced, can be recovered if thought advantageous. Carbon is added to the smelt to reduce the remaining iron and scavenge the oxygen from the melt. Small additions of calcium oxide are added to the smelt combined with calcium oxide from the red mud to optimize the basicity of the slag. The mixture, now in liquid form, separates into iron and slag. The iron is poured out from the furnace for recovery. After cooling, the iron can be sold as pig iron. The slag, now rich in titanium is ready to be processed further. The evaluation of the titanium content in the slag is an essential factor in determining whether the extraction of the metal is economically viable. If viable, the hardened slag containing high amounts of titanium and low amounts of iron is utilized to recover the remaining titanium constituents by either carbo-chlorination or conversion from perovskite to rutile. Smelting the magnetic product of red mud is performed by the U.S. Bureau of Mines (3). The results are as follows. The magnetic product of the sample that is simultaneously sintered and reduced, leached and magnetically separated (similar to the modified simultaneous sintering and reduction sequence) is heated in an induction furnace. A fluid melt is observed at 1480°C by optical pyrometer. Iron recovery reaches 95.5%. Microprobe analysis discovers, "...hollow spherical particles containing metallic iron, some $CaTiO_3$ and a matrix of glassy slag" (3). Recovery of titanium is not performed on this sample. A smelting experiment is also performed at the Colorado School of Mines (not performed by the author). The sample is first dried, leached and reduced with 100% excess carbon. Smelting is performed at 1650°C. After, the iron is reported to be at least 90% pure. The slag contains 22% CaO, 19% FeO, 7.5% SiO_2, 29% TiO_2, and 22.5% other constituents (Mn, P, S, Al etc.). Results suggest smelting successfully performs liquid separation of the iron from the other red mud constituents. Drawbacks to smelting include high energy costs to melt the red mud and the large volume of slag produced. However, smelting the processed red mud in either the modified simultaneous or the separate sintering and reduction sequence does merit some serious consideration due to its ability to separate iron from other red mud constituents.

5.4.3 FERRO-TITANIUM PRODUCTION

Direct production of ferro-titanium (Fe-Ti) from alumina depleted red mud is also theoretically investigated. The ores generally used for Fe-Ti production are rutile, ilmenite, titanomagnetite and perovskite. Ferro-titanium is produced by the application of aluminothermic reduction using an electric arc furnace or non-electric reducing smelter. The overall charge material for ferro-titanium production includes 37% TiO_2, 26.5% FeO, 23% Fe_2O_3, 6% CaO, 2.5% SiO_2, 3% Al_2O_3 and 2% other material. The product contains

27% Ti, 3.5% Si 7% Al, 0.1% S and P, the rest allowing for iron. It is emphasized that, if alumina-depleted red mud is used as ferro-titanium charge, significantly lower titanium oxide and higher iron oxides exist in the mud compared with other charge. The addition of rutile in the charge is therefore necessary to produce a commercial grade Fe-Ti. It is also suggested that if the alumina depleted red mud is smelted as presented above, both titanium and lime concentration increase in the slag making it a candidate for Fe-Ti charge. However, iron ore would have to be supplemented to the slag to satisfy the charge requirement. It is observed, after Fe-Ti production using alumina depleted red mud as the charge only 75% of titanium is recovered. The slag remains rich in titanium and aluminum and its volume is substantial. One way to improve titanium concentration in the red mud is to electromagnetically concentrate it. However, the lean fraction could not be used for further recovery and its volume could prove to be abundant. If, after weighing the pros and cons of the process, Fe-Ti production seems applicable then the following course of action is suggested. The alumina depleted red mud is mixed with rutile in a 1:1 ratio and reduced aluminothermically at 1600-1700°C to produce Fe-Ti. The slag, after cooling and communiting, is recycled to the Bayer's process for alumina recovery. The resulting red mud, now rich in titanium, is suitable for processing for TiO_2 recovery via acid-leaching. This method embodies both positive and negative aspects, their degree depending on what value is placed on various steps throughout the process. However, the application does maintain to be a solution with noteworthy benefits and should be seriously considered.

6
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

The objective of this study is to determine the feasibility and sequence of extracting alumina, iron and titanium oxide from red mud generated from North Coast Jamaican bauxite. Overall, this investigation has expanded the knowledge of red mud and identified the possibilities and limitations of extracting various constituents from this material.

6.1 CONCLUSIONS

The success of extracting alumina, iron and titanium oxide varies greatly due to the inherent material characteristics of red mud. The removal of alumina from the mud via sintering and leaching proves to be successful. The results are as follows.

- As much as 83% of the alumina and almost 100% of the sodium oxide are recovered from the red mud when sintering at 1050°C for two hours using 50% excess sodium carbonate above stoichiometry followed by leaching with 5g/l NaOH at 65°C for 1.5 hours using a 0.6 A/C ratio and washing at 100°C for 15 minutes using 10 grams of red mud per liter of distilled water.
- The leach liquor produced is appropriate for reintroducing into the Bayer process stream.

- Alumina recovery is suspected to improve with more refined particle size.

The approach to iron extraction including reduction, magnetic separation and/or smelting, if necessary, does not prove to be successful. Results are as follows.

- At least 90% reduction of the iron is achieved when the red mud is reduced at 1050°C for 2 hours using 200% excess carbon above the stoichiometry covered by a fine layer of calcium oxide.
- The inability to magnetically separate the iron from the remaining red mud constituents leads to a failure in iron extraction.

The approach to titanium oxide extraction through carbo-chlorination or conversion of perovskite to rutile is summarized by the following.

- Because titanium oxide extraction is contingent upon the separation of iron out of the existing red mud, it remains to be unsuccessful.

Two sequences for removal are employed during experimentation, recognized as the modified simultaneous sintering and reduction sequence and the separate sintering and reduction sequence. The modified simultaneous sintering and reduction sequence consists of drying, simultaneously sintering and reducing, leaching, washing, magnetically separating, smelting if necessary or further processing and carbo-chlorinating or converting perovskite to rutile to recover all three value added products. The separate sintering and reduction sequence incorporates the same processing steps except the reduction occurs after washing instead of during sintering. The results from both of these sequences are as follows.

- The exposure of the iron to leaching and washing during the modified simultaneous sintering and reduction sequence induces a passivating oxide layer to form on the iron, spoiling the effects of full reduction.
- The calcium oxide layer carried over from reduction during the modified sintering and reduction sequence detracts from alumina recovery if the oxide occurs in excess.

- The separate sintering and reduction sequence produces slightly better alumina extraction and iron reduction results.
- The separate sintering and reduction sequence is the more efficient sequence for extraction of value added products and is therefore recommended.

Other results are generated aside from the main conclusions that provide additional insight into the behavior and characteristics of red mud. These results include the following.

- Sodium, after undergoing a sharp increase in content after sintering, is decreased to below 1% by the process of washing. Satisfactory conditions for sodium dissolution include washing for fifteen minutes at 100°C using a 2g/l red mud to distilled water ratio.
- The removal of zinc is not observed during reduction, however, cadmium is able to be completely eliminated if reduction occurs at 1050°C.
- During leaching, iron, titanium and calcium do not dissolve into solution.
- Radioactive elements such as uranium and thorium exist in the red mud at 2 and 0.85 PPM. However, their concentration is increased with further processing including sintering, leaching, washing and reducing to as high as 4.7 and 8.5 PPM respectively.
- The red mud, prior to processing, exhibits unusual magnetic characteristics caused by either inherent particle size or aluminum solubility in iron.
- The reduced iron in the red mud, determined via Mössbauer analysis, converts back to a more stable oxide after a period of time.

Because of the inability to extract two out of the three constituents from the red mud, some alternative routes for utilization are suggested. These suggestions include selling the red mud after prior processing to a blast furnace operation to use as feed for iron making, smelting the red mud to recover pig iron and slag rich in titanium and then extracting the titanium from the slag through sulfation and finally using titanium enriched red mud as feed for ferro-titanium production. These are just suggestions and should be further researched and developed if such ideas are applicable.

6.2 RECOMMENDATIONS FOR FUTURE RESEARCH

This thesis is successful at focusing in on the ability of current technology to remove the three aforementioned constituents from red mud as well as identifying the intrinsic difficulties with the methods of extraction. Based on the data gathered in this thesis, future work involves the following. The Achilles' heel of extraction of value added products from red mud produced from North Coast Jamaican bauxite revolves around the ineffectiveness to magnetically separate the iron from the remaining elements. This inability is most likely attributed to the microscopic features present in the red mud, the compounds present and the interaction of these various compounds and the iron phases observed via Mössbauer. Thus thorough investigation into these characteristics might aid in explaining the behavior during magnetic separation as well as other processes. Based on this work, research into more sophisticated techniques for magnetic separation should be accomplished. Confirmation and optimization of the extraction processes performed in this thesis should be acquired. Lastly, if magnetic separation is not practicable the option of smelting followed by extraction of titanium from the slag should be experimentally investigated. Throughout the research, more possibilities for the utilization of red mud after current processes have been executed should be examined to allow for more options to be considered. Overall, the information provided in this thesis will add to the existing body of knowledge on the waste product known as red mud. However, plenty of research is still necessary before any commercial operation is put into use.

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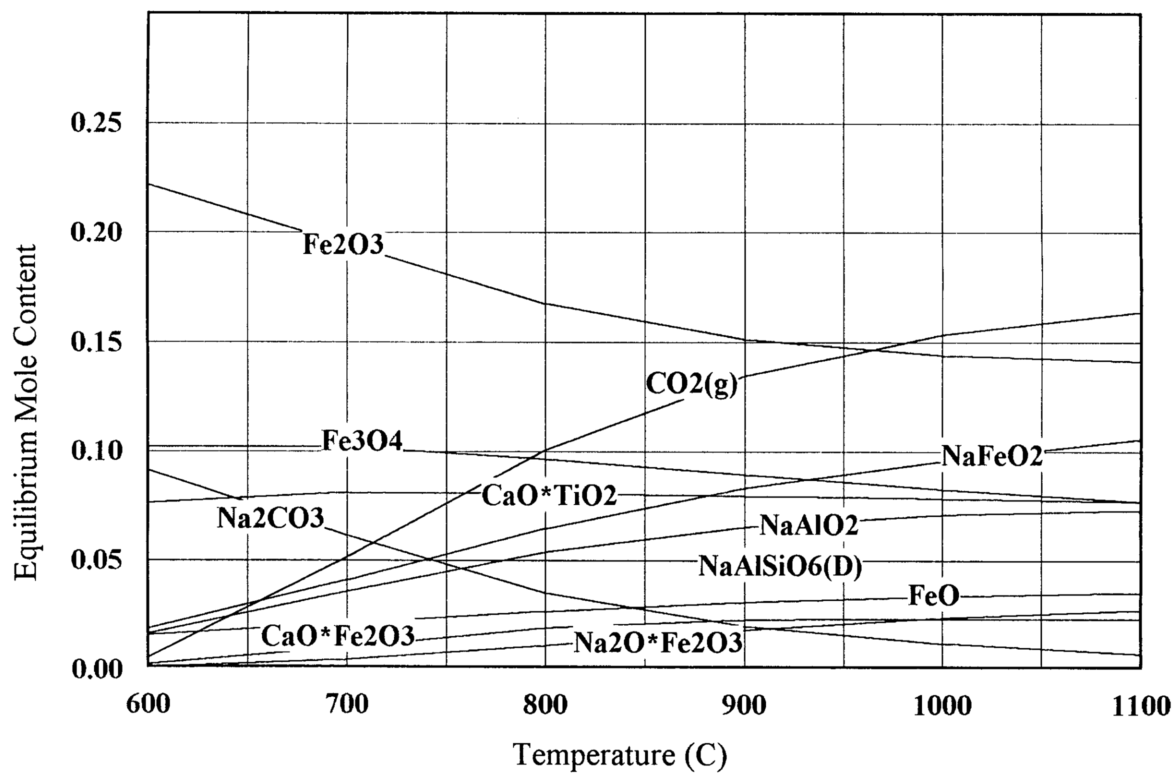
APPENDIX A
CONDITIONS AND RESULTS OF ALUMINA EXTRACTION

	Sintering Conditions			Leaching Conditions			Washing	Comments
Run #	Temperature (^oC)	Excess soda %	Sequence sim./sep.	A/C Ratio	Excess Caustic (%)	Recovery Al2O3 (%)	Recovery Al2O3 (%)	
1	850	50	sep.	0.6	100	66.7	76.8	
2	950	50	sep.	0.6	100	67.4	81.4	
3	1050	50	sep.	0.6	100	69.6	83.1	
4	950	0	sep.	0.6	100	62.7	66.2	
5	950	50	sim.	0.6	100	66.9	75.3	no CaO added
6	1050	50	sep.	0.6	0	59.9	76.0	
7	1050	50	sim.	0.6	150	39.9	54.3	CaO added

*sim. = modified simultaneous sintering and reduction sequence
sep. = separate sintering and reduction sequence

APPENDIX B

EQUILIBRIUM PRODUCTS FORMED IN RED MUD AFTER SINTERING AT VARIOUS TEMPERATURES USING 50% EXCESS SODIUM CARBONATE



* Starting Composition: 71g Fe2O3, 12g Al2O3, 7g TiO2, 7g CaO, 3g SiO2 and 18g Na2CO3.

Calculation performed by HSC software.

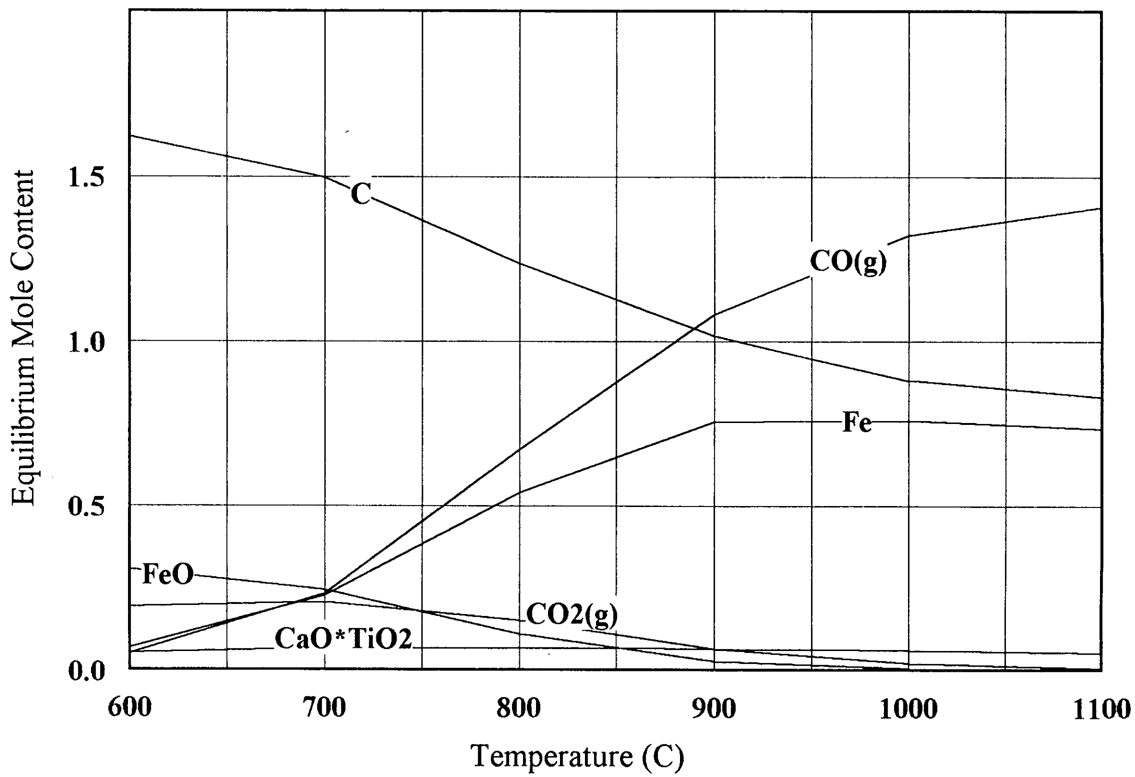
APPENDIX C
CONDITIONS AND RESULTS OF REDUCTION EXPERIMENTS

	Reduction Conditions					Weight Loss			Mossbauer Analysis				
Exp. #	Time hr.	Temp. C	xs C %	CaO top g	Sequence sim./sep.	%Lost %	Th. Loss %	Difference %	Fe %	FeO %	Fe3O4 %	Fe2O3 %	other %
1	2	900	300	yes	sim.	17.6	22.6	5	32	54	6	0	8 Fe/Fe3O4
2	4	1050	300	yes	sim.	26.4	22.6	-3.8	92	5	-	-	3 Fe2+
3	2	1050	300	yes	sim.	26.5	22.6	-3.9	93	4	-	-	3 Fe2+
4	2	1050	200	yes	sep.	25.6	24.1	-1.5	96	3			1 non-mag
5	2	1050	200	no	sep.	25.2	24.1	-1.1	88		8	3	1 non-mag
6	2	1050	100	yes	sep.	29.8	25.9	-1.2	81	0	13	4	2 non-mag

*sim. = modified simultancous sintering and reduction sequence
sep. = separate sintering and reduction sequence

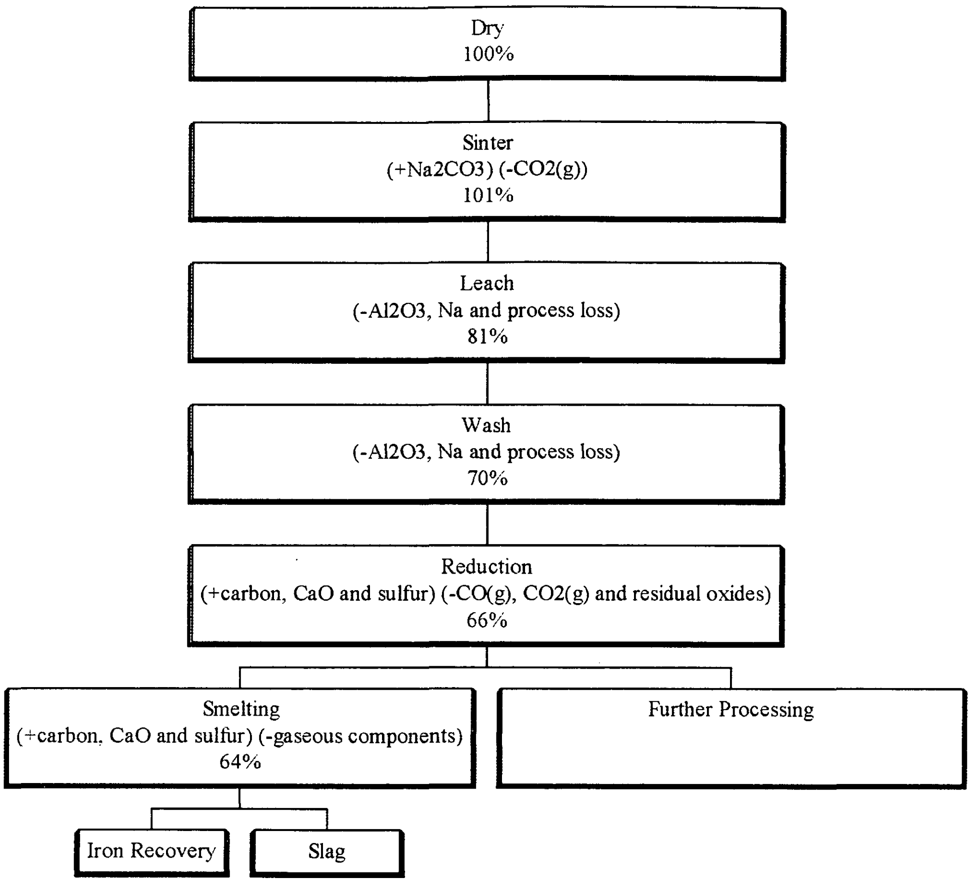
APPENDIX D

EQUILIBRIUM PRODUCTS FORMED IN RED MUD AFTER REDUCING AT VARIOUS TEMPERATURES USING 200% EXCESS CARBON



* Starting Composition: 71g Fe_2O_3, 12g Al_2O_3, 7g TiO_2, 7g CaO, 3g SiO_2 and 32g C.
Calculation performed by HSC software.

APPENDIX E
PERCENT WEIGHT LOSS OR GAIN AFTER PERFORMING VARIOUS EXTRACTION PROCESSES



+ Weight Gain
- Weight Loss
process loss- loss of product from coherency to containers and filters

APPENDIX F
SAMPLE CALCULATION FOR BLAST FURNACE ADDITION

For sample calculations, an average composition of different components in the charge is considered. The composition of red mud is altered three times to produce various results. Comparison of these results can then be assessed. All three red mud calculations followed the same calculational path. Results are presented following the calculation. For this sample calculation, the iron ore, coke, lime, red mud and final product are composed of the following. Note that the iron ore, coke, lime and final product compositions do not change throughout all calculations.

Compositions of Iron Ore, Coke, Lime, Leached and Reduced Red Mud and Final Product Required for Blast Furnace Calculation

Sample	Fe	FeO	Fe_2O_3	CaO	MnO	MgO	Al_2O_3	TiO_2	C	SiO_2
iron ore	-	-	92	1	1	1	3	-	-	2
coke	-	-	-	-	-	-	5	-	75	20
lime	-	-	-	95	-	-	2	-		3
red mud	65	10	-	11	-	-	2	9	-	3
final product	92	-	-	-	1 Mn	-	-	-	5	2 Si

For every 1000 kg of hot metal, 100 kg of red mud is supplied to blast furnace.

* 65% of 100 kg of red mud is Fe.

$$(0.65)(100) = 65 \text{ kg of Fe}$$

* Amount of Fe in hot metal.

$$(0.92)(1000) = 920 \text{ kg of Fe}$$

* Quantity of FeO in red mud.

$$(0.10)(100) = 10 \text{ kg of FeO}$$

* FeO reduction.

$$FeO + C = Fe + CO$$

$$10kgFeO * \frac{1molFeo}{71.85kgFeO} * \frac{1molFe}{1molFeO} * \frac{55.85kgFe}{1molFe} = 7.77kgFe$$

$$10kgFeO * \frac{1molFeo}{71.85kgFeO} * \frac{1molC}{1molFeO} * \frac{12.01kgC}{1molC} = 1.67kgC$$

* Amount of Fe from FeO in red mud.

7.77 kg Fe

* Amount of carbon necessary for FeO reduction.

1.67 kg C

* Quantity of Fe in hot metal after final red mud subtraction.

$$920-65-7.77 = 847.2 \text{ kg of Fe}$$

*Fe_2O_3 reduction.

$$Fe_2O_3 + 2C = 2Fe + CO_2 + CO$$

$$847.2kgFe * \frac{1molFe}{55.85kgFe} * \frac{1molFe_2O_3}{2molFe} * \frac{159.7kgFe_2O_3}{1molFe_2O_3} = 1211.3kgFe_2O_3$$

$$847.2kgFe * \frac{1molFe}{55.85kgFe} * \frac{2molC}{2molFe} * \frac{12.01kgC}{1molC} = 182.2kgC$$

* Quantity of Fe_2O_3 necessary for hot metal.

1211.3 kg Fe_2O_3

* Measure of C required for Fe_2O_3 reduction.

182.2 kg of C

* Quantity of iron ore brought in.

1211.3 kg Fe_2O_3/.92 = 1316.6 kg of ore

* Amount of Si necessary for hot metal.

(1000 kg) (0.02) = 20 kg of Si

* SiO_2 reduction.

$$SiO_2 + 2C = Si_{(in\ Fe)} + 2CO$$

$$20kgSi * \frac{1molSi}{28.09kgSi} * \frac{1molSiO_2}{1molSi} * \frac{60.09kgSiO_2}{1molSiO_2} = 42.8kgSiO_2$$

$$20kgSi * \frac{1molSi}{28.09kgSi} * \frac{2molC}{1molSi} * \frac{12.01kgC}{1molC} = 17.1kgC$$

* Quantity of SiO_2 required for hot metal.

42.8 kg SiO_2

* Amount of carbon necessary for SiO_2 reduction.

17.1 kg C

* Measure of Mn required for hot metal.

(0.01)(1000) = 10 kg Mn

* MnO reduction.

$$MnO + C = Mn + CO$$

$$10kgMn * \frac{1molMn}{54.94kgMn} * \frac{1molMnO}{1molMn} * \frac{70.94kgMnO}{1molMnO} = 12.91kgMnO$$

$$10kgMn * \frac{1molMn}{54.94kgMn} * \frac{1molC}{1molMn} * \frac{12.01kgC}{1molC} = 2.19kgC$$

* Amount of MnO necessary for hot metal.

12.91 kg MnO

* Quantity of C required for MnO reduction.

$$2.19 \text{ kg C}$$

* Amount of C necessary for hot metal.

$$(1000)(0.05) = 50 \text{ kg C}$$

* Total amount of C necessary for reduction and hot metal.

$$1.67 + 182.2 + 17.1 + 2.19 + 50 = 253.2 \text{ kg of C required overall}$$

* Total amount of coke required.

$$253.2/0.75 = 337.6 \text{ kg of coke}$$

* Total amount of SiO_2 overall.

$$67.5 + 3 + 26.3 = 96.8 \text{ kg } SiO_2$$

* Quantity of SiO_2 in slag.

$$96.8 - 42.8 = 54 \text{ kg } SiO_2$$

* Total amount of Al_2O_3 in slag.

$$(0.03)(1316.6) + (0.05)(337.6) + (0.02)(100) = 58.4 \text{ kg } Al_2O_3$$

* Measure of MgO in slag.

$$(0.01)(1316.6) = 13.2 \text{ kg MgO}$$

* Measure of MnO in slag.

$$(0.01)(1316.6) = 13.2 \text{ kg MnO}$$

$$13.2 - 12.91 = 0.3 \text{ kg of MnO in slag}$$

* Measure of TiO_2 in slag.

$$(0.09)(100) = 9 \text{ kg } TiO_2$$

* Amount of CaO required.

$$(0.95x(\text{CaO lime}) + 13.2(\text{CaO iron ore}) + 0.3(\text{MnO}) + 13.2(\text{MgO}) + 11(\text{red mud CaO}))/(54(SiO_2) + 58.4(Al_2O_3) + 9(TiO_2) + 0.03x(SiO_2 \text{ lime}) + 0.02x(Al_2O_3 \text{ lime})) = 1$$

$$x = \text{lime} = 93 \text{ kg}$$

$$88.4 \text{ kg CaO}$$

$$1.86 \text{ kg } Al_2O_3$$

2.79 kg SiO_2

* Slag formation.

$$13.2\ (MgO) + 0.3\ (MnO) + 56.79\ (SiO_2) + 9\ (TiO_2) + 60.26\ (Al_2O_3) + 112.55\ (CaO)$$
$$= 252.1 \text{ kg of slag}$$

Composition of Slag

5.2% MgO	3.57% TiO_2
0.12% MnO	23.9% Al_2O_3
22.5 % SiO_2	44.6% CaO

Results of Blast Furnace Calculation Produced from Various Starting Red Mud Compositions

kilograms of red mud	coke consumed (kg)	slag produced (kg)	lime consumed (kg)
none	356	245	98
100 (37% Fe) (presented in thesis)	346	284	98
100 (65%Fe) (presented above)	338	252	93