Recovery of value-added products from red mud

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Abstract

The major waste product of the alkaline extraction of alumina from bauxite (Bayer Process) is known as red mud. Approximately one ton of red mud is produced for every two tons of bauxite mined. The red mud produced from Jamaican bauxite is rich in hematite, alumina and titanium oxide. It has been shown that more than 90% (by weight) alumina can be recovered from red mud by soda ash sintering and caustic leaching. Hematite can be carbothermically reduced with a degree of metallization of more than 94%, resulting in attempts for magnetic separation. These separations are desirable because there are no waste products generated. Consequently, there is an opportunity for complete utilization of the waste material. Conversely, the preseparated material could be charged through the tuyeres in an iron blast furnace, or it could be smelted to produce pig iron. If smelted, the concentration of titanium oxide in the slag would be high enough to justify its recovery by an established acid-leach process. This paper describes the results of alumina recovery and the plans for titanium oxide recovery from red-mud. In addition, the situation of ongoing efforts in iron extraction, particularly, the method of magnetic separation of the reduced material. The problems associated with the use of reduced red mud as an alternative to direct-reduced iron (DRI) is also discussed. A critical assessment of the recovery sequence chosen for the products is described based on economics.

Key words: Red mud, Waste product utilization, Alumina recovery, Titanium oxide, Iron

Introduction

The pyrochemical extraction of alumina from bauxite leaves behind process waste called red mud. Red mud produced from Jamaican bauxite 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. This work has determined the possibility of extracting various value-added products from red mud produced from north coast Jamaican bauxite, and the work has developed the sequence of extraction for the various products. In addition, intrinsic characteristics of the red mud have been identified, and some potential commercial applications for the products have been recommended.

The removal of alumina, iron and titanium oxide from red mud can be approached in a number of ways. The composition of bauxite varies widely around the world and requires different conditions in the Bayer process for successful alumina extraction. After processing, the different bauxites result in varying red mud compositions. The former US Bureau of Mines examined the extraction of these three constituents from Jamaican red mud (Fursman et al., 1970). The extraction of alumina entails combining the mud with sodium carbonate at high temperatures to form sodium aluminate, a process 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 or partially 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 in a number of ways. The classical Kroll Process subsequent to carbochlorination is possible if the titanium oxide is in the form of rutile. 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 and, for this reason, should only be performed after the other constituents are removed. Thus, the sequence of removal of the value-added products is a vital issue for success in extraction.

The sequence thoroughly investigated in this work comprises the separate sintering and reduction steps to recover alumina followed by iron. The red mud is dried, sintered, leached and washed to remove the alumina. The material is then reduced and magnetically separated and smelted, if necessary, to recover iron. The remaining nonmagnetic 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 com-

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Table 1 — Composition of dried north coast Jamaican Bauxite and the generated red mud and trihydrate

Compound	Percent in bauxite	Percent in red mud	Percent in trihydrate
Al_2O_3	56.4	11.7	11.0
SiO_2	0.7	2.5	0.8
CaO	1.2	6.6	2.1
TiO_2	4.3	7.1	6.7
Fe_2O_3	35.1	67.7	77.2
Others*	2.3	4.4	2.3

*P, S, Cr, Mn, Zn and Cd

position to Portland cement, providing an avenue for complete utilization of red mud in an ideal situation. The extraction process mentioned above demonstrates the use of well-established technologies. 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 abide by the normal behavior of uncontaminated compounds. The red mud, thus, behaves with some degree of unpredictability. However, using the composition listed in Table 1, the aluminum industry could annually recover 24, 2.5 and 4.3 Mt (27, 2.8 and 4.7 million st) of Fe_2O_3, TiO_2 and Al_2O_3, respectively, if such metal retrieval processes are effective (Piga et al., 1993).

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 could be used as an ingredient for iron making or as a pigment for pottery making. The nonmagnetic portion can be applied in building materials or supplemented back into the Bayer process. However, recovery of the iron is low (Braithwait, 1982). Another investigator reduces the iron with chlorocarbons before magnetic separation and uses the resulting magnetic portion as feed for iron making (Agency of Ind. Sci. Tech., 1997).

Another research suggests drying the red mud, blending with lime and ground coal and feeding the mixture into a machine that agglomerates it into 12.7-mm- (0.5-in.-) diam balls. Subsequently, 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 high-quality steel is produced. The final product yields about 98% to 99% iron (Guccione, 1971). 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 (Dakatos et al., 1978). 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 to 9 MPa. This solution is supplemented into the Bayer process for increased alumina recovery (Cresswell and Milne, 1981). One approach uses 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 (Vachon et al., 1994). 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. 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 (Vereinigle Aluminum-Werke, 1971).

The simultaneous recovery of aluminum, iron and titanium has been investigated by a number of researchers. One method uses 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 (Baetz and Lightbourne, 1972). The former US Bureau of Mines 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 one hour. After leaching, the blend is washed and magnetically separated in a Davis tube, leaving both a magnetic and nonmagnetic compound. The nonmagnetic 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 hrs 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 stoichiometric. 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 1,480°C, suggesting almost full reduction. The principal components after smelting include alpha iron, austenite and $CaTiO_3$. This work 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 (Fursman et al., 1970). It should be noted that the presence of high levels of lime does not allow the application of carbo-chlorination and Kroll Process for the recovery of titanium.

Experimental studies

The optimized sequence of steps is shown in Fig. 1. The figure shows the separate sintering and reduction sequence used to extract alumina, iron and titanium oxide from red mud.

Drying and sintering. The intent of a drying operation is to eliminate the moisture and some of the volatiles from the red mud. First, a sample of the red mud is weighed to a tenth of a gram and placed in a MgO crucible. The crucible is then heated to 400°C at a rate of 3°C/min. This temperature is maintained for up to two hours in a N_2 atmosphere, with the N_2 being feed at a rate of 16 to 24 cm^3/s (2 to 3 cu ft/hr). The crucible is then cooled at a rate of 3°C/min, and the red mud is weighed. After drying, the red mud is ground and sieved to -70 mesh (212 mm) to provide for improved contact between constituents in subsequent reactions.

Sintering is performed to react the sodium carbonate with alumina forming water-soluble sodium aluminate. The alumina content is determined using SEM-EDS analysis. Using the predetermined alumina content, the amount of sodium carbonate is calculated based on

$$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2(g) \qquad (1)$$

Depending on the experiment, the amount of sodium carbonate varies from the stoichiometric value to a maximum of

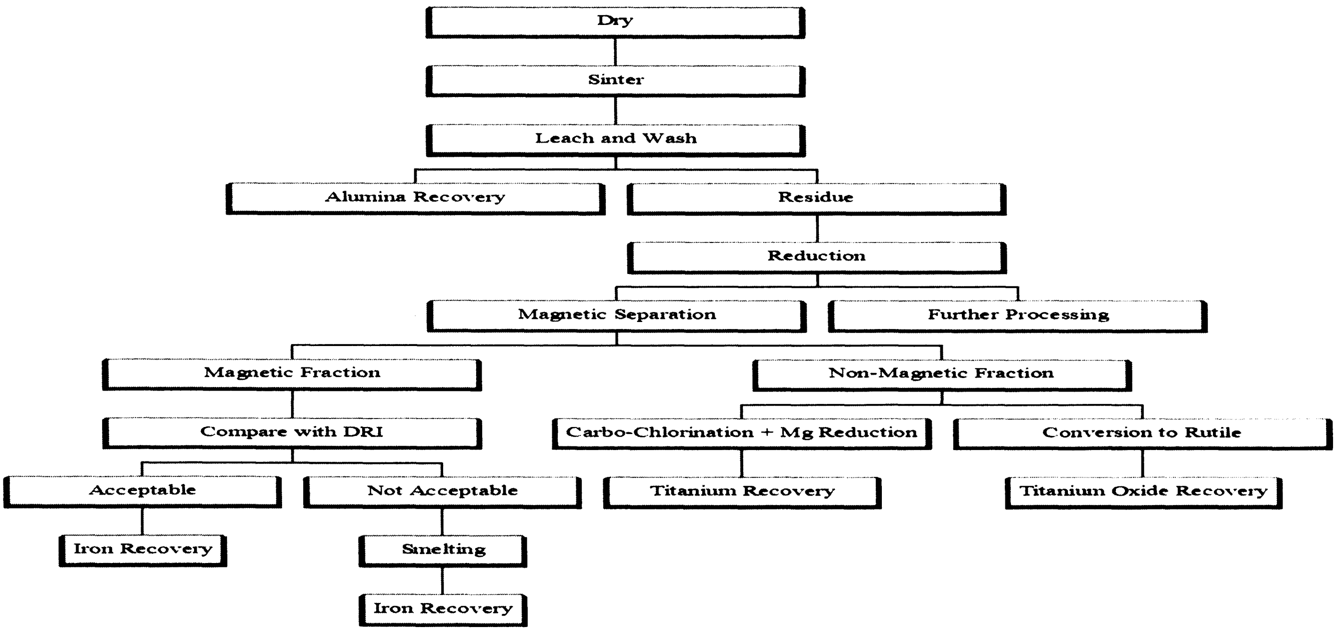

Figure 1 — diagram of the separate sintering and reduction sequence used to extract alumina, iron and titanium oxide from red mud.

100% excess. A MgO crucible is used to contain the mixture and is inserted into the furnace. The sample is heated at a rate of 2°C/min to the specified temperature in a N_2 atmosphere, with a N_2 flow rate of 30 cm^3/s (4 cu ft/hr). The temperature of sintering is 1,005°C. The time of sintering is 4 hrs in all experiments. The sample is cooled at a rate of 3°C/min and is again weighed after cooling.

Leaching and washing. The objective of leaching is to dissolve the sodium aluminate product into solution based on

$$NaAlO_2(s) = Na^+ + AlO_2^- \qquad (2)$$

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 leaching solution required per kilogram of sintered and reduced red mud has been determined using the graph shown in Fig. 2. This figure is used to calculate the caustic required for leaching by first determining the amount of sodium oxide contained in the mud from sintering (sodium carbonate) and then subtracting this value from 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 the experiments. Excess caustic ranging from zero to 100% is used depending on the experiment. Upon reaching 65°C, the red mud is added to the solution, stirred for 2 hrs and filtered. After leaching, residual amounts of sodium remain in the red mud residue. A wash is performed to increase the alumina recovery as well as to dissolve the sodium compounds. The temperature range for the washing experiments performed is 70°C. The ratio of red mud to distilled water is 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 is 2 hrs. The mud is again filtered, dried and weighed after leaching and washing.

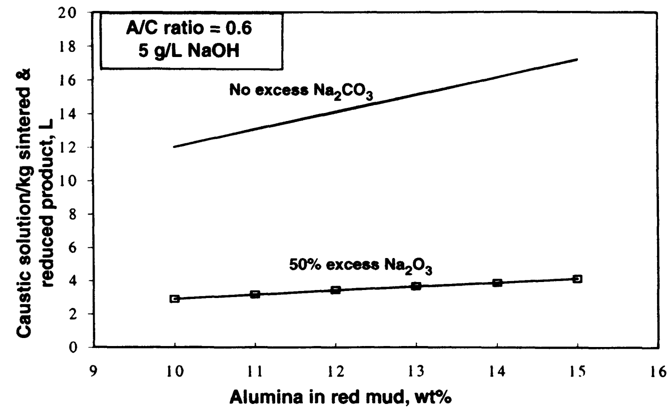

Figure 2 — Requirment of caustic solution for leaching experiments performed in the extraction of alumina from red mud.

Reduction of iron. The focus of reduction is to get iron into a magnetic form in preparation for magnetic separations. Magnetite and elemental Fe are both magnetic. For a complete reduction of the iron, the carbon content is calculated using the iron oxide content and the following reduction reaction

$$Fe_2O_3 + 3C = 2Fe + 3CO(g) \qquad (3)$$

And for a partial reduction of the iron, the carbon content is calculated using the iron oxide content and the following reduction reaction

$$3Fe_2O_3 + C = 2Fe_3O_4 + CO\ (g) \qquad (4)$$

The amount of carbon is varied from 100% excess of stoichiometry to 300% excess. Petroleum coke is used as the reductant. The red mud and coke are measured out and ground to -70 mesh. The mixture is then placed in a MgO crucible.

Depending on the experiment, a CaO powder layer is placed on top of the mixture. The crucible is placed into the furnace and heated at a rate of 3°C/min up to the required temperature and held for 2 to 4 hrs. A N_2 atmosphere is used at a flow rate of 24 to 32 cm^3/s (3 to 4 cfh). The temperature ranges from 600° to 1,100°C for partial and full reductions. Afterwards, the sample is cooled at a rate of 3°C/min and then

Table 2 — Iron compounds detected in red mud by Moßbauer characterization.

Compound	Description
Fe_2O_3	Hematite, also described as magnetic Fe_2O_3; a canted antiferromagnetic that displays a very weak magnetic signal
Fe_3O_4	Magnetite, magnetic
FeO	Wüstite, nonmagnetic
Fe	Iron usually in the form of ferrite, ferromagnetic
Fe/Fe_3O_4	Not able to decipher between Fe and Fe_3O_4
Nonmagnetic	Iron constituent that displays nonmagnetic characteristics; could be austenite
Magnetic oxide	Fe_3O_4 or Fe_2O_3
Fe^{2+} and Fe^{3+}	Iron depleted of two or three electrons; could be combined with other red mud constituents such as silicon; displays magnetic and nonmagnetic characteristics

Table 3 — Conditions and results of alumina extraction.

	Sintering conditions		Leaching conditions			Washing
Run	Temp., °C	Excess soda, %	A/C ratio	Excess caustic, %	Rec. Al_2O_3, %	Rec. Al_2O_3, %
1	850	50	0.6	100	66.7	76.8
2	950	50	0.6	100	67.4	81.4
3	1,050	50	0.6	100	69.6	83.1
4	950	0	0.6	100	62.7	66.2
5	950	50	0.6	100	66.9	75.3
6	1,050	50	0.6	0	59.9	76.0
7	1,050	50	0.6	150	39.9	54.3

weighed. The material is then analyzed using Moßbauer Spectroscopy.

Magnetic separation is performed on the red mud to exclusively separate the iron from the remaining constituents by both a crude wet and a Davis tube separation. Both the magnetic and nonmagnetic materials are then dried. Analysis of the solid product at various stages is performed be SEM-EDAX, XRD and Moßbauer spectroscopy (Table 2). The leach solutions were analyzed by atomic absorption spectroscopy.

Characterization. Thermo-gravimetric analysis and differential thermal analysis (TGA/DTA) are used to observe weight loss and enthalpy behavior during reduction. Two tests are performed with varying amounts of carbon at 100% and 200% excess of stoichiometry. The experiments consist of heating the sample at 20°C/min from room temperature to 1,050°C and holding for five hours in an inert atmosphere of argon.

Extraction of alumina. 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 increases the tendency of the reaction to occur by increasing its change in Gibbs energy. Amount of sodium carbonate influences the amount of sodium aluminate formation. Concentration of sodium hydroxide solution, time for leaching, temperature of leaching and A/C ratio all remained constant. Therefore, leaching behavior was only affected by the volume of leach liquor. Washing the residual sodium aluminate from the red mud is an important step in improving alumina recovery. The washing conditions are kept constant at 100°C for 15 minutes using a ratio of 10 g of red mud per liter of distilled water. The results from the experiments on alumina extraction are summarized in Table 3.

Alumina extraction increases as temperature increases. At 850°C, sodium aluminate forms, but not all of the alumina available for reaction is converted. At 1,050°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. Alumina recovery subsequent to washing demonstrates the true extent of sodium aluminate formation. 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. As the excess of 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, the washing conditions mentioned previously are not appropriate for complete dissolution of the remaining sodium aluminate. Complete alumina extraction does not occur under any condition. This observation is possibly due to the availability of the alumina to react with the sodium carbonate and the kinetic limitations of the reaction. Alumina extraction is a feasible process and its oxide can be successfully recovered to as much as 84% by sintering at 1,050°C using 50% excess sodium carbonate and leaching is performed using 100% excess caustic followed by a wash.

A thermodynamic analysis is performed on red mud during sintering using 50% excess sodium carbonate and is shown in Fig. 3. 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.

Extraction of iron. The processes to extract iron includes reducing the iron oxide to elemental iron or magnetite, magnetically separating the iron from the red mud, evaluating the iron product for commercial use and smelting (if necessary) to recover iron as a value added product and investigation for use of the nonmagnetic material.

Results and discussion

Each of these steps depends on a number of variables, significantly altering the individual end products. These variables include the carbon content, temperature, time and the presence of a calcium oxide layer, which maintains a reducing atmosphere. Table 4 summarizes the results gathered from experiments performed on the complete reduction of the iron. It should be noted that the source of carbon is petroleum coke, which is not the best reductant for iron oxide because it lacks volatile matter and moisture. Attempts were made to use graphite as a source for carbon in reduction. But graphite proved deficient in comparison to petroleum coke. The table

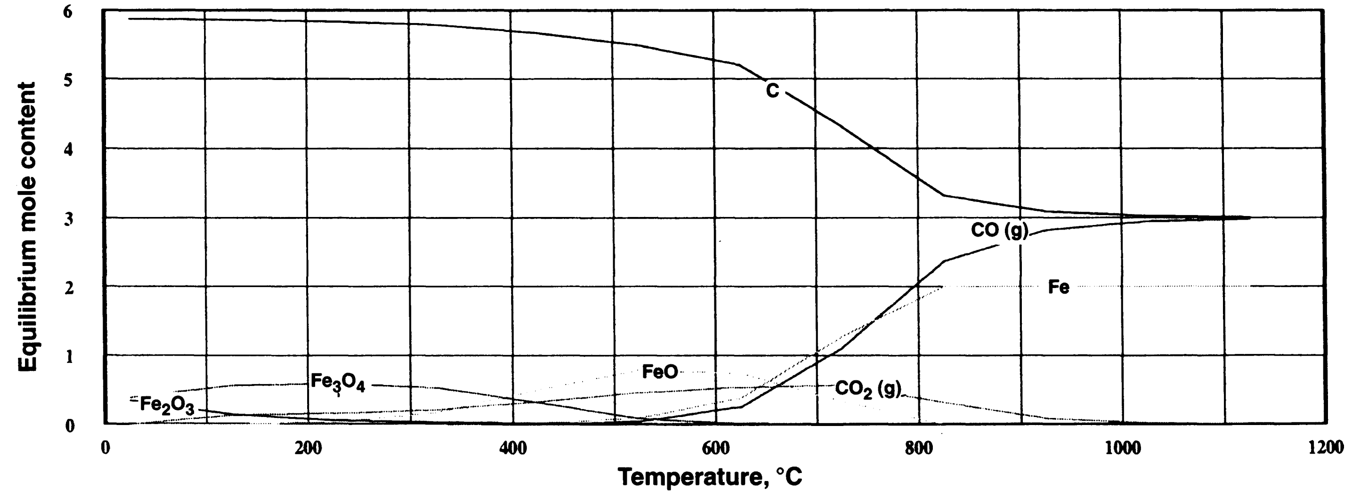

Figure 3 — Equilibrium products in red mud after sintering at various temperatures using 50% excess sodium carbonate. Starting composition: 71 g Fe_2O_3, 12 g Al_2O_3, 7 g TiO_2, 7 g CaO, 3 g SiO_2 and 18 g Na_2O_3.

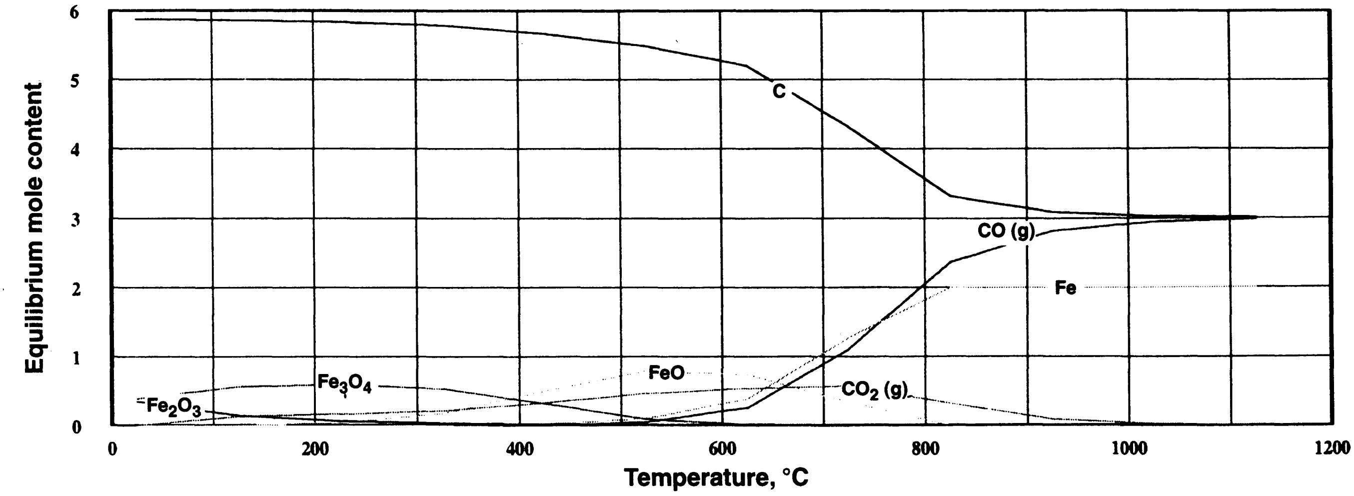

Figure 4 — Effect of temperature on the equilibrium iron products formed during reduction of Fe_2O_3 using 200% excess carbon.

Table 4 — Conditions and results of reduction experiments.

	Reduction conditions			Weight loss			Moßbauer analysis				
Exp.	Time, hr	Temp., °C	xs C, %	Lost, %	Th. loss, %	Diff., %	Fe, %	FeO, %	Fe_3O_4, %	Fe_2O_3, %	Other, %
1	2	650	300	17.6	22.6	5	32	5	55	0	8 Fe^{2+}
2	4	1,050	300	26.4	22.6	-3.8	92	5	-	-	3 Fe_3C
3	2	1,050	300	26.5	22.6	-3.9	93	4	-	-	3 Fe_3C
4	2	1,050	200	25.6	24.1	-1.5	96	3			3 Fe_3C
5	2	1,050	200	25.2	24.1	-1.1	88		8	3	1 nonmag
6	2	1,050	100	29.8	25.9	-1.2	81	0	13	4	2 nonmag

shows whether reduction has taken place (weight loss) and shows the extent of reduction (Moßbauer analysis).

As temperature increases, reduction also increases, as seen by the weight loss and products detected by the Moßbauer. Different temperatures prefer different oxide states. Figure 4 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). 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 and the results of the experiments, it was concluded that to achieve almost full reduction, temperatures around 1,050°C should be used. It was found, in an attempt to ensure adequate energy for reduction, that small increases in temperature above 1,050°C caused the iron to agglomerate (sinter), resulting in poor reduction. Time has no effect on the reduction conditions, except that a minimum time is required for complete reduction, which was achieved in approximately 2 hrs. A layer of calcium oxide does increase the amount of reduction in the iron, as seen by the Moßbauer results and weight loss differences. As mentioned above, the calcium oxide layer promotes a more reducing environment by trapping the carbon monoxide involved during reduction. There is a disadvantage using lime because calcium and titanium form perovskite, which is suspected to possess an affinity for the iron. X-ray diffraction verifies the existence of perovskite, and magnetic separations support this theory of association. The addition of calcium encourages the affiliation. As carbon content increases from 100% excess to 200%

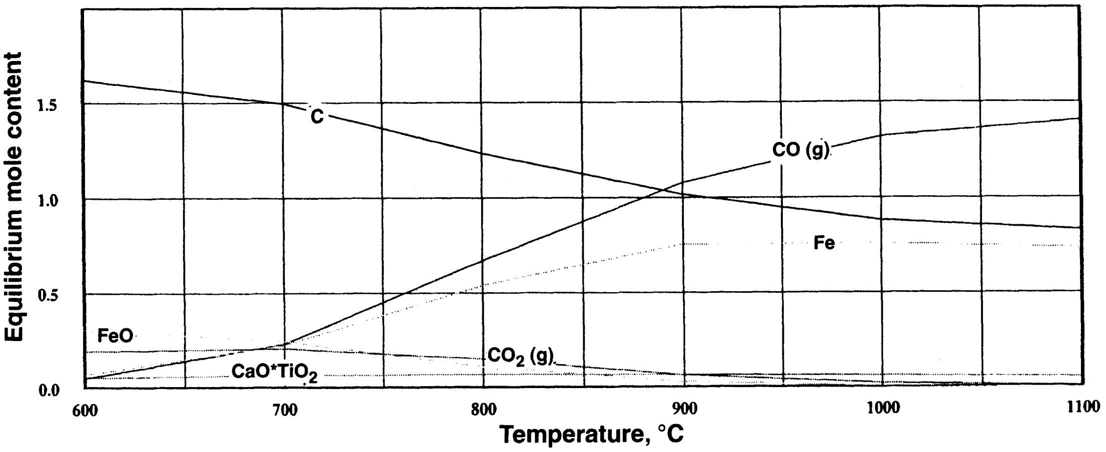

Figure 5 — Equilibrium products formed in red mud after reducing at various temperatures using 200% excess carbon. Starting composition: 71 g Fe_2O_3, 12 g Al_2O_4, 7 g CaO, 3 g SiO_2 and 32 g C.

excess, almost complete reduction is observed via the Moßbauer results. The effects of carbon content are further examined by performing TGA/DTA. Two samples were separately heated up to 1,050°C at a rate of 20 °C/min and held for five hours in an argon atmosphere. The only variable in these experiments was carbon content.

Large drops in weight occured at 630°C for 100% excess carbon and at 930°C for 200% excess carbon. Weight losses over the entire temperature cycle are 21.7% and 33.6% for 100% and 200% excess C, respectively. Stoichiometrically, the weight loss should be 26.1% for 100% excess carbon and 24.0% for 200% excess carbon. In the 100% excess C sample, a sudden drop in weight occurs at 630°C, which promotes Fe_3O_4 formation. In the 200% excess C sample, weight loss occurs at 930°C, which promotes products such as Fe and FeO. As carbon content increases, the temperature at which measurable reduction occurs 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 (Bodsworth and Bell, 1972). To achieve almost full reduction at 1,050°C, 200% excess carbon is sufficient.

As high as 95% reduction of iron oxide to elemental iron is attained by reducing the red mud at 1,050°C for 2 hrs containing 200% excess carbon content and a calcium oxide layer. A thermodynamic analysis is performed on red mud during reduction using 200% excess carbon presented in Fig. 5. Based on the results of these experiments, attempts were made to control the reduction and yield a high concentration of magnetite. The reaction could not be regulated to prevent the continuation of reduction. This experimentation produced limited success with a conversion of less than 50% in all efforts. Therefore, there were no magnetic separations attempted on this partially reduced material. More investigations in this area are planned.

Magnetic Separation. Magnetic separation is performed to separate the reduced iron from the remaining mixture. There were three methods investigated: crude wet, crude dry and Davis Tube magnetic separations. Several tests were performed in an attempt to separate the nonmagnetic 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 6 shows the magnetic and the nonmagnetic composition of two trials of Davis tube separation on red mud. Figure 7 shows the same separation but omitting iron for better resolution of subsidiary constituents. Optimum results would display 100% iron in the magnetic product and the remaining constituents in the nonmagnetic product. It should be noted that, in addition to iron, calcium and titanium also report to the magnetic product, while sulfur, phosphorus and silicon segregate to the nonmagnetic product. Iron also distributes to the nonmagnetic portion of the red mud. All other constituents appear to be about equally divided. Iron, calcium and titanium appear intimately mixed, or exhibit some type of affinity with each other, in all magnetic separations. 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. Under the assumption that this affiliation occurred in the sintering portion of the extraction process, the magnetic separation was attempted on the raw red mud and trihydrate materials after being subjected to a full reduction only. The results of these separations showed no difference in the final compositions. Possibly during reduction, the manganese and sulfur react with the help of carbon to form manganese sulfide, a nonmagnetic compound. The presence of iron in the nonmagnetic product could be due to residual FeO remaining from reduction. Magnetic separation is not a completely successful procedure, as is readily apparent, but continued efforts will be devoted to this objective.

Iron product and smelting. After magnetic separation, the final step in iron recovery is the evaluation of the iron product. The red mud, after an unsuccessful magnetic separation, contains up to 65% reduced iron and oxides with the balance elements: calcium, aluminum, sodium, titanium, manganese, silicon, phosphorous and sulfur. This product does not compare with the direct reduced iron, which is typically 90% iron. Smelting can be performed on the unseparated red mud. If performed, smelting should be successful, recovering pig iron in the molten phase. Metallurgical techniques such as sulfation and carbo-chlorination are suggested for the extraction of titanium oxide. Conversion of perovskite to rutile, via sulfation, is a prerequisite to carbo-chlorination. However, H_2SO_4 used in the sulfation step forms iron sulfates. The unseparated, reduced red mud is not a practical material for this process

Table 5 — Composition and weight change in red mud after various extraction processes.

Process	Fe_2O_3, %	FeO, %	Fe, %	Al_2O_3, %	TiO_2, %	CaO, %	SiO_2, %	Other, %	Wt%
Dried at 400°C, 1 hr	67.7	-	-	11.7	7.1	6.6	2.5	4.4	100
Sintered at 950°C, 2 hr, 50% excess soda	56.4	-	-	12.7	6.7	8	2.4	13.8	101
Leached at 65°C, 1.5 hr, 100% excess caustic	66.0	-	-	5	8.1	11.1	2.5	7.3	81
Washed at 100°C, 15 min, 10g/L	69.3	-	-	2.8	8.4	12.5	1.9	5.1	70
Reduced at 1,050°C, 2hr, 200% excess C; CaO layer	-	5.2	36.5	6.7	14.8	19.8	3.7	13.3	66
Smelted at 1,650°C	-	19	>90	-	29	22	7.5	22.5	64

because of the high iron concentration. Thus, recovery of titania from red mud requires that iron be removed prior to sulfation. However, the nonmagnetic portion of the separated red mud is suitable for sulfation. After sulfation, during carbo-chlorination, chlorine reacts with several constituents besides titanium oxide, such as lime. Carbo-chlorination is not an adequate process for the extraction of titanium oxide in the presence of a large quantity of lime. There is a large quantity of lime in the separated and unseparated products.

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. Table 5 shows the material-balance flow sheet.

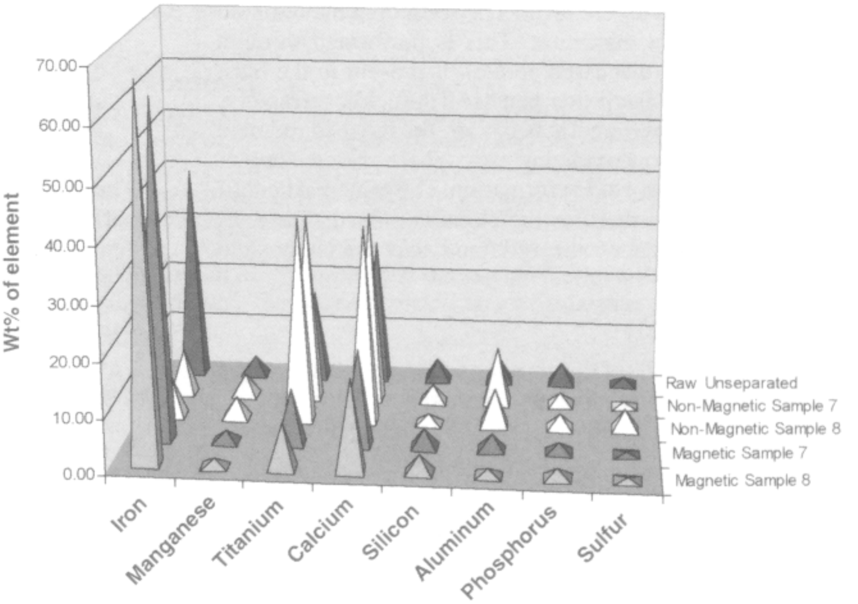

Figure 6 — Davis tube separation of red mud (all constituents).

Blast furnace supplement. The red mud contains approx. 40% fully reduced iron, 5% iron oxide (FeO), 17% titanium oxide, 20% calcium oxide, 4% alumina and 2% silicon oxide after processing, with the balance being the following constituents in order of decreasing quantity: manganese, sulfur, phosphorus and sodium.

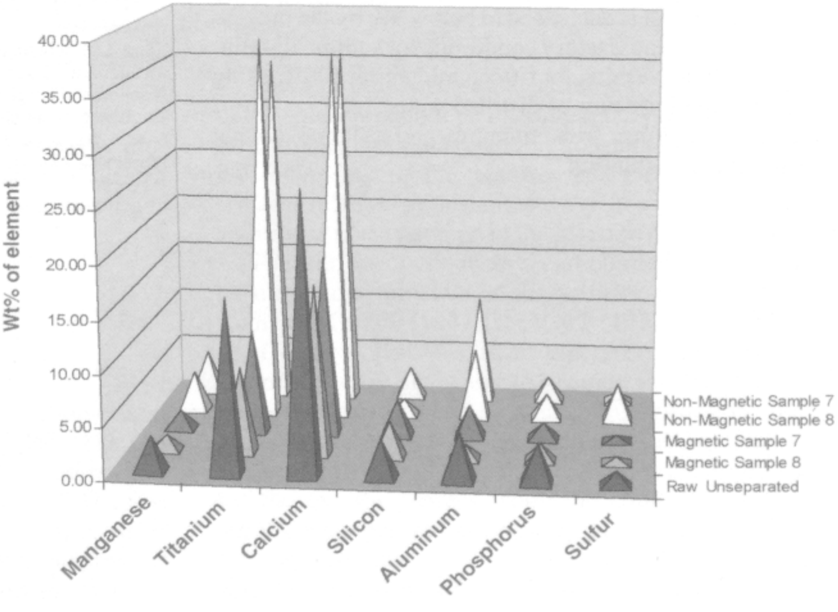

Figure 7 — Davis tube separation of red mud (nonmagnetic constituents).

A potential application for alumina depleted and reduced red mud could be in the iron making blast furnaces. A preliminary calculation is made on adding 100 kg of red mud to one ton of hot metal. 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 6. The TiO_2 serves as a blast furnace hearth protector, acting as an acidic component by enhancing the silica rich refractory. The red mud also contains calcium oxide that, 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, this constituent does not increase the slag melting point. The uranium and thorium present in the red mud oxidize in the furnace and, therefore, they 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

Table 6 — 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	13	5	37	20	-	-	6	15	-	4
Final product	92	-	-	-	1 Mn	-	-	-	5	2 Si

the steel. The red mud is in powder form and ought to be added to the furnace at the tuyere level. The sodium in the red mud should be kept to a minimum. This is performed through extensive washing (discussed above). If present in the blast furnace, sodium, a basic oxide, 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.

Conclusions

- As much as 83% of the alumina and almost 100% of the sodium oxide are recovered from the red mud by:
  - sintering at 1,050°C for two hours using 50% excess sodium carbonate above stoichiometry,
  - leaching with 5g/L NaOH at 65°C for 1.5 hrs using a 0.6 A/C ratio and
  - washing at 100°C for 15 min using 10 g of red mud per liter of distilled water.
- At least 94% reduction of the iron is achieved when the red mud is reduced at 1,050°C for 2 hrs using 200% excess carbon above the stoichiometry covered by a fine layer of calcium oxide.
- 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 2 g red mud per liter of distilled water.
- During leaching, iron, titanium and calcium do not dissolve into solution.
- The red mud, prior to processing, exhibits unusual magnetic characteristics caused by either inherent particle size or aluminum solubility in iron.
- There are promising results in the avenue of magnetic separation, with success providing an opportunity for complete utilization of the material.

These investigations are continuing. In light of these pending efforts, some alternative routes for utilization are suggested. These suggestions include using the red mud after prior processing in a blast furnace, smelting the red mud to recover pig iron and slag rich in titanium and then extracting the titanium from the slag through sulfation.

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