

# OPPORTUNITIES FOR HIGH VOLUME COMMERCIAL PRODUCTS CONVERSION FROM BAUXITE RESIDUE

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## Abstract

*The alkaline extraction of alumina from bauxite ore [Bayer Process] generates a major waste product known as red-mud. Approximately, a tonne of red-mud is produced for every two tonnes of bauxite ore that is mined. The primary aluminium production generates approx. 120 million tonnes of red mud each year globally. The red-mud produced from Jamaican bauxite is rich in hematite, alumina and titanium oxide. It has been shown that, over 90 wt% alumina can be recovered from red-mud by soda-ash sintering and caustic leaching that can be reverted back to the Bayer Process. Hematite can be reduced with a degree of metallisation of over 94 % or over 92 % of the hematite can be partially reduced to magnetite. A completely reduced material could be charged through the tuyeres in an iron blast furnace or smelted to produce pig iron. A viable material balance has been included in this paper. This paper will describe the successful efforts of iron and alumina recovery. The problems associated with the use of reduced red-mud, as an alternative to direct-reduced iron [DRI] have been discussed.*

## Introduction

Red mud is the bauxite residue generated from the digestion stage of the Bayer's process to extract alumina from the bauxite ore. This is a potential solid waste and has a global reserve of 2.7 billion tonnes.<sup>1</sup> The production of one tonne of aluminium yields about 1.5-4 tonnes of red mud depending on the characteristics of the bauxite ore used. The high dependence of red mud composition on the bauxite ore makes processing red mud in a single universal route is highly improbable. The processes developed for processing red mud are not economical which leaves the option to dispose it as a waste.

Red mud being basic in nature poses a difficulty in its efficient disposal. The lack of which could cause a high degree of environmental pollution, ground water pollution. Ajka Aluminum refinery red mud storage breakout in Hungary, October 2011 was the biggest incident involving red mud causing widespread damage to property and life.

Chemically, red mud contains about Fe<sub>2</sub>O<sub>3</sub>: 67 %, Al<sub>2</sub>O<sub>3</sub>: 12 %, TiO<sub>2</sub>: 7.1 %, CaO: 6 %, SiO<sub>2</sub>: 2 %. In addition to these, red mud contains some trace elements such as: K, Cr, V, Ni, Ba, Cu, Mn, Pb, Zn, Sc, Ga, also as oxides.

Most of the research on the application of red mud is being done in the area of construction materials like cements and bricks.<sup>6-8</sup> Red mud utilisation as catalysts, adsorbents for waste water treatment has been widely researched.<sup>2-5</sup> Red mud was also used in ceramics which utilised from 0 wt% to 50 wt%. But the role of red mud in glass-ceramics is strongly affected by the thermal treatment.<sup>9-10</sup>

Some efforts have been made in the area of metal recovery from red mud for the metals Fe, Al, Ti, Na, V, Sc, and Ga.<sup>11-16</sup> But very few of them have been put into commercial scale. So we have picked up this aspect of red mud processing termed as “High volume low value products form red mud” for our study using the Jamaican Bauxite residue.

## **Recovery of Valuable Metals from Red Mud**

### **Recovery of Aluminium and Sodium from Red Mud**

Red mud contains about 2.2 % - 33 % of alumina.<sup>17</sup> Alumina is recovered either by forming sodium aluminate (soda ash roast) or by incorporating organic reagents hydrometallurgically. Zhang et al. recovered alumina hydro chemically by the formation of grossular hydrogarnet. In a work by Li Zhong et al., about 87.8 % of alumina from the red mud was extracted using mild hydro-chemical process conditions utilising NaOH pressure leaching which is essentially a repeat of the Bayers process.<sup>18</sup>

Smelting was tried on red mud by Bruckard et al. which was mixed with calcium carbonate at 1400 °C. The Al and Na could be easily recovered due to the phase transformation into (Na,Ca)<sub>2-x</sub>(Al,Fe<sup>3+</sup>)<sub>2-x</sub>Si<sub>x</sub>O<sub>4</sub>.<sup>20</sup> The slag was subjected to water leaching at 60 °C, 55 % Al and 90 % Na could be recovered at 50 % pulp density.

Li et al. have attempted to devise a simultaneous sintering process for alumina recovery and converting hematite to magnetite. They found out that sintering temperature and amount of carbon have great influence on alumina recovery.<sup>21</sup> A high recovery of 75.7 % Al, 80.7 % Na can also be obtained by the soda lime roasting followed by the water roasting of red mud.<sup>22</sup>

## Recovery of Iron from Red Mud

Iron is the major constituent in red mud. The concentration of Fe in iron oxides varies between 6.8 wt% and 71.9 wt%, depending on the grade of bauxite.<sup>23,24</sup> A prior reduction of the hematite in red mud transforms it into a magnetic product which can be separated by magnetic separation. Li et al. suggested that pulsating magnetic current utilisation would provide better separations than the conventional magnetic current. HGMS can separate magnetic particles of size less than 100 µm.<sup>25</sup> It was observed that weakly magnetised particles are attracted.

Xiangong et al. told that an addition of calcium, sodium or magnesium salt can improve the efficiency of carbon based direct reduction of iron in red mud. Jayasankar et al. has proposed that addition of 10-12 % dolomite would increase iron recovery to 71 %. A recovery of 94.5 wt% Fe can be obtained by employing 6 % Na<sub>2</sub>SO<sub>4</sub> and 6 % Na<sub>2</sub>CO<sub>3</sub> in the mixture.

The soda ash roasting and leaching process by Liu et al., described in the previous section, generates a leach residue consisting of magnetite, hercynite and TiFe<sub>2</sub>O<sub>4</sub>. The iron recovery decreases because of agglomeration of ferrous phases and other impurities.

Acid leaching of recovering iron also was investigated, a high recovery of iron 97.46 % Fe can be obtained at calcination temperature of 600 °C and subsequent leaching in 6M H<sub>2</sub>SO<sub>4</sub>.

## Experimental

### Drying and sintering

The intent of a drying operation is to eliminate the moisture and some of the volatiles from the red mud. The red mud sample is heated to 200 °C. The sample is then ground to < 180 µm.

Sintering is performed for the reaction of sodium carbonate with alumina forming water soluble sodium aluminate.



The sodium carbonate content is varied from stoichiometric amount to 100% excess. The sample is heated in a MgO crucible in N<sub>2</sub> atmosphere. The temperature of sintering ranges from 850 °C to 1100 °C. The time of sintering is 2 hours. The sample is cooled and weighed.

## Leaching and washing

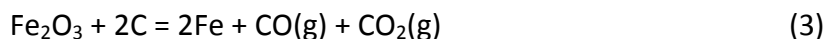
Sodium carbonate roasting is generally followed by the water/sodium hydroxide leaching dissolving sodium aluminate into the solution.



A wash is performed to increase the alumina recovery as well as to dissolve the sodium compounds. The temperature range varies between 25 and 100 °C for 5-30 minutes. The ratio of red mud to water varies between 2 and 50 g/l.

## Reduction and magnetic separation

The objective of these experiments is to reduce the hematite to metallic iron and followed by magnetic separation to separate the iron.



The amount of carbon is varied from 100 % to 300 % excess. Petroleum coke is used as the reductant. CaO powder layer is placed on top of the mixture in the furnace in N<sub>2</sub> atmosphere. The temperature of reduction ranges from 900 °C to 1100 °C.

A magnetic separation is performed on the red mud to exclusively separate the iron from the remaining constituents by both, wet and dry magnetic separation. Both the magnetic and non-magnetic materials are dried, if wet method is used. Analysis of the solid product at various stages is performed by SEM-EDAX, XRD and Mossbauer spectroscopy.

## Results and Discussion

### Extraction of Alumina

Sintering depends on several factors including temperature, amount of sodium carbonate. Concentration of sodium hydroxide solution, time for leaching, temperature of leaching and A/C ratio remained constant. The washing conditions are kept constant at 100 °C for 15 minutes using a ratio of 10 g/l of red mud to distilled water.

Alumina extraction increases as temperature increases, as shown in the results tabulated in Table 1. At 850 °C sodium aluminate does form, but not all of the alumina is converted. At 1050 °C extraction efficiency is increased. Excess sodium carbonate and caustic added increases the formation of sodium aluminate and

extraction of alumina respectively. Alumina is recovered to as much as 84 % by sintering at 1050 °C using 50 % excess sodium carbonate and leaching at 100 % excess caustic followed by a wash.

**Table 1:** Conditions and results of alumina extraction

Run #	Sintering Conditions			Leaching Conditions		Washing
	Temperature	Excess Soda	A/C Ratio	Excess Caustic	Recovery	Recovery
	°C	%			Al <sub>2</sub> O <sub>3</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)
1	850	50	00.6	100	66.7	76.8
2	950	50	00.6	100	67.4	81.4
3	1050	50	00.6	100	69.6	83.1
4	950	0	00.6	100	62.7	66.2
5	950	50	00.6	100	66.9	75.3
6	1050	50	00.6	0	59.9	76
7	1050	50	00.6	150	39.9	54.3

### Extraction of Iron

The reduction of iron oxide and magnetic separation depends on a number of variables including the carbon content, temperature, time, and the presence of a calcium oxide layer which maintains a reducing atmosphere. Table 2 summarises the results of reduction. 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 the extent and occurrence of reduction, are weight loss calculations and Mössbauer analysis.

As temperature increases, reduction also increases. From the results of experiments it is concluded that temperatures around 1050 °C should be used for complete reduction.

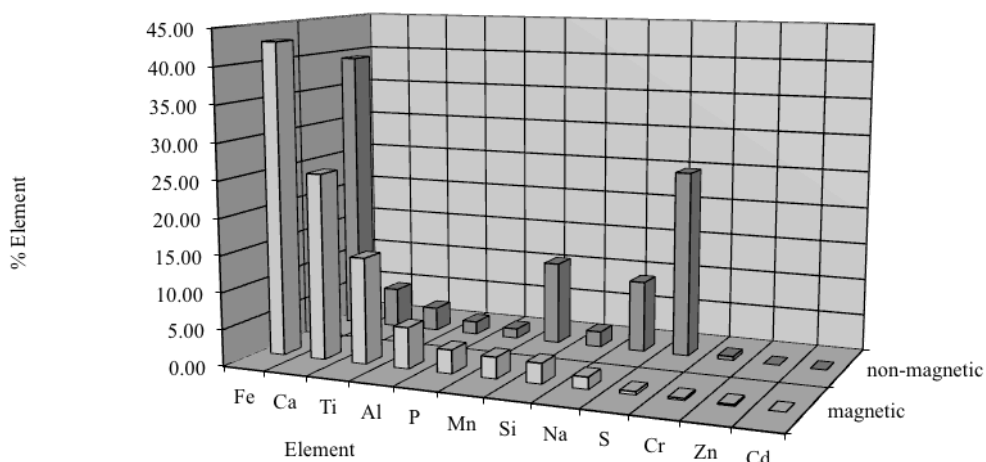
A minimum time is required for complete reduction which was achieved in approx. 2 hours. A layer of calcium oxide does increase the amount of reduction in the iron by trapping carbon dioxide gas as seen by the Mössbauer results and weight loss differences. As carbon content increases from 100 % excess to 200 % excess, almost complete reduction is observed. 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.

**Table 2:** Conditions for reduction and Mössbauer analysis

Reduction Conditions			Weight Loss			Mössbauer Analysis			
Exp #	Time	Temp	xs C	Lost	Th Loss	Difference	Fe	FeO	Fe <sub>3</sub> O <sub>4</sub>
	hr	°C	%	%	%	%	%	%	%
1	2	900	300	17.6	22.6	5	32	54	6
2	4	1050	300	26.4	22.6	-3.8	92	5	
3	2	1050	300	26.5	22.6	-3.9	93	4	
4	2	1050	200	25.6	24.1	-1.5	96	3	
5	2	1050	200	25.2	24.1	-1.1	88		8
6	2	1050	100	29.8	25.9	-1.2	81	0	13

### Magnetic separation

A magnetic separation is performed to separate the reduced iron out of the remaining red mud. Wet and dry magnetic separation is used. The reduced red mud contains iron combined with titanium, aluminium, calcium, silicon oxides and residuals of sulphur, zinc, manganese, sodium, chromium and phosphorus as shown in Figure 1. From Figure 1, it is concluded that magnetic separation of red mud is difficult. It was observed that iron, calcium, titanium and aluminium segregate to the magnetic product while sulphur, manganese and sodium segregate to the non-magnetic product. Iron is also distributed into the non-magnetic portion of the red mud. It has been suggested that titanium is combined with iron in the bauxite residue.<sup>21</sup> Calcium oxide is supplemented to the Bayer process and can react with titanium oxide to form perovskite ending up in redmud. This perovskite can attach itself to the iron separating into the magnetic fraction. The presence of iron in the non-magnetic product could be due to residual FeO remaining from reduction.



**Figure 1:** Elemental distribution in the magnetic and non-magnetic fraction of reduced red mud

## 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 40 % reduced iron and oxides and elements of calcium, aluminium, sodium, titanium, manganese, silicon, phosphorous, sulphur, zinc and chromium. Smelting can be tried on the unseparated red mud.

## Material balance

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 3 shows the material balance flow-sheet. 'Other' represents the Na<sub>2</sub>O, rare earth elements, Zn, Cr and Cd oxides, etc.

**Table 3:** Composition and Weight Change in Red Mud after Various Extraction Processes

Process	Fe <sub>2</sub> O <sub>3</sub>	FeO	Fe	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	SiO <sub>2</sub>	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% xs soda	56.4	-	-	12.7	6.7	8	2.4	13.8	101
Leached at 65 °C 1.5 hr. 100% xs 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 1050 °C 2 hr. 200% xs C; CaO layer	-	5.2	36.5	6.7	14.8	19.8	3.7	13.3	66
Smelted at 1650 °C	-	19	>90	-	29	22	7.5	22.5	64

## Blast furnace supplement

A potential application for alumina depleted and reduced red mud could be in the iron making blast furnaces. A preliminary calculation is made upon adding 100 kg of red mud to 1000 kg 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 4.

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 slag is separated from the hot metal and cooled where these deleterious constituents are consequently entrapped in a glassy matrix. The sodium content of red mud is also reduced. The fine nature of redmud does not allow its charging into the blast furnace from the top before pre-reduction unless agglomerated. Therefore, the addition is suggested at the tuyere level. Full reduction of iron oxides cannot be accomplished in BF at the tuyere level, therefore, pre-reduction is suggested. Alternatives would include converting redmud into a DRI type product or consider reactors other than blast furnaces.

**Table 4:** Composition of Iron Ore, Coke, Lime, Alumina-depleted and Reduced Red Mud and Final Product Required for Blast Furnace Calculations

Sample, %	Fe	FeO	Fe <sub>2</sub> O <sub>3</sub>	CaO	MnO	MgO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	C	SiO <sub>2</sub>
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

## Conclusions

- 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 followed by leaching with 5 g/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.
- 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 covered by a fine layer of calcium oxide.
- Sodium content is decreased to below 1 % by washing. Satisfactory conditions for sodium dissolution include washing for fifteen minutes at 100°C using a 2 g/l red mud to distilled water ratio.

Because of the inability to magnetically separate iron after reduction, some alternative routes for utilisation are suggested like blast furnace supplement, smelting to recover iron as pig iron.



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