Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 357–361

AN INVESTIGATION ON CHARACTERIZATION AND THERMAL ANALYSIS OF THE AUGHINISH RED MUD

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Red mud is insoluble, fine-grained waste residue which is generated as a by product during the production of alumina from the Bayer process. In this article, the thermal behavior of Aughinish red mud was investigated using thermal gravimetric analysis (TG) and differential thermal analysis (DTA). For identification of oxide and mineral phases in the red mud sample, XRD method, scanning electron microscopy (SEM), EDAX were used. Iron (30.4%), aluminium (23.6%) and titanium (17.85%) oxides are major oxides in the sample. Two endothermic peaks were shown on DTA curve. The total mass loss in the red mud was found to be 10.1%, which was associated with moisture and water molecules in gibbsite and boehmite phases.

Keywords: *alumina, Aughinish red mud, DTA curve, iron oxide, thermal analysis*

Introduction

Aluminium is a very important metal which is used everywhere from packing to aerospace industries. It is produced from alumina, using the Hall–Heroult cell [1, 2]. Alumina is extracted from bauxite by the Bayer process [3, 4]. The process can be classified into five stages; mixing, digestion, precipitation, clarification and separation. In the digestion stage, gibbsite ($Al(OH)_3$) and boehmite ($AlO(OH)$) are dissolved in the mixture of bauxite and caustic soda, at temperature between 150–250°C, according to the reactions (1) and (2);

- Monohydrate alumina

$$Al_2O_3\cdot H_2O+Na(OH)\cdot 3H_2O= \\ =NaAl_2O_3(OH)+4H_2O+\text{red mud}_{\text{insoluble}} \quad (1)$$

- Trihydrate alumina

$$Al_2O_3\cdot 3H_2O+Na(OH)\cdot 3H_2O= \\ =NaAl_2O_3(OH)+6H_2O+\text{red mud}_{\text{insoluble}} \quad (2)$$

Digestion stage is most important step in the Bayer process. To yield high sodium aluminate solution depends on the used parameters in the digester. The solution of the sodium aluminate, $NaAl_2O_3(OH)$, commonly known as ‘pregnant liquor’, is cooled, diluted and seeded with aluminium three hydroxide ($Al(OH)_3$, gibbsite) crystals and agitated for a period of time to precipitate the alumina which is then separated from the resulting spent liquor [4, 5].

$$NaAlO_2+2H_2O=Na(OH)+Al(OH)_3 \quad (3)$$

The cream-cloured aluminium hydroxide is thickened by the removal of water, before going to the calcination stage, at over 1000°C [5, 6]. A fine, white powder of anhydrous alumina is formed. The following reaction gives the calcination operation;

$$Al_2O_3\cdot 3H_2O=Al_2O_{3(s)}+3H_2O_{(g)} \quad (4)$$

Various gangue minerals, such as hematite, anatesa, or rutile and desilication products (DSP) are not dissolved and remain as an insoluble solid phase, which is, called red mud. DSP is a complex sodium-aluminium-silicate waste of variable composition, which may include other oxides present in the solution. A typical desilication product is $Na_2Al_2O_3\cdot SiO_2\cdot 1/5(Na, Al)\cdot nH_2O$. Iron oxide content gives its colour and liquid waste is red brown colour.

Chemical and mineralogical compositions are main importance for utilization of red mud for industrial applications. They determine any mechanical, physical properties and transformation reactions, which will take place during the heating of red mud. Thus, the potential use of red mud depend upon the chemical properties of the bauxite fed stock of the Bayer process and this in turn is dependent on the geography of the area from which the bauxite is mined [4, 7].

Mineral phase of red mud can be classified into two groups. Unchanged mineral phases of red mud come from the origin of bauxite ore without any transformation during the Bayer process treatment. The old mineral phases are iron, titanium and un-reacted alumina phases. Formed phases are formed during the digestion stage as a result of the caustic soda addition.

The studies on the utilization of red mud were started at the beginning of the alumina production. There are many investigations of looking at red mud as

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1388–6150/$20.00

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a new potential source for industrial applications [8–14], rather than the storage of it as a waste material. Due to the increasing environmental costs associated with the storage the utilization of red mud is economically more feasible for the recovery of both major and minor valuable metals in the red mud.

Pyro-metallurgy is imported process for production of many products. Final properties of any products depend on treatment parameters as well as compositions and mineral phases of used materials. To understand which mineral undergoes phase transformation and relationships between reactions, transformations and mineral phases, it is essential to know basic chemical and mineral compositions of raw materials. Differential thermal analysis is most common method for investigations of thermal properties and reactions, which may take place during the heating or cooling of sample. Any exothermic or endothermic reactions occur in sample during heating treatment can be observed on DTA curve. Generally, it is used at constant heating rate at around 10°C min^{-1}.

Experimental

Material

Red mud (slurry) material was provided from the Aughinish alumina plant in Ireland. The plant imports its bauxite from Guinea and South Africa [15]. Red mud sample was dried in an ordinary oven at 100°C for 12 h and then ground and characterized using X-ray diffraction, SEM EDAX and TG/DTA.

Simultaneous thermal analysis

To examine the thermal stability of the red mud, simultaneous thermal analysis, Seiko, was used. The thermal analysis experiment was carried out using following conditions;

Sample mass	20–30 mg
Heating rate	10°C min^{-1}
Temperature range	20–1200°C
Crucible	Pt
References material	alumina
Atmosphere	air

SEM and EDAX

The scanning electron microscope was used to examine the surface and morphology of the Aughinish red mud sample. Specimens were prepared by placing a little amount of red mud on aluminium holder using double-sided sticky tape and then they were coated with gold layer by vacuum evaporation, as the red mud samples are not conductive. Air drying silver was applied on the edges of the gold-coated samples for electrical connection to earth.

Energy disperse analysis of X-ray was used for the basic chemical analysis of the red mud sample. In this experiment, the prepared red mud sample was coated with carbon by vacuum evaporation.

X-ray

X-ray diffractometer was used for the determination of phases present in the red mud sample. The fine ground powder was compacted into the XRD sample holders. The obtained X-ray peaks were identified by comparison of the diffraction values and relative intensity obtained with those in the JCPDS file using the APD programme. The analysis was carried out at 40 kV, 50 mA, CuK_α as a X-ray source.

Results and discussion

Characterization of the red mud

The X-ray diffraction pattern of the Aughinish red mud sample is given in Fig. 1. The identified mineral phases in the sample are hematite (Fe_2O_3, card no. 33-0664), rutile (TiO_2, card no. 21-1276), perovskite ($CaTiO_3$, card no. 22-0153), quartz (SiO_2, card no. 18-1166), sodalite ($Na_2O\cdot Al_2O_3\cdot SiO_2$, card no. 16-0612), boehmite {AlO(OH), card no. 21-1307}, goethite {FeO(OH), card no. 26-0792}, gibbsite {$Al(OH)_3$, card no. 33-180}, calcium alumina silicate {$Ca_2Al_2(SiO_4)(OH)_8$, card no. 03-0798}.

Basic chemical analysis of the sample is given in Table 1. There are some variations in the chemical composition of the red mud with other red mud samples [5, 6, 16]. Iron oxide, aluminium oxide and titanium oxide are the major constituents of the Aughinish red mud.

Figure 2 shows the picture of the red mud powder. As seen from this figure, the red mud composed of very fine particle size where the particle size ranges from a few microns to over 20 μm. Red mud powder

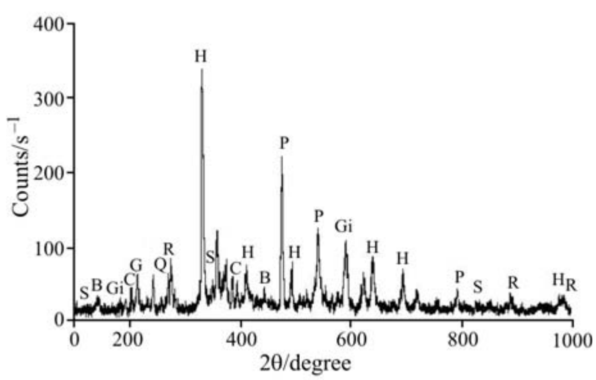


Fig. 1 X-ray diffraction pattern of the sample as received form

Table 1 Common mineral phases in red mud sample [19]

Formed phase	Phase form	Old phase	Phase form
Cal. Al. silicate	$Ca_2Al_2(SiO_4)(OH)_8$	Hematite	Fe_2O_3
Perovskite	$CaTiO_3$	Goethite	$FeO(OH)$
Sodalite	$Na_6[Al_6Si_6]_{24}(CO_3)_2{\cdot}2H_2O$	Quartz	SiO_2
Calcite	$CaCO_3$	Boehmite	$AlO(OH)$
Sod. titanate	Na_2TiO_3	Rutile	TiO_2
Concrinite	$Ca_2Na_6[Al_6Si_6O_{24}](CO_3)_2{\cdot}2H_2O$	Gibbsite	$Al(OH)_3$
Al. silicate	–	Kaolinite	$Al_4[Si_4O_{10}](OH)_8$
		Ilmenite	$FeTiO_2$

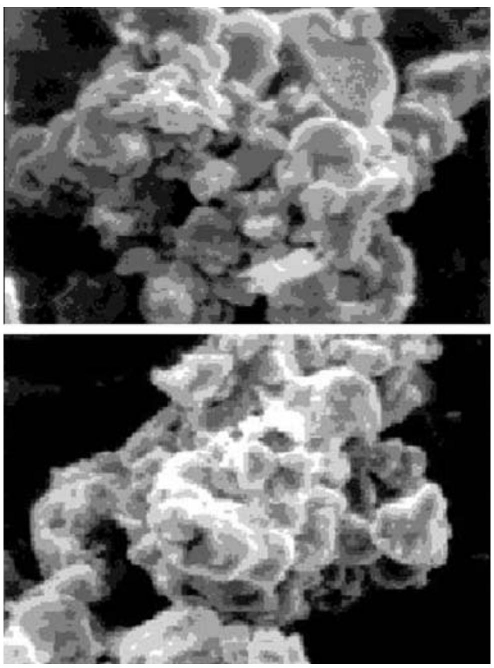


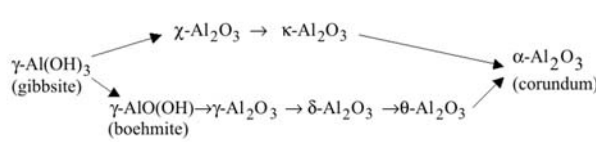
Fig. 2 SEM pictures of the red mud sample (9000×)

has a variety of different morphology, some individual particle look flake, and spherical particles. Red mud is fine sized (70–90%<12 μm). There may be particle size differences between the unchanged with the new-formed mineral. The coarse particle would be belonging to the old mineral oxides. The density of the mud is around 2.75 g cm^{-3} and it is distinctly alkaline pH 12.7. Sodium oxide content in the red mud sample is due to the addition of caustic soda for the recovery of aluminium content of the bauxite ore. It is possible to say that very fine particle may belong to sodium/aluminium minerals in the red mud powder. The large particle may belong to iron mineral groups or the unchanged minerals in the bauxite ore.

Thermal analysis

Since chemical compositions of bauxite and red mud vary, DTA curves of them will be different form. Red mud contains many mineral phases (Table 2), such as kaolinite, quartz, chlorides. Thermal characteristics of red mud can vary sample to sample. For example, quartz is major oxide in many red mud, shows a small peak, as a result of α/β transition at 570°C. If kaolinite is major mineral phase in red mud sample, it shows nearly straight line.

There are different suggestions on the differential thermal analysis curve of gibbsite [17, 18]. Makenzie [17] states that gibbsite shows an endothermic peak between 320–330°C corresponding to a decomposition reaction forming x-Al_2O_3 on DTA curve. There may be small peak or inflection of variable size on peak within 250–300°C range and small peak at temperature between 500–550°C. The first peak is due to the formation of boehmite {y-AlO(OH)} and the second peak is the dehydration of the formed boehmite phase. There is different approach on the DTA curve of gibbsite. According to Lodding [18], at constant heating rate, gibbsite partially dehydroxylates to boehmite a temperature 250°C and the remain part of the gibbsite goes to a transition alumina at about 330°C. He suggests that, two separate endothermic peaks can be seen on DTA curve. According to Mackenzie observation, the decomposition of gibbsite, anhydrous alumina is formed and the dehydroxylation proceeds to the anhydrous alumina. But Lodding [17] suggests that, boehmite forms at the onset of dehydroxylation during this transformation and it forms a layer around the un-reacted gibbsite preventing further dehydroxylation until higher temperature is reached. The decomposition of gibbsite is given in the following equation.



Equation (5)

There are several intermediate transition phases of alumina until to the α-Al_2O_3, corundum structure. All endothermic peaks of intermediate phases may not observe on the DTA curve.

Table 2 Chemical composition of the bauxite used and the red mud generated in the Aughinish alumina plant with other red mud samples

Oxides	The bauxite used in the plant [15]/mass%	Aughinish red mud [13]/mass%	Jamaican red mud [6]/mass%	Turkish red mud [16]/mass%	Indian red mud [5]/mass%
Al_2O_3	56.2±3.9	23.6	16.4	20.24	18.2
Fe_2O_3	10.2±4.13	30.4	42.3	39.84	33.1
TiO_2	4.0±1.2	17.85	6.0	4.15	19.6
SiO_2	1.4±1.6	9.65	8.0	15.24	8.8
CaO	0.07±1.2	6.4	9.0	1.80	2.7
Na_2O	–	5.3	4.6	9.43	5.8
other	±	6.8	13.7	0.48	11.8
total	78.6±13.4	100	100	99.97	100
L.O.I.	6.5±1.4	10.1	10.2	8.79	9

However, the dehydration of goethite, FeO(OH), is more simple than gibbsite. Geothite decomposes to hematite and water as in the following equation;

$$\text{goethite}\rightarrow\text{hematite}+\text{water}_{(g)}$$

$$2\alpha\text{-FeO(OH)}_{(s)}\rightarrow Fe_2O_{3(s)}+H_2O_{(g)} \quad (6)$$

Endothermic peaks on DTA can be explained with dehydration and decomposition of mineral phases in red mud. It is possible to observe formation of new phase and re-crystallization reactions as an exothermic peak on DTA curve.

The results of the differential thermal analysis (DTA) and thermal analysis (TG) of the red mud sample are given in Fig. 3. There are three endothermic peaks on the DTA. According to the above explanations, it is likely that for the Aughinish red mud, the first two endothermic peaks between 271 and 314°C, on the DTA curve, can be associated with the dehydration of gibbsite to form both boehmite and χ-alumina [9]. The third endothermic peak at 358°C can be explained the decomposition of the goethite to hematite.

The result of the thermogravimetric analysis (TG) of the red mud sample is given in Fig. 3. It can be seen from the TG curve, there is very little mass loss up to 120°C in the red mud sample. But the mass loss of the sample is very rapid between 120–358°C. There are three endothermic peaks on DTA curve of the sample within this temperature range. The mass loss observed of the sample was 2.8%, which can be explained with the loss of physical water content of the sample. There is also very rapid mass loss in the sample at 271–314°C temperature range. The mass loss is associated with the loss of water from the gibbsite and goethite phases. The total mass loss of the red mud is 10.1% until 1200°C. It is good agreement with the DTA curve of the sample. The endothermic peaks came cross to loose of water from gibbsite and goethite phases.

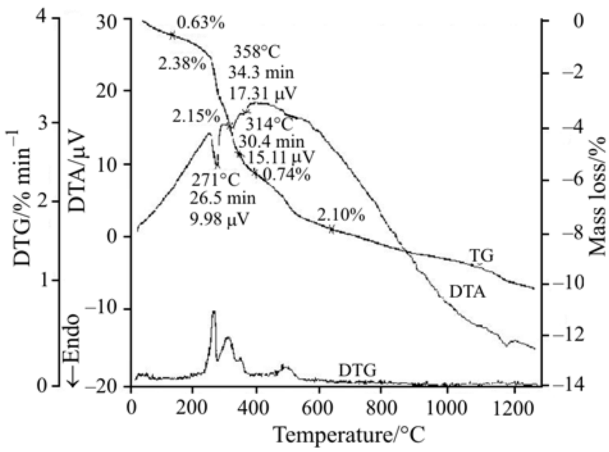


Fig. 3 TG/DTA curve for the red mud sample

Conclusions

The Aughinish red mud sample was characterized. Following statements can be made up on the results;

It was very fine-grained powder with density of 2.75 g cm^{-3} and ready to any mineral processing and separation.

It contains considerable amount of the valuable oxides, iron, titanium and aluminium hydroxides. Total iron oxide content of the sample is 30%. It is reducible and can be separated by magnetic separation techniques.

The un-recovered sodium aluminate content is very high in the sample. The recovery of aluminium hydroxides can increase by improving the washing conditions or the re-washing of the red mud slurry. Titanium oxide is third major phase with 18% content.

Two endothermic peaks were determined on the DTA curve of the red mud sample and 10.1% of the total mass loss was observed on the TG of the sample.

For the characterization and analysis of rare elements in the red mud needs to be further investigated of these elements.

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Received: December 3, 2004
In revised form: April 7, 2005

DOI: 10.1007/s10973-005-6419-z