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THE INFLUENCE OF SODA ADDITIVE ON THE THERMAL PROPERTIES OF RED MUD

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Abstract

The dehydration and decomposition of the red mud from Seydişehir Aluminum factory, mixed with soda were investigated under dynamic and isothermal conditions. Soda was added to the red mud samples as much as 50, 100 and 150 mass% of Na_2CO_3 of the red mud sample's mass. To determine the effect of soda additive on the red mud's thermal properties, using TG and DTA techniques simultaneously under atmospheric conditions. Furthermore, the original red mud sample's XRD and IR spectrum curves were investigated. It seems that the temperatures of the endothermic peaks of the red mud decreased with the amount of soda added. However the endothermic peak's temperature readings showed that the melting of soda increased gradually with the quantity of soda used.

Keyword: DTA, effect of soda, IR, red mud, TG, thermal properties

Introduction

Red mud is a waste material which is produced during alumina production using the Bayer process. Approximately 35–40% of the processed bauxite ore is transferred to the red mud waste dump and this means that millions of tones of waste product is discarded polluting the environment. The red mud contains Fe_2O_3, Al_2O_3, SiO_2, TiO_2 etc. from bauxite ore, flocculent that was added before flotation and alkaline oxide residue from the washing process. There hasn't been an economic technology developed yet or a plant scale application to utilize this waste material, which amounts to nearly 3 million tons in Seydişehir up to now [1].

Disposal of any solid waste raises issues such as space/real estate industry, cost of disposal and pollution, which by now becoming pressing problems. Obviously, these factors are also present in the red mud disposal. As the red mud contains a large amount of valuable chemicals, such as Al_2O_3, Na_2O and TiO_2, there is a need for developing a technology to recover of at least some of the important chemicals [2].

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In the literature there is a study on the thermal behavior of the red mud, the solid-state transformations and solid-liquid phase transitions within the interval 120–1400°C. The use of thermal analysis (TG, DTG and DTA) coupled with a gas-mass spectrometry for detecting possible gas release, and of X-ray diffraction methods seem to be well suitable for the problem at hand [3].

In another study, the effect of reduction of pressure on the shapes of the TG, DTG and DTA curves, mass-spectra of hydroxide and carbonate phases was investigated using some typical Hungarian red mud. They used a Mettler thermobalance for the investigations connected to a gas analyzer. The pressure change caused different decomposition rates of the phases and resulted in a better separation of the overlapping thermal curves. Red mud was also identified by IR and X-ray methods [4].

Approximately 3 million tons of red mud is wasted from Seydişehir Aluminum Factory, similarly to aluminum production plants all over the world. The possibility of recovering valuable compounds from this waste material hasn't been investigated yet. The aim of this preliminary study is to investigate the thermal behavior of the red mud as well as to study the effectiveness of soda addition; evaluating the decomposition of the compounds in the red mud residue.

Experimental

In this study, the red mud was analyzed by chemical, XRD, IR and thermal methods. The thermal studies were carried out on the red mud without and than with, by the addition of 50, 100, 150 mass% pure Na_2CO_3 of the red mud mass content. Thermal analysis curves were obtained dynamically. A Netzsch equipment was used to record the differential thermal analysis (DTA) and thermogravimetric analysis (TG) curves simultaneously. The heating rate rose between 25–1400°C by 10°C min^{-1}. The mass of the samples were 200 mg. The thermal reactions were determined under atmospheric conditions. X-ray studies were carried out by Shimadzu XRD-6000 equipment with CuK_α radiation (λ=1.5405 Å). Before recording the Fourier transform infrared (FTIR) spectra, the red mud was dried at 378 K. FTIR spectra was recorded from 4000 to 400 cm^{-1} (100 scans) on samples in KBr pellets using Mattson Infinity series FTIR spectrophotometer.

Results and discussion

The chemical analysis of the red mud used in this study is given in Table 1.

The XRD peaks and FTIR spectra of the red mud are shown in Fig. 1 and Fig. 2, respectively. From the interpretation of the XRD peaks in Fig. 1, it was understood that the red mud contains hematite (Fe_2O_3), gibbsite ($Al(OH)_3$), sodium aluminum carbonate silicate ($Na_5Al_3Si_3O_{15}$), boehmite (AlO(OH)), diaspore (AlO(OH)) and calcite ($CaCO_3$).

From the FTIR spectrum in Fig. 2, 3650–3130 cm^{-1} region, a broad peak which corresponds to OH vibrations appears as a result of hydration due to the presence of

Table 1 The chemical analysis of red mud

Compounds	%	Compounds	%
Al_2O_3	20.24	CaO	1.80
Fe_2O_3	39.84	CO_2	1.92
SiO_2	15.27	Other	0.48
TiO_2	4.15	LOI(at 900°C)	8.79
Na_2O	9.43		

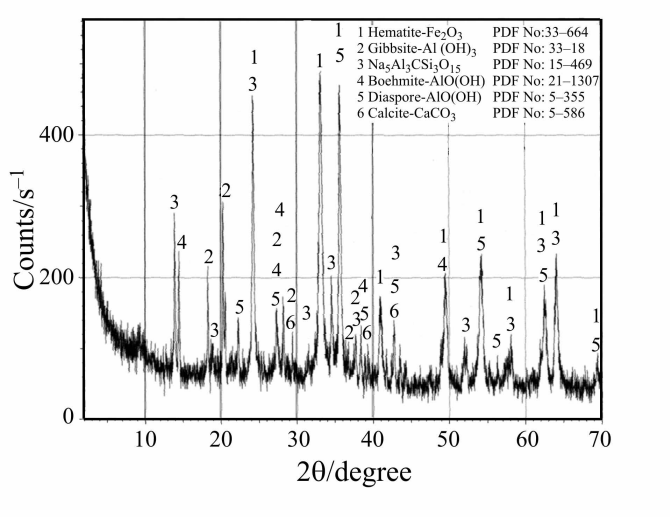

Fig. 1 XRD peaks of the red mud

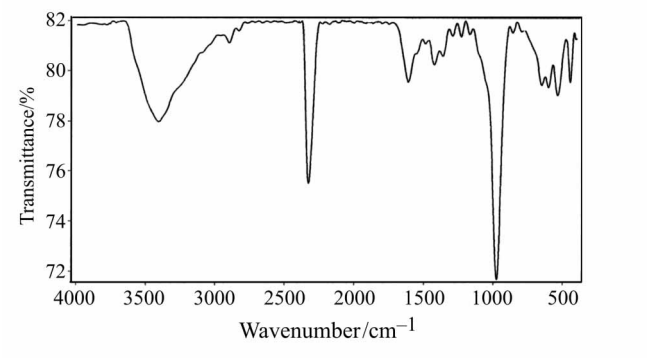

Fig. 2 FTIR spectra of the red mud

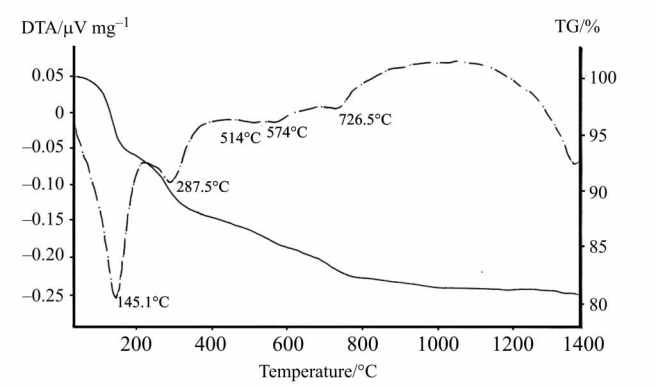

Fig. 3 TG and DTA curves of the red mud

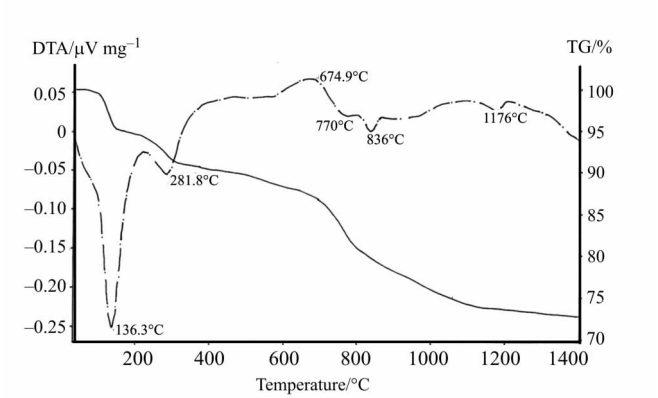

Fig. 4 TG and DTA curves of the mixture of red mud with 50 mass% Na_2CO_3

H_2O in the red mud. The peaks at 2920 and 1450 cm^{-1} represent the existence of $CaCO_3$. 1630, 550 and 440 cm^{-1} are for the stretching vibrations of Fe^{3+}–O^{2-} bond. The peaks at 980 cm^{-1} is for the SiO_2. In the same way peak at 620 cm^{-1} also represents Al^{3+}–O^{2-} bond. These results are consistent with the results obtained from the XRD analysis of the red mud.

The results of the thermal analysis of red mud are presented in Figs 3–6. Figure 3 represents the thermal analysis curves of the red mud received from Seydişehir Aluminum factory.

Between 25–1400°C the total amount of mass loss of original red mud sample was found 19.2%. Starting from the room temperature a rapid increase in the mass loss rate is observed with increasing temperature. This loss (7.6%) was estimated from TG by taking DTA curve into account which produced an endothermic peak at 145.1°C. This loss is attributed to the physical water content of the red mud. The

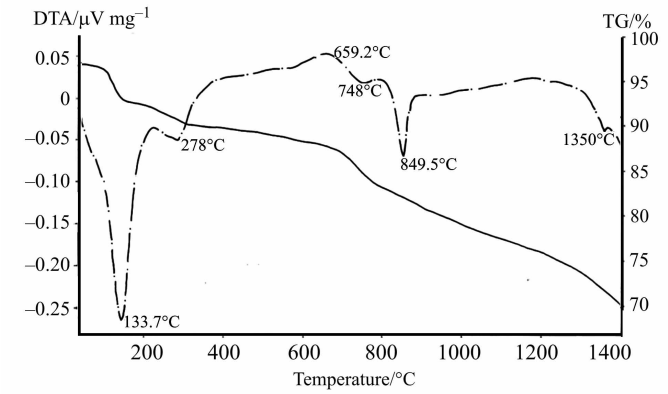

Fig. 5 TG and DTA curves of the mixture of red mud with 100 mass% Na_2CO_3

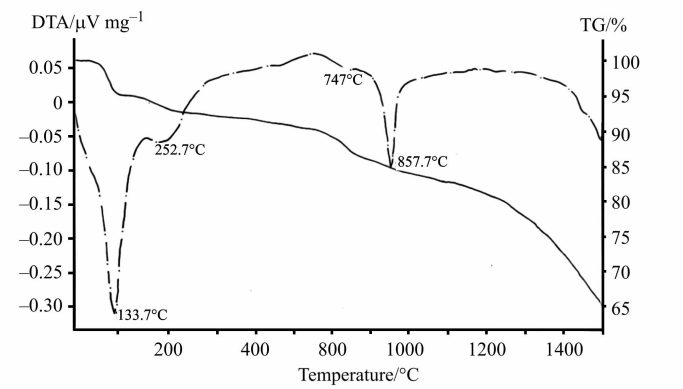

Fig. 6 TG and DTA curves of the mixture of red mud with 150 mass% Na_2CO_3

evaporation of the physical water is completed at about 229°C. A 4.84% of the mass loss occurred between the range of 229–395°C due to the decomposition of gibbsite that was deduced from the interpretation of the endothermic peak at 287.5 C in DTA. Two other endothermic peaks are observed (Fig. 3). These peaks occurred at 514 and 574°C in DTA, respectively. The endothermic peaks at these temperatures together with the mass loss of 0.99 and 0.91%, refer to the decomposition of boehmite and diaspore. Similar experimental observations has been reported by Shiskin [5]. An endothermic peak starting at about 680°C and ending at 776°C resulted from the decomposition of calcite. This calcite decomposition caused 1.7% of the mass loss and due to this, DTA curve revealed a maximum endothermic peak which is seen at 726.5°C in DTA. It is known that calcite decomposes at less than 950°C [6]. The low mass loss without revealing a peak, occurs after 776°C is related to sodium aluminum carbonate silicate decomposition in the red mud.

Figures 4–6 show the TG and DTA results of the red mud mixed with 50, 100 and 150 mass% of soda. As it was mentioned earlier, in the experiment soda was added by the ratio of soda over the red mud mass content. The TG and DTA curves of the mixture of red mud with 50 mass% Na_2CO_3 are given in Fig. 4.

The estimated total mass loss was 27.15% between the temperatures of 25 to 1400°C. The first endothermic peak in DTA, which has a maximum at 136°C, refers to the physical water release between the temperatures of 25–222°C. In this temperature range 5.59% mass loss is occurred. As shown in Fig. 4 a second endothermic peak is clearly seen between the temperatures of 222–391°C. This DTA reveals a peak at 281.8°C and the mass loss was estimated 4.17% between these temperatures. The mass loss, took in that temperature range is resulted from the dehydration of gibbsite in the red mud. In the temperature range of 391–674.9°C, 3.28% mass loss was estimated. The mass loss is believed to be caused by the decomposition of boehmite, diaspore and a small amount of soda, as we already stated in our previous studies [6, 7]. In Fig. 4 an endothermic peak is observable, with a maximum at 770°C. In this peak range (674.9–795°C), 5.86% of the mass loss has been recorded, and proved that $CaCO_3$, Na_2CO_3 and sodium aluminum carbonate silicate decompose together. The sharp endothermic peak at 836°C indicated that soda has started to melt in addition to the decomposition of Na_2CO_3. It is well known that soda melts at 851°C and decomposes at about the same temperature. The reason for the soda starting to decompose at such a low temperature can be attributed to the catalytic effects of the contaminants in the sample [7]. DTA curve produced a small endothermic peak at 1176°C between the temperature of 1100–1200°C and resulted in approximately 0.53% mass loss. The reason for this mass loss is believed to occur as the result of both the decomposition of soda and the sublimation of sodium oxide. Furthermore, it has also been reported in the literature that the sublimation of pure Na_2O is possible at the temperatures above 917°C [8].

The thermoanalytical curves of the red mud mixtures with 100 and 150 mass% Na_2CO_3 are demonstrated in Figs 5 and 6, respectively. In the mixture we added 100 mass% soda to the red mud: a total amount of 30.85% mass loss was estimated. It changed to 35% in the mixture of 150 mass% soda added to the red mud sample.

Studying Figs 5 and 6, two major can be drawn. Firstly; the endothermic peak temperatures seem to decrease as the amount of added soda increasing. For example, the endothermic peak related to the physical water release appeared at 145.1°C in case of the original red mud sample. This peak has shifted to 136.3, 133.7 and 133.7°C for the 50, 100 and 150 mass% soda addition to the red mud mixtures, respectively. In a same manner the decomposition temperatures of gibbsite and calcite/sodium aluminum carbonate silicate are decreased by the increased amount of soda. Secondly, increased amount of soda addition resulted in decreased rate of mass loss up to 800°C. In spite of the fact that the total amount of mass loss increased with soda addition, the rate of mass loss shows different characteristics compare with the original (without soda added) red mud that has almost completed at 800°C (Fig. 3). Comparing Figs 4–6, it is clearly seen that the addition of increasing amount of soda to the mixtures caused significant amount of mass loss beyond the temperature of

800°C. The increasing rate of mass loss with the increasing amount of soda added to the mixture at high temperatures is attributed to the decomposition and sublimation of soda. Another characteristic can be observed in the soda and red mud mixture, is, that an endothermic peak is visible between the temperature range of 836–857.7°C while the original red mud sample does not exhibit this kind of curve in DTA. The peak temperature shows a gradual increment with the increasing soda content. The reason for this increment is not yet clearly understood, however, soda produces alkali compounds with Al_2O_3, Fe_2O_3, etc. in the red mud. It is believed that these alkaline compounds increase the melting temperature of soda. As a matter of fact, between the approximate temperature of 800 and 1100°C the rate of mass loss decreases by the increase of soda content in the mixture. This fact can be clearly seen from the TG curves in Figs 4–6.

Conclusions

The total mass loss values between the temperatures of 25–1400°C were calculated to increase as increasing the content of soda addition. The temperatures of endothermic peaks related with physical and chemical water release and, the decomposition of calcite and/or sodium aluminum carbonate silicate in red mud were decreased with increasing the amount of soda added. The temperature of endothermic peak which also showed the melting of soda increased gradually with the quantity of soda. The amount and the rate of mass losses in soda added mixtures decreased up to 1100°C related with the increasing amount of soda addition. On the other hand, the rate of mass loss showed a significant increment beyond the temperature of 1100°C with the addition of soda to the red mud. Since the increasing amount of soda needed high temperatures for calcination, the addition of 100 and 150 mass% soda has not shown an advantage in a technological point of view.

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