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EFFECT OF ALKALINE ADDITIVES ON THE THERMAL PROPERTIES OF BAUXITE

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Abstract

The dehydration and decomposition bauxite mixed with alkaline compounds were investigated under dynamic and isothermal conditions. Alkaline compounds (CaO or/and Na_2CO_3) were added to bauxite samples in various mole fractions (0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 of CaO). To determine the effect of alkaline additives on the thermal properties of bauxite, TG, DTG and DTA techniques were used simultaneously under atmospheric conditions.

Keywords: alkaline, bauxite, TG-DTG-DTA

Introduction

Bauxite is not only a single mineral but a chemical mixture of a trihydrate such as gibbsite and monohydrates, diasporite and boehmite [1]. The term bauxite is used for compounds containing a small fraction of silica, alkaline soil and high fraction of alumina, formulated as $Al_2O_3 \cdot nH_2O$ [2, 3]. The term bauxite ore is applied for bauxites which are economically mineable at present or in the foreseeable future, containing not less than 45–50% Al_2O_3 and not more than 20% Fe_2O_3 and 3–5% combined silica [4]. Earlier studies indicated that it consisted of 43 elements including mainly aluminium, iron, silicon, titanium, calcium and magnesium.

Diasporite, an α-monohydrate ($Al_2O_3 \cdot H_2O$), differs from boehmite. Optical examinations revealed that diasporite contained prismatic or thin tabular orthorhombic crystals [4, 5]. It is usually found in clay stones and dolomite or crystalline schists together with corundum and emery-stone. Its Mohs hardness is 6.5–7.0 and specific gravity 3.3–3.5 g cm^{-3} [6, 7].

Approximately 90% of the extracted bauxite, the most important aluminium ore, is used in the production of alumina and aluminium [2, 8]. It is also used for abrasives, for chemical and refractory manufacture, and for the preparation of

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high-alumina cements. Additionally, it can be used for filtration operations [1, 8, 9].

The thermal changes occurring during calcination of gibbsitic, boehmitic and diasporic bauxites have been examined by TG, DTG, DTA, X-ray analysis and IR spectroscopic methods. The effects of the type (wet or dry) and time of grinding of gibbsitic and diasporic bauxites on the TG, DTG and DTA curves have been investigated [10]. Moreover, the thermal analysis studies of pure gibbsite, boehmite and kaolinite and some bauxites containing these three minerals, alone or in mixtures, have been studied by calorimetry and simultaneous TG-DTG-DTA methods. The results obtained have been compared with those of X-ray studies [11].

Thermoanalytical studies on various bauxites from different countries were made together with thermosonimetry, and the activation temperatures were determined. Also, in simultaneous thermoanalytical and thermosonimetric studies, the behaviour of composite carbonates and sulphates was investigated in detail [12, 13]. The mineral compositions of complex bauxite ores were determined following thermoanalytical studies, whereas the changes in the crystal structure of Al_2O_3 compounds were investigated by X-ray analysis over the calcination temperature of 950°C [14, 15]. It has been estimated that Turkey has a potential of 430 million tones of bauxite, of which 20.6 million tones are in the vicinity of Mugla [16]. The purpose of the present study is to determine the effectiveness of alkaline additives in the thermal analysis of this bauxite, sold as an ore rather than using it in alumina industry.

Experimental

Four samples obtained from Savran, Göbekdagi, Yaglidag and Kayaderesi in the vicinity of Mugla-Milas were cleaned and ground to ~200 mesh. A homogeneous mixture was prepared using equal amounts of these samples, and chemically analysed. The chemical analysis of the ore is given in Table 1.

The equivalent amount of alkaline compounds to form aluminate, silicate, ferrate and titanate was calculated. It was added to bauxite in an excess of 20%

Table 1 The chemical analysis of the bauxite mixture

Compound	%	Compound	%
Al_2O_3	57.91	FeS_2	1.02
Fe_2O_3	21.33	CO_2	1.65
SiO_2	3.84	other	0.52
TiO_2	2.20	mass loss	11.08
CaO	2.10	total	*100.00*

and contained CaO in various mole fractions (0.0, 0.2, 0.4, 0.6, 0.8, 1.0). The bauxite samples thus prepared were ground and mixed thoroughly in an agate mortar. These almost homogeneous mixtures were calcinated dynamically. For this purpose a Netzsch equipment was used which is capable of simultaneously recording the DTA, TG, rough measurement TG_1 and DTG curves simultaneously as functions of the temperature. The thermal events were examined under atmospheric conditions. The heating rate and the sensitivity were 10°C min^{-1} and 0.2 mV, respectively. All samples were kept at 200°C for 4 h and cooled; then the curves were recorded.

Results and discussion

The thermoanalytical curves of bauxites from the vicinity of Mugla-Milas obtained by dynamic simultaneous method are shown in Fig. 1 [17]. The total mass loss of the bauxite mixture after calcination was found as 10.93%. The rapid mass loss continued up to 585°C as indicated by the TG curve which showed the completion of the dehydration of the ore. This was supported by chemical analysis, and by an endothermic DTA peak at 550°C. A gradual mass loss was observed between 585 and 700°C. However, an increase in the mass loss rate was observed between 700–830°C. A 2% mass loss above 585°C indicates the decomposition of the mineral (release of CO_2, SO_2). This situation showed that the decomposition of pyrite an carbonates occurred at lower temperatures because of the catalytic effect of SiO_2 and Fe_2O_3 etc. present in the bauxite [18, 19]. An endothermic peak in the DTA curve starting at 585°C and ending at 780°C resulted from the interference by CO_2 and SO_2 release.

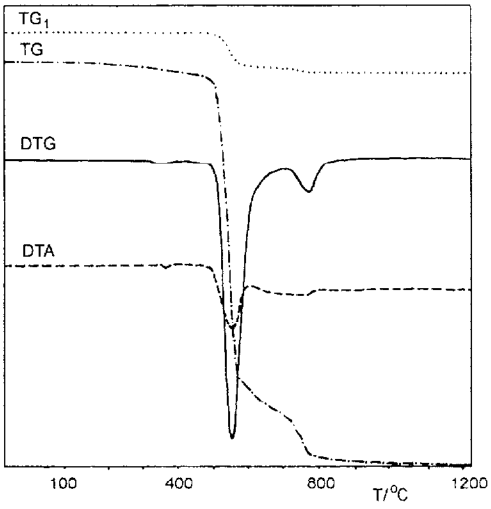

Fig. 1 Thermal analysis of bauxite from Mugla

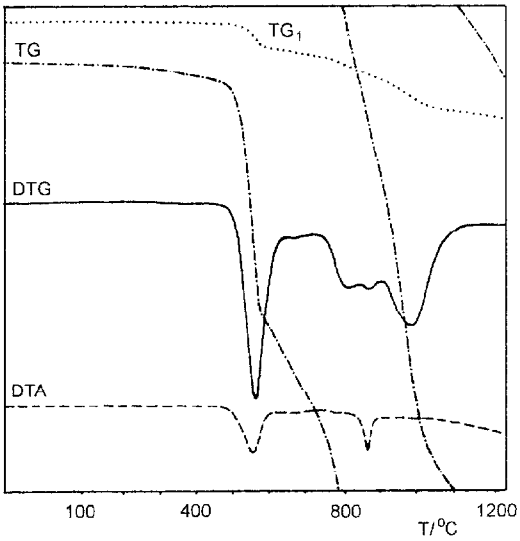

Fig. 2 Calcination of bauxite mixed with alkaline additive (mole fraction of CaO 0.0)

The TG, DTG and DTA curves obtained for the calcination of the sample mixed with only Na_2CO_3 (at a 0.0 mole fraction of CaO ($X_{Na_2CO_3}$: 1.0)) are given in Fig. 2. The total mass loss was 25.13% up to about 1200°C. The TG and DTG curves revealed that the mass loss occurred rapidly at about 460°C, resulting in a 6.53% mass loss, and the process became slower above 570°C. A 13% mass loss was found when it was calculated with regard to the original bauxite sample in the mixture. However, the total mass loss of the original pure bauxite mixture was found to be 10.93%. This showed that the decomposition of Na_2CO_3 took place together with the dehydration of bauxite in the given temperature ranges. It was shown as a big peak in the DTG curve between 460–620°C and as an endothermic peak in the DTA curve at 555°C. It is well known that Na_2CO_3 melts at 851°C and decomposes at about this temperature. The reason that its decomposition occurred at a lower temperature in this study, can be the catalytic effects of the contaminants present in bauxite.

A rapid increase in the rate of mass loss was observed at temperatures above 570°C, although the total mass loss was 18.60% between 570–1200°C. It was deduced from the curves that this event was not fully completed. It was shown that above 725°C the rate of mass loss increased again because of the decomposition of the bauxite and Na_2CO_3, causing three peaks of various heights in the DTG curve. The endothermic peak in the DTA curve at 860°C can be ascribed to the melting Na_2CO_3 or some reaction products occurring in the solid phase.

The TG, DTG and DTA curves of a bauxite sample mixed with an alkaline additive with a mole fraction of CaO of 0.2 ($X_{Na_2CO_3}$:0.8) are shown in Fig. 3. The mass loss of the sample between 440–1200°C was 26.54%. Regions of rapid

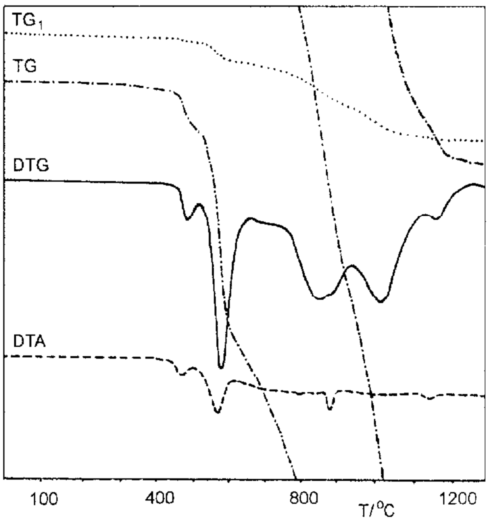

Fig. 3 Calcination of bauxite mixed with alkaline additive (mole fraction of CaO 0.2)

mass loss were exhibited consecutively in the temperature ranges of 440–500, 500–645, 735–930, 930–1110 and 1110–1200°C. All the peaks in the DTA curve were endothermic, appearing at 460, 570, 880 and 1130°C. The most interesting peak was the one at 460°C, which was not present in the curve of the sample containing bauxite and Na_2CO_3 only (Fig. 2). This difference is due to the presence of CaO. We believe that CaO absorbed humidity from the environment during grinding with bauxite or during the waiting period before the analysis, and thus some $Ca(OH)_2$ was formed. Dehydration took place as a result of the reaction, indicated by an endothermic peak at 460°C. Calculation of the mass loss between 500 and 645°C in the TG curve supported the assumption of the dehydration of bauxite in addition to the decomposition of Na_2CO_3. This was also confirmed by the DTA peak at 570°C. The mass loss above 930°C corresponded to the sublimation of Na_2O and decomposition of bauxite and Na_2CO_3. The mass loss due to sublimation of Na_2O was shown by the last part of TG curve and as a peak between 1100 and 1200°C in the DTG curve, as well as a small endothermic peak at 1130°C in the DTA curve. The sublimation of pure Na_2O above 917°C has also been reported in the literature [20].

The TG, DTG and DTA curves of a bauxite sample homogenized with an alkaline additive with a mole fraction of CaO of 0.4 ($X_{Na_2CO_3}$:0.6) are presented in Fig. 4. The mass loss was calculated as 24.62%. The peak due to the mass loss between 425 and 515°C in the TG curve was ascribed to the dehydration of hydrated CaO, and this corresponded to 2.15% mass loss. This was seen as an endothermic peak at 470°C in the DTA curve. The mass loss corresponding to the DTG peak between 515 and 630°C, was also calculated from the TG curve, and

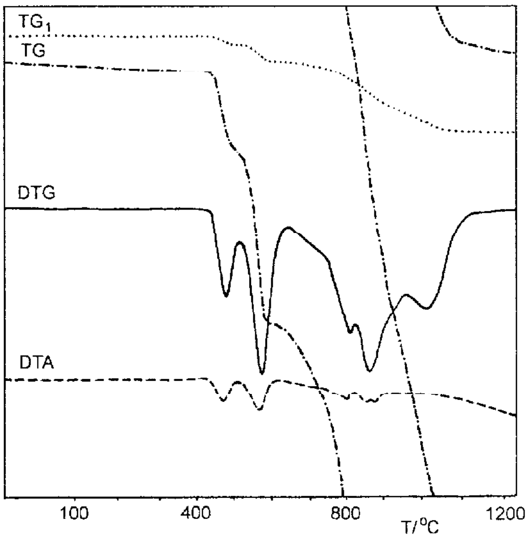

Fig. 4 Calcination of bauxite mixed with alkaline additive (mole fraction of CaO 0.4)

was assumed to be due to the dehydration of bauxite. The characteristic peak at 570°C in the DTA curve supports this assumption. The mass losses corresponding to the peaks between 630 and 820 and 820 and 960°C belonged to the decomposition of bauxite and Na_2CO_3. These were seen as endothermic peaks at 800 and 870°C in the DTA curve. The mass loss between 960 and 1100°C can be explained by the sublimation of Na_2O.

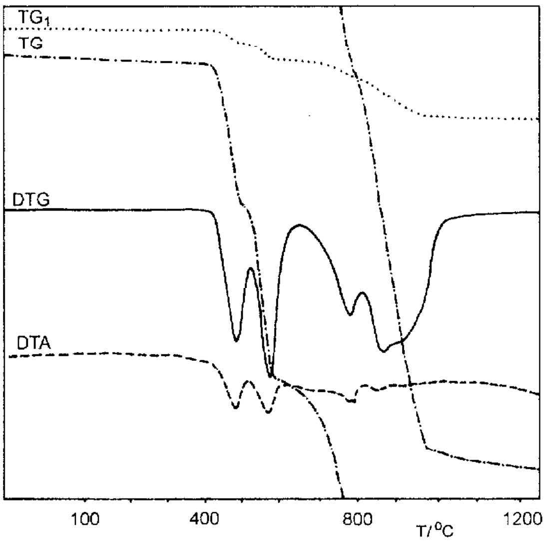

Fig. 5 Calcination of bauxite mixed with alkaline additive (mole fraction of CaO 0.6)

The thermoanalytical curves of a bauxite sample homogenized with an alkaline additive with a mole fraction of CaO of 0.6 are shown in Fig. 5. The total mass loss was calculated from the TG curve as 22.94%. The first mass loss between 410 and 515°C was due to the loss of humidity and decomposition of $Ca(OH)_2$, and was seen as an endothermic peak at 480°C in the DTA curve. The mass loss observed above 515°C was due to the dehydration of bauxite, and was represented by an endothermic peak at 560°C. However, TG curve indicated that the dehydration of bauxite was not complete. A mass loss between 640 and 890°C showed that also the decomposition of Na_2CO_3 took place in addition to the dehydration and decomposition of bauxite. These were shown as endothermic peaks at 780 and 850°C in the DTA curve.

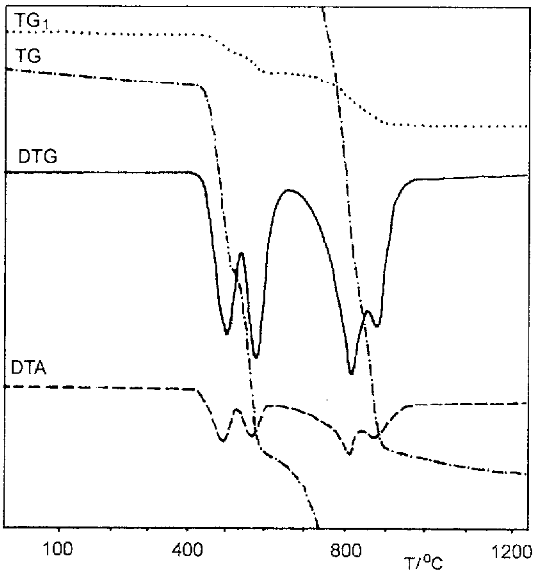

Fig. 6 Calcination of bauxite mixed with alkaline additive (mole fraction of CaO 0.8)

The TG, DTG and DTA curves of a bauxite sample homogenized with an alkaline additive with a mole fraction of CaO of 0.8 ($X_{Na_2CO_3}$:0.2) are given in Fig. 6. The total mass loss was calculated as 22.18%. The first mass loss of 5.28% shown by the peak between 420°C and 535°C in the DTG curve belonged to the release of absorbed water and dehydration of the formed $Ca(OH)_2$. This endothermic event was seen at 490°C in the DTA curve. The second mass loss reflected by the peak between 535 and 655°C in the DTG curve was due to the dehydration of bauxite, and this event caused an endothermic DTA peak at 570°C. Calculations revealed that the mass loss did not stop in this temperature range, and continued up to 655°C with a decreasing rate. The mass loss above 655°C was due to the decomposition of bauxite and Na_2CO_3 (endothermic peak at

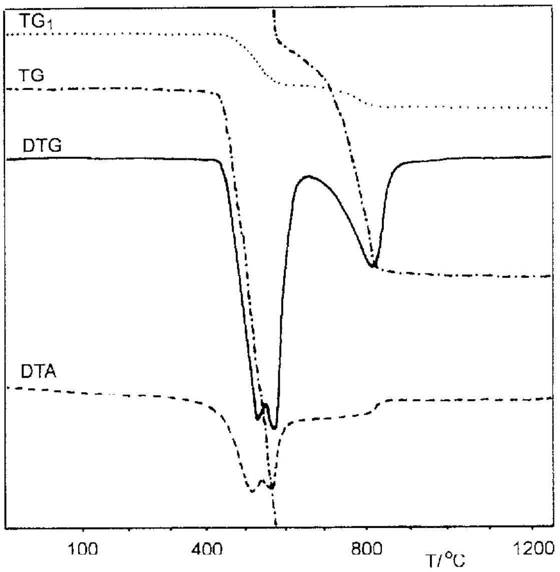

Fig. 7 Calcination of bauxite mixed with alkaline additive (mole fraction of CaO 1.0)

875°C) and sublimation of Na_2O. In other words, all the reactions took place one after another or simultaneously.

The TG, DTG and DTA curves obtained by calcination of bauxite sample mixed with only CaO (X_{CaO}=1.0, $X_{Na_2CO_3}$:0.0) are given in Fig. 7. The total mass loss was calculated as 17.04%. Two different peaks between 410 and 530 and 530 and 640°C in the DTG curve indicating important mass losses interfered with each other. The mass loss in this region was due to the physically adsorbed water content, the chemical water absorbed by $Ca(OH)_2$ and partial dehydration of bauxite. The corresponding peaks in the DTA curve show endothermic reactions almost superimposed. The mass loss between 640 and 880°C in the DTG curve was calculated as 5.28% from the TG curve. The maximum mass loss due to the decomposition of bauxite in the mixture was calculated as 1.28% from chemical analysis. As reflected by these values, the dehydration of bauxite continued also in the last region. Some peaks which characterized mixtures containing Na_2CO_3 in the last region of the DTG curve were not present. This confirms the sublimation of Na_2O assumed in previous cases. Analysis of the curves reveals that the mixture became stable above 900°C.

When the calcination of the original bauxite sample was examined in detail, the dehydration and decomposition reactions were found to end above 800°C. The mixture of bauxite with only CaO behaved similarly, and all reactions were completed at about 850°C. However the mass loss during the calcination of bauxite with added CaO and Na_2CO_3 and with Na_2CO_3 only stopped at about 1200°C because of the decomposition of the Na_2CO_3 present.

Conclusions

These studies indicate that the endothermic peak temperatures belonging to the dehydration of bauxite increase in the presence of added CaO. The endothermic peak temperatures of the dehydration of $Ca(OH)_2$ which occurs before the dehydration of bauxite in the presence of CaO increase with the amount of added CaO.

It may be possible to evaluate the applicability of diasporitic bauxites for production of alumina based on solid-state reactions if an alkaline substance is added and preheating is applied. Additionally, the preheating temperature should be lower than the sublimation temperature of Na_2O to prevent loss of Na_2CO_3, i.e. the preheating temperature should not be as high as 1200°C.

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