



Thermal characterization and kinetic analysis of non-isothermal decomposition process of Bauxite red mud. Estimation of density distribution function of the apparent activation energy

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ABSTRACT

Thermal characterization and kinetic analysis of non-isothermal decomposition process of Bauxite red mud were carried out using thermogravimetry (TG), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC), differential thermal analysis (DTA) and Fourier transform infrared spectroscopy (FTIR). It was found that the investigated decomposition was a complex heterogeneous process, which included two main decomposition stages and one sub-stage. The overall decomposition process consisted of the series of parallel and competitive reactions, which originated from the decomposition of various chemical species and solid-state transformations. This behavior was confirmed by the appearance of different forms of density distribution functions of apparent activation energy values. Furthermore, the conversion range of $0.10 \leq \alpha \leq 0.30$, with a constant value of the apparent activation energy ($146.4 \text{ kJ mol}^{-1}$) for the second stage of the overall process, belongs to calcite decomposition, which takes place through a two-dimensional diffusion mechanism.

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1. Introduction

The Bayer process is a worldwide adopted technology for alumina production, by reacting ground bauxite ore with caustic soda, under heat and pressure (Habashi, 1997; Wang et al., 2008). The resulting sodium aluminate solution is subsequently cleaned, decomposed and calcinated into alumina, whereas red mud represents the undissolved waste material separated from the solution (Habashi, 1997). Depending on the quality of bauxite, 0.3–2.5 tonnes of red mud is generated per tonne of alumina produced (Adamson et al., 1963). Therefore, disposal of the red mud is a major problem due to the vast amounts and its highly alkaline nature. It was reported that the slurry washed with 1000 times its mass of distilled water still reaches a pH of 10.5 (Habashi, 1997). In the alumina industries around the world, deep thickening to recover alumina and soda followed by wet-slurry or dry storage are the most common practices for red mud disposal (Piga et al., 1993). The mineral and chemical compositions of the red mud depend on the quality of bauxite, and to a lesser degree, the operational process parameters. Different red mud samples contain 11–45 wt.% Al_2O_3 , 5–66 wt.% Fe_2O_3 , 1–16 wt.%

SiO_2 , 6–25 wt.% TiO_2 and 3–8 wt.% Na_2O (Adamson et al., 1963). From the mineralogical point of view, hematite (Fe_2O_3), goethite (FeOOH), gibbsite ($\text{Al}(\text{OH})_3$), and boehmite (AlOOH), calcium oxides, titanium oxides (anatase and rutile), and aluminosilicate minerals (sodalite, cancrinite) are commonly found (Wang et al., 2008). Some of the minerals originate from the parent bauxite, some are modified and some (like sodalite and cancrinite) or created during the bauxite treatment.

Many studies have investigated different applications of red mud in order to utilize this industrial waste and minimize its environmental impact. From the recent literature which summarizes the scientific research results and patents, it can be concluded that applications include red mud as an adsorbent material for treatment of water polluted with heavy metals, inorganic ions, organic compounds, viruses and bacteria, for gas cleaning, soil remediation, in catalysis, as well as for preparation of construction materials, such as cement, glass-ceramics, fired and non-fired building materials, etc. (Bhatnagar et al., 2011; Liu et al., 2009, 2011; Wang et al., 2008).

From the aspect of red mud utilization, thermal treatments or activations are often necessary. Consequently, the chemical/mineralogical compositions, thermal properties as well as the decomposition kinetics at elevated temperatures are of great importance and need to be understood. In the literature, several researches have studied red mud from different sources by thermal analysis and the other

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techniques (Atasoy, 2005; Lin, 2004; Pascual et al., 2009; Sglavo et al., 2000). All of them have approved that this material has a complex behavior. Based on the literature survey, there is no information about the detailed kinetic analysis of the red mud decomposition process, where the combined “model-fitting/model-free” kinetical approach (Vyazovkin and Wight, 1999) was used, together with statistical analysis. Also, the data about the derivation of the density distribution function (ddf) of the apparent activation energy ($f(E_a)$), for such complex material during non-isothermal decomposition process, were not found.

Accordingly, in this study we focused our investigation on the thermal behavior of the red mud, including the solid-state transformations during the heating, within the temperature interval of 20–900 °C. The red mud sample from Bosnia and Herzegovina (“Birač” Alumina factory) was used, and the material was characterized by thermogravimetry (TG), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC), differential thermal analysis (DTA) and the Fourier transform infrared spectroscopy (FTIR).

For the purpose of kinetic study, the combined kinetic approach which involves applying the “model-free” (isoconversional) and the modelistic (“model-fitting”) methods was used (Khawam and Flanagan, 2005). These methods allow us to perform complete kinetic triplets for the investigated decomposition process. Furthermore, in this article, the Miura's procedure (Miura, 1995; Miura and Maki, 1998) for finding the experimental form of the density distribution function (ddf) of the apparent activation energy ($f(E_a)$) was applied. The corresponding theoretical ddf 's for the considered decomposition process were also derived. For such a complex heterogeneous process, the obtained density distribution functions of the apparent activation energy values enable us to better describe the mechanism of the process, which can be represented by the analytical form of the reaction mechanism function. The results collected in this article provide a better understanding of the physical and chemical characteristics of the tested material, and also the kinetics of degradation at elevated temperatures, which can be useful both from a fundamental and from a practical point of view.

2. Materials and methods

The investigated red mud sample was supplied from the “Birač” Alumina factory. After settling, the clear supernatant was decanted. The remaining dense slurry was dried in an electrical oven at 105 °C for 24 h, and powdered using mortar and pestle.

The chemical analyses of such sample have revealed that it consisted of: SiO₂ (12.62%), Fe₂O₃ (42.42%), Al₂O₃ (18.08%), TiO₂ (4.63%), CaO (2.86%), and Na₂O (8.92%), whereas the lost of ignition was 7.93% (Smičklas et al., 2013).

Thermal analyses were performed on an SDT-Q 600 (TA Instruments) equipment for simultaneous differential thermal analysis (DTA)/differential scanning calorimetric (DSC) measurements and also for the thermogravimetric (TGA) analysis. The samples were heated from ambient temperature up to 900 °C at three different heating rates ($\beta = 10 \text{ °C min}^{-1}$, 15 °C min^{-1} and 20 °C min^{-1}) in a nitrogen (N₂) flow with the rate of $\varphi = 100 \text{ cm}^3 \text{ min}^{-1}$. Decomposition temperature calculations were performed from the obtained data using the Universal analysis 2000 software.

To get a better insight into the processes provoked by heat treatment, the original red mud powder as well as several samples prepared by annealing the red mud at different temperatures was characterized by Fourier transforms infrared (FTIR) spectrometry. The annealed samples were prepared by heating the starting material at the temperatures of $T = 200 \text{ °C}$, 400 °C , 600 °C , 800 °C and 900 °C in the electrical furnace, for 3 h. All FTIR spectra were recorded in the $4000\text{--}400 \text{ cm}^{-1}$ region, using Bomem MB 100 FTIR spectrometer. Ten scans per spectrum were collected, with a resolution of the 4 cm^{-1} , using the potassium bromide pellet technique.

3. Theoretical background

In the thermogravimetric measurements, the degree of decomposition (conversion) can be calculated as follows:

$$\alpha = \frac{m_o - m_T}{m_o - m_f} \quad (1)$$

where α is the degree of decomposition; m_T , m_o and m_f are the actual, initial and final mass of the sample, respectively. A typical kinetic equation for the investigated process can be expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

where $d\alpha/dt$ is the decomposition rate, $f(\alpha)$ is the function of α , depends on the particular decomposition mechanism (function of reaction mechanism). In Eq. (2), $k(T)$ is the temperature dependent decomposition rate constant, which can be expressed by the Arrhenius equation:

$$k(T) = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where A is the pre-exponential factor (min^{-1}), E_a is the apparent activation energy (J mol^{-1}), R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the absolute temperature (K). Substituting the Eq. (3) into Eq. (2), we obtain

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right)f(\alpha) \quad (4)$$

If the temperature of a sample is changed by a constant value of β (the linear heating rate) ($\beta = dT/dt$), the variation of the degree of decomposition can be analyzed as a function of temperature. Therefore, the reaction rate gives:

$$\beta \cdot \frac{d\alpha}{dT} = A \cdot \exp\left(-\frac{E_a}{RT}\right)f(\alpha) \quad (5)$$

Separating the variable and rearranging and integrating Eq. (5), it can be obtained:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_o}^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (6)$$

where $g(\alpha)$ is integral form of the reaction mechanism function, and T_o is the starting temperature of non-isothermal experiment. Eq. (6) cannot be expressed by a simple analytical form since its right-hand side corresponds to a series of infinite γ functions. In mathematical practice, Eq. (6) can be expressed in the following form (Vyazovkin and Wight, 1998):

$$g(\alpha) = \frac{A}{\beta} \int_0^\alpha \exp\left(-\frac{E_a}{RT}\right) dT = \frac{AE_a}{\beta R} p(x) \quad (7)$$

where an approximation is introduced for the lower limit of the integral on the right-hand side of Eq. (6) as $T_o \rightarrow 0$, bearing in mind that the value of temperature T_o in practical cases is very small. The variable $x = E_a/RT$ is the reduced apparent activation energy, while $p(x)$ represents the temperature or exponential integral which cannot be exactly calculated (Flynn, 1997). For the different solid state reaction mechanisms, $f(\alpha)$ and $g(\alpha)$ have different expressions (Turmanova et al., 2008).

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