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STUDY OF KINETICS OF REACTION OF TITANIUM RAW MATERIALS WITH SULPHURIC ACID

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The reaction of ilmenite titanium raw materials with sulphuric acid has been studied in a non-isothermal- non-adiabatic type calorimeter. The influence of different starting conditions, temperature and ilmenite particle-size distribution on the thermo-kinetics of the reaction was investigated. A kinetic model is presented for this heterogeneous system for a specified ilmenite particle-size distribution and starting temperature. On the basis of this model and experimentally determined parameters it is possible to analyse by simulation the autothermic reaction of digestion of different titanium ores with sulphuric acid.

Keywords: heterogeneous system, kinetic model, titanium raw materials

Introduction

Ilmenites and slags are the basic raw materials in the production of titanium dioxide using the sulphuric acid method. This process is mainly non-continuous. In the first step the raw material is ground and dried, followed by mixing with sulphuric acid, and the reaction is started by heating with steam. This reaction is strongly exothermic and the reaction mixture reaches temperatures of over 200°C. It is very important to know the rate, thermal effects and other kinetic parameters of this reaction. This information is required for optimum and safe operation of this reaction. In the literature models are presented [1, 2] to simulate this reaction, but the starting condition are quite different and the solution is very complex. In order to estimate the kinetic parameters, a special quasi-adiabatic calorimeter has been constructed and a mathematical model is proposed for the process.

Experimental

The reaction of ilmenite with sulphuric acid was observed in the quasi-adiabatic calorimetric system. The calorimeter was built using a Dewar flask,

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equipped with a glass stirrer, an electric calibration heater and a temperature sensor.

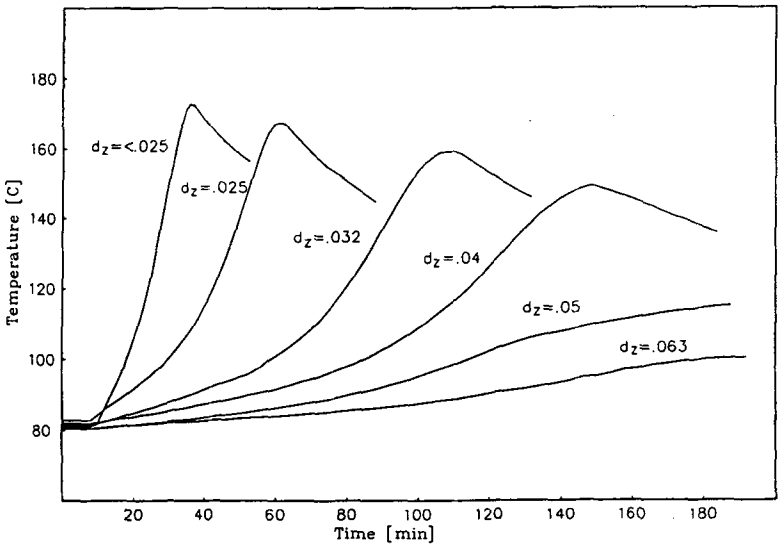

Fig. 1 Temperature changes in the calorimeter for different particle sizes of ilmenite

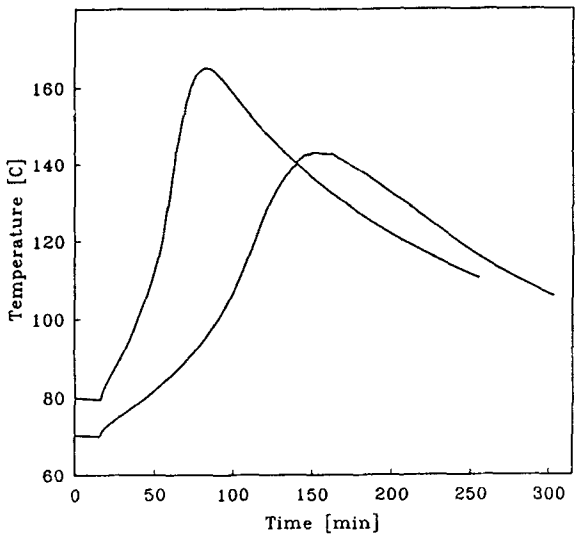

Fig. 2 Observed temperature changes in calorimeter for different starting temperatures

The sulphuric acid of known concentration was placed in calorimeter together with ground ilmenite. The size of the ilmenite particles plays a very important role during reaction. In the experiment the ilmenite particles were separated into specific size ranges. When the initial temperature was reached the reaction was started by mixing both reactants. The temperature changes during reaction for different particle sizes of ilmenite are shown in Fig. 1 and for different starting temperatures in Fig. 2.

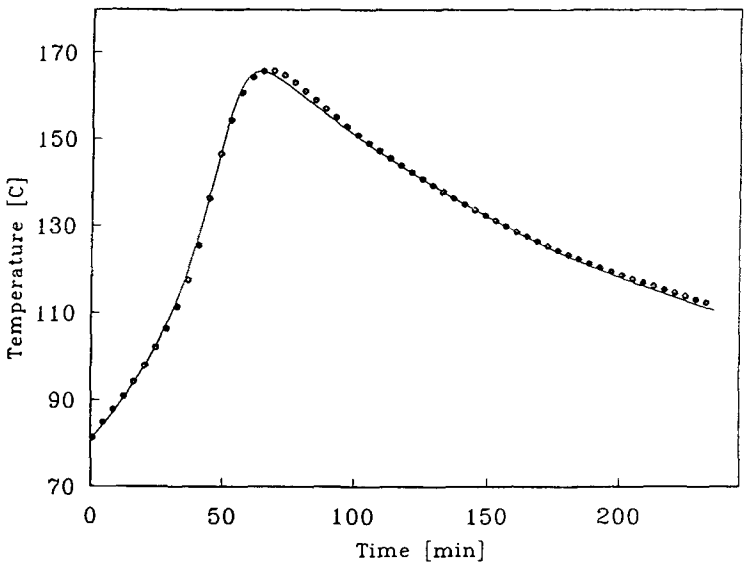

Fig. 3 Comparison of observed and calculated values of temperatures in calorimeter

Model

In the study of temperature changes in the calorimeter the following assumptions were made:

– only one kind of chemical reaction is proceeding in the system,

– the sepcific heat of the reaction mixture is constant and does not depend on the temperature,

– the heat conduction of the reaction mixture is sufficiently high that the temperature is uniform throughout the mixture.

In a heterophase system the interfacial surface plays a very important role. The rate of reaction depends mainly on the interfacial surface and to a lesser extent on the degree of transformation. The kinetic equation takes the form:

$$d\alpha / dt = k_r S \quad (1)$$

where: S – interfacial surface, $k_r = k_o \exp(-E/RT)$
For spherical particles the interfacial surface depends on the degree of transformation:

$$S = S_o (1 - \alpha)^{2/3} \tag{2}$$

The energy balance for this calorimetric system and assumptions take the form:

$$(k + m_r c_{pr})\, dT/dt = m_i H_r k_o S - k_s (T - T_o) \tag{3}$$

where: k –calorimetric constant; m_r –mass of reaction system; c_{pr} –heat capacity of reaction system; m_i – mass of ilmenite sample; H_r –heat of reaction

The process is described by a system of ordinary differential Eqs (1–3), which can be solved by one of numerical method for boundary condition:
for $t = 0$, $T = T_o$, $\alpha = 0$.

On the basis of the experimental data it is possible to estimate parameters and compare experimental temperature changes with theoretical calculated from Eqs (1–3) (Fig. 3).

It is possible to simulate temperature changes for different starting tempratures and different particle-size distributions of ilmenite if the particles are assumed to be spherical.

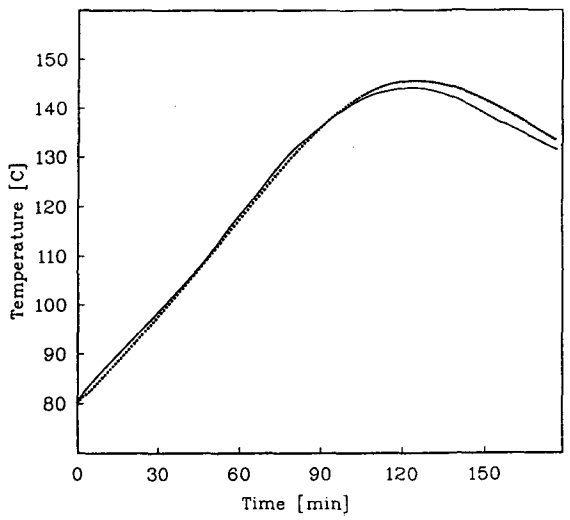

Fig. 4 Comparison of temperature changes for reaction of ilmenite (—) (particle size range 0.04–0.063 mm) with that calculated from the model (· · · ·)

Results

Using the experimental measurements in the simple mathematical model presented, the thermal effects and macro kinetic parameters were calculated. A comparison of temperature changes for the reaction of ilmenite (particle size range 0.04–0.063 mm) with the calculated temperature changes from the model is presented in Fig. 4. The parameters were estimated on the basis of the reaction of sulphuric acid with ilmenite (particle size range 0.02–0.04 mm). They show good agreement. The results of the investigation of this reaction indicate that the process rate and efficiency of digestion depend mainly on the initial temperature and particle size. The proposed method can be used to calculate the thermal effects and kinetic parameters of the reaction and the determination of the reactivity of different new materials.

References

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Zusammenfassung — In einem nichtisothermen-nichtadiabatischem Kalorimeter wurde die Reaktion des Titanrohstoffes Ilmenit mit Schwefelsäure untersucht. Dabei wurde der Einfluß verschiedener Ausgangsbedingungen, der Temperatur und der Partikelgrößenverteilung des Ilmenits auf die Thermokinetik der Reaktion geprüft. Für eine bestimmte Partikelgrößenverteilung und Ausgangstemperatur wird ein kinetisches Modell für dieses heterogene System gegeben. Anhand dieses Modelles und experimentell bestimmter Parameter ist es möglich, mittels Simulation die autothermische Reaktion des Aufschließens verschiedener Titanerze mit Schwefelsäure zu analysieren.