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KINETIC MODEL FOR THE REACTION OF ILMENITE WITH SULPHURIC ACID

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Abstract

The kinetic of the reaction ilmenite with sulphuric acid was studied using non-adiabatic and non-isothermic calorimetric device system. The kinetic model based on interphase surface and kinetic models found in literature which are usually applied were tested.

The best agreement between experimental and calculated values was found with model based on first order of reaction and model of contracting volume.

Keywords: calorimetry, ilmenite, interphase surface, kinetics, model

Introduction

In the process of obtaining titanium dioxide by sulphate method, titanium raw materials, ilmenites or titanium slags are digested at high temperature and in the concentrated solution of sulphuric acid. As a result of an exothermic reaction, the temperature of the reacting mixtures grows up to about 200°C. The reaction product is a mixture of sulphate of titanium(IV), iron(II), iron(III), magnesium and other metals, which are present in raw material.

Thermal power of the reactor, in which titanium raw material is digested, in the period of the main run of the reaction can reach about 10 MW. The uncontrolled run of the reactor creates a dangerous possibility of explosion of the reaction mixture.

The aim of the presented investigations was the research of the rate of reaction of Norwegian ilmenite with sulphuric acid by the method of non-isothermic calorimetry and the determination the kinetic model of this process.

Experimental

Natural ilmenite is a concentrate most often received by the method of flotation from solid magma rocks or from alluvial sands. These raw materials are characterised by high content of titanium dioxide and oxides of iron, magnesium and other metals such as manganese, chrome, niobium.

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Ilmenite from the south of Norway was applied in the investigations of the reaction of ilmenite with sulphuric acid. The elemental composition of ilmenite determined by spectrometer of X-ray fluorescence XRF PHILIPS PW1480 was as follows: TiO_2 – 44.4%, FeO – 34.8%, Fe_2O_3 – 11.6%, MgO – 4.1% and SiO_2 – 2.1%.

Investigations of phase composition on X-ray diffractometer PHILIPS with goniometer PW 1820 and with controller PW 1710 showed, that the main crystallographic phase of ilmenite is iron - titanic oxide $FeTiO_3$.

Ilmenite before measurement was dried at 105°C to constant mass, and then grounded in Fritsch sphere mill to the moment when the remainder on 40 μm sieve was 15%.

Ilmenite reaction with sulphuric acid was investigated in non-isothermic and non-adiabatic calorimeter. The main unit of the apparatus was a calorimetric vessel volume about 0.6 dm^3, equipped with a heater, a stirrer and a temperature Pt 100 sensor. The calorimetric vessel was placed in thermostatic jacket. Schematic diagram of apparatus was presented in Fig. 1.

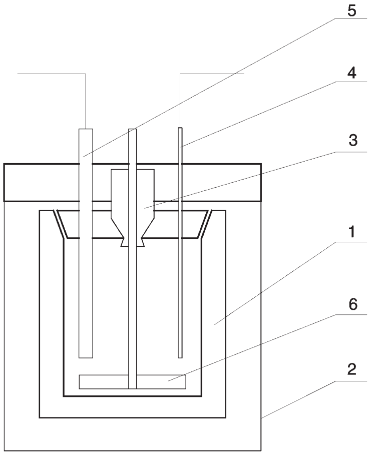

Fig. 1 Apparatus used for thermokinetic investigations. 1 – calorimetric vessel, 2 – thermostat, 3 – dosage vessel, 4 – temperature sensor, 5 – heater, 6 – stirrer

The calorimetric vessel was connected with the feeder of ilmenite. The reaction begins when ilmenite was introduced into the calorimetric vessel filled with sulphuric acid.

The installed electric heater served to calibrate the calorimeter (determination of calorimetric constant, time constant and heat transfer coefficient).

The used sample of ilmenite was about 100 g and mass of sulphuric acid of concentration 84% was about 400 g.

In Fig. 2 was presented the temperature run of reaction ilmenite with sulphuric acid in calorimeter at the starting temperature 80°C and in concentration of sulphuric acid 84%.

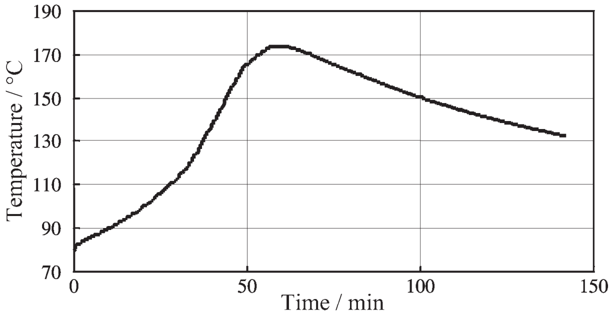

Fig. 2 Temperature changes in calorimeter during reaction ilmenite with sulphuric acid

After the beginning of the reaction the temperature began growing quickly in the calorimetric vessel. At the moment when almost all mass of ilmenite was reacted, the diminution of the heat stream takes place, which is visible as a slight maximum on the graph. When the maximum of the temperature was reached, the amount of the heat reaction was smaller than the heat losses and the temperature decreases.

Theoretical

Reaction of ilmenite with sulphuric acid, solid–liquid system, proceed on an interphase surface. Processes of mass transport to and from interphase surface, inflow of sulphuric acid to the area of the reaction and outflow dissolution product of the reaction from the reaction area play an important role in this reaction. Driving module of this processes is difference of concentrations among area of reaction and environment.

It can be assumed, that products of the reaction dissolve partly, and remainders create porous structure, which is not a barrier for processes of mass transport. As the reaction is carried on with excess of sulphuric acid, it can be accepted, that the concentration of sulphuric acid is constant during the reaction.

This reaction is exothermic, the heat of reaction is the reason for the increase of the temperature of the reactionary mixture. The increase of the temperature influences the expansion of the reaction rate. On constructing a kinetic model the following assumptions were accepted; all particles are of identical dimension and shape, the enthalpy of the reaction is constant and is not dependent on temperature, the heat conduction of the reaction mixture is sufficiently high, that temperature is identical in given moment in all sample, and specific heat of the reaction mixture is constant and does not depend on temperature.

The reaction rate according to this assumption can be expressed with equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{1}$$

where: α – degree of transformation, A – pre-exponential coefficient, E – activation energy.

The reaction temperature is not constant and the second equation is necessary in order to describe this dependence. In case of calorimetric systems we can use balance equation of heat flow:

$$K\frac{\mathrm{d}T}{\mathrm{d}t}=\frac{\mathrm{d}Q}{\mathrm{d}t}-\beta T(t) \tag{2}$$

where: K – calorimetric constant, Q – heat amount generated during reaction, β – coefficient of heat losses.

In Eq. (2) the left side determines heat accumulation in calorimetric system, and the right side determines the difference between heat of stream generated in calorimetric vessel and heat losses to environments. We receive in consequence the following system of differential equations:

$$\begin{aligned} K\frac{\mathrm{d}T}{\mathrm{d}t}&=\Delta H_\mathrm{r}\frac{\mathrm{d}\alpha}{\mathrm{d}t}-\beta T(t)\\ \frac{\mathrm{d}\alpha}{\mathrm{d}t}&=A\exp\left(-\frac{E}{RT}\right)f(\alpha) \end{aligned} \tag{3}$$

The solution of the equation system (3) requires a kinetic equation. In literature series of kinetic models with different factors influencing the reaction rate was described [1]. Models describing phenomena of nucleation belong to popular kinetic models. Avrami equations [2] take into account this type of process. To reactions in which occur process of diffusion, belongs oxidising of metals (gas+solid), reactions between solids and reactions in liquid–solid system. The simpliest equation taking into account diffusion processes is the parabolic equation [3].

Kinetic models taking into account influence of surface change on rate of reaction are qualified as models of disappearing geometry. Example of this kinetic type is reaction of solid in sphere form, which decrease during reaction until complete disappearances.

In heterogeneous systems quantity of interfacial surface plays an essential role. The surface of the reaction is closely connected with the degree of transformation. Degree of transformation is defined by

$$\alpha=\frac{m_0-m}{m_0} \tag{4}$$

where: m – mass present, m_0 – initial mass.

For spherical particles dependence of interfacial surface on degree of transformation we get by substituting mass and surface of particle:

$$S=S_0(1-\alpha)^{2/3} \tag{5}$$

This equation was presented in paper [4].

We can use similar considerations for particles of simple regular solids, for example, particles in shape of cylinder.

Substituting mass of particle in shape of cylinder

$$m=\frac{\rho\pi D^2 L}{4} \tag{6}$$

and surface

$$S=\pi DL+\frac{\pi D^2}{2} \tag{7}$$

into Eq. (4) we receive

$$S=\pi D_0 L\left[\frac{L(1-\alpha)}{L_0}\right]^{\frac{1}{2}}+\frac{\pi D_0^2 L(1-\alpha)}{2L_0} \tag{8}$$

For the case when the cylinder shape nears to needles i.e. $L>>D$ and the length of this needles does not change in time of reaction i.e. $L=L_0$, Eq. (8) will simplify and we obtain:

$$S=S_0(1-\alpha)^{1/2} \tag{9}$$

For the case of particles in shape of cylinder when both diameter and length change in time of reaction in the following way

$$\frac{D}{L}=\text{const.} \tag{10}$$

we obtain

$$S=S_0(1-\alpha)^{2/3} \tag{11}$$

This equation is identical with Eq. (5) obtained for spherical particles.

Next shape in our consideration is particle of rectangular prism of edges A, B and C. We assumed, this dimension in time of reaction changes in following way

$$\begin{gathered}\frac{\mathrm{A}}{\mathrm{B}}=\text{const.}\\ \frac{\mathrm{B}}{\mathrm{C}}=\text{const.}\end{gathered} \tag{12}$$

After transformation we obtain Eq. (11).

From this considerations it can be concluded that for reaction of ilmenite (irregular shape of particles) with sulphuric acid we can take the kinetic equations into account

$$f(\alpha)=(1-\alpha)^{1/2} \tag{13}$$

and

$$f(\alpha)=(1-\alpha)^{2/3} \tag{14}$$

In [1] we found rate equations used in kinetic analyses of solid state reactions. These kinetic models take geometric factors, chemical controls and diffusion into consideration and are used to describe processes of thermal transformations.

Substituting this kinetic equations to system of Eq. (3), we can calculate the value of the pre-exponential factor and activation energy and determine the best fitting model.

Results and discussion

To find the value of parameters in the equation system (3) the experimental data and non-linear regression were used. This is an iterative procedure to find out the minimum of sum of square deviations.

$$\Sigma(T_{\mathrm{i\,exp}} - T_{\mathrm{i\,cal}})^2 = \min \tag{15}$$

To solve this function the algorithm on the basis of Marquart method was applied. In this algorithm during each iteration the system of differential Eq. (3) by the Runge–Kutta method was solved.

Calculations were carried out for experimental data of ilmenite with sulphuric acid and for kinetic models. Results of calculations are in Table 1.

Table 1 Results of calculation

$f(\alpha)$	$\Sigma(T_{\mathrm{i\,exp}}-T_{\mathrm{i}})^2$
$(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	1288.2
$\alpha(1-\alpha)$	27832.9
$(1-\alpha)^{1/2}$	179.4
$(1-\alpha)^{2/3}$	104.7
$(1-\alpha)$	51.2
$(1-\alpha)^2$	178.8
$1/\alpha$	42207.9
$[-\ln(1-\alpha)]^{-1}$	16321.5
$(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	10485.2
$[(1-\alpha)^{-1/3}-1]^{-1}$	10486.5

In Table 1 we present the sum of squares deviations for kinetic model.

The best fitting of experimental data we received for the kinetic models of contracting volume and for model of chemical reaction of first order. In both cases lowest value of sum of squares deviations was received. The activation energy for the kinetic model of contracting volume Eq. (11) was E=41.44 kJ mol^{-1} and for reaction of first order was E=49.54 kJ mol^{-1}.

Remaining equations taking into account diffusion show considerably worse fitting to given experimental. Equations taking into account occurrence of nuclei (Avrami equation) do not give a good fitting, either.

The calculations show, that diffusion processes and transportation of mass from and to interfacial surface do not decide about the reaction rate. The main units having influence on the reaction rate are the interfacial surface and chemical kinetics in reaction of ilmenite with sulphuric acid. The obtained results confirm earlier assumptions accepted.

The experimental value of heat of reaction ilmenite with sulphuric acid was obtained from the experiment. Taking into account suitable corrections we received the value of 1.12 kJ g^{-1}.

During reaction of ilmenite with sulphuric acid, the chemical reaction can be assumed and presented below:

$$\begin{gathered} TiO_2+H_2SO_4 \rightarrow TiOSO_4+H_2O \\ Fe_2O_3+3H_2SO_4 \rightarrow Fe_2(SO_4)_3+3H_2O \\ FeO+H_2SO_4 \rightarrow FeSO_4+H_2O \\ MgO+H_2SO_4 \rightarrow MgSO_4+H_2O \end{gathered}$$

On the basis of these reactions it is possible to calculate the theoretical value of heat reaction. The result of heat calculation for ilmenite is 0. 997 kJ g^{-1}.

Conclusions

Presented results of calculations and theoretical considerations lead to the conclusion that the reaction rate of ilmenite with sulphuric acid mainly depends on the quantity of interfacial surface and chemical reaction. In this case process of mass transport does not influence on the reaction rate. It confirms the assumption, that products of reaction dissolve partly, and the remainders create a porous structure which in not a barrier for process of mass transport.

Theoretical considerations about particles shape of solids lead to the conclusion, that kinetic Eq. (11) could be used to particles in a more complicated shape, together with particles in an irregular shape. The assumption about the constant ratio of main dimensions of particles in time of reaction could be applied to the particles in irregular shapes. Experimental results confirm this assumption.

The assumption about constant specific heat of reaction mixture in time of reaction is close to real conditions. The measured specific heat of substrate and the product of reaction was on the same level about 1.5 J g^{-1} K^{-1}.

Differences from real conditions were in the assumption about identical dimensions of particles in reaction mixture. It is very difficult to fulfil this assumption, in our experiment the dimensions of particles were in the range from 1 to 40 μm.

The rest of assumptions are consistent with real condition of reaction.

The tested kinetic model of reaction of ilmenite with sulphuric acid is very simple and could be used in simulation of production technology, especially to determine conditions for safety run of reaction.

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