

# Influence of particle size distribution on thermokinetics of ilmenite with sulphuric acid reaction

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**Abstract** The knowledge about kinetics of the reaction titanium raw materials with sulphuric acid is very important from the reason of influence of initial conditions of reaction on efficiency, quality and safety. One of the very important parameter, which influence on kinetics of this reaction is distribution of particles sizes of raw material. Presented results of investigation of reaction thermokinetics of ilmenite with different particles sizes, obtained in special construction of calorimeter, demonstrated very great influence of this parameter on rate of reaction with sulphuric acid. On the base of experimental investigation the kinetic model of this reaction was elaborated which takes into account density of particles sizes distribution described by the function of Rosin–Rammler. Presented model was tested on the base of experimental data of ilmenite with sulphuric acid reaction.

**Keywords** Calorimetry · Thermokinetic of reaction · Particles size distribution

## Introduction

Sulphate technology of titanium pigments production is widely used and has large industrial meaning. In this technology, reaction of titanium raw material with sulphuric acid is the first step of the process [1]. Titanium raw material is mixed with sulphuric acid and reaction is

initiated by heating. Conditions of reaction have great influence on efficiency, quality and safety.

Series of parameters have influence on kinetics of this reaction, for example, such as temperature, acid concentration or the size of particles of titanium raw material. The special meaning in this reaction has the last parameter i.e. particles sizes distribution. Very often the result of inappropriate grinding of the raw material, is the incomplete reaction or what is worse, thermal explosion in case of very fine grinding.

The size of the interphase surface in the liquid (gas)–solid system and particle size distribution are the essential parameters, which have the significant influence on reaction, what is the subject of series of papers [2–10]. In reaction of solid with liquid, the chemical process can begin when both reacting substances are in contact. The surface of solid is the place of contact and therefore surface area is so important parameter. This suggests that, the changes of surface area (size of particles) of raw material influences on the reaction rate [2].

In theoretical models of the reaction kinetics, it was assumed, that particles are spherical and in the same size. In real system we have however solid particles with different dimensions and in consequence this particles size distribution have influence on rate of reaction. This suggests that, particles size distribution is very important parameter in this type of reaction.

## Experimental

The reaction of sulphuric acid with titanium raw materials is strongly exothermic. Except of heat emitted in reaction, can be emitted vapours and gases, in extreme cases enough intensely, what creates danger of explosion. The strongly

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corroding environment and high temperature of reaction are additional problems in investigation. Investigation of thermal effects and kinetics of this reaction was realized in specially constructed calorimetric system described elsewhere [13]. This calorimetric system consists of calorimetric vessel and thermostatic shield. The calorimetric vessel was equipped with heater, temperature sensor, stirrer, batcher and safety valve.

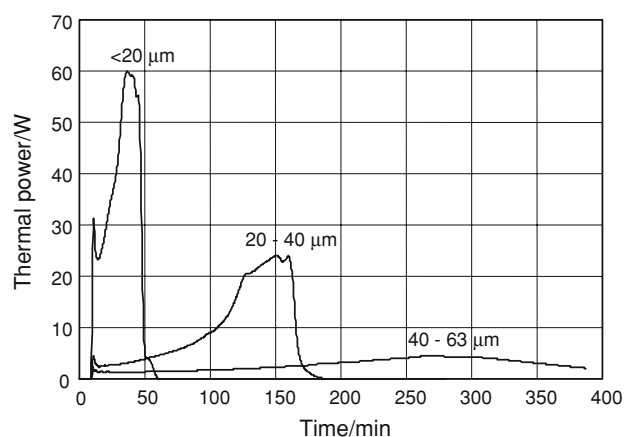
As raw material to investigations of reaction with sulphuric acid was used ilmenite obtained from deposits in South Norway. Composition of ilmenite determined by XRF method was as follows:  $\text{TiO}_2$ —44.4%,  $\text{FeO}$ —34.8%,  $\text{Fe}_2\text{O}_3$ —11.6%,  $\text{MgO}$ —4.1% and  $\text{SiO}_2$ —2.1%.

The sample of ilmenite before measurement was dried and grounded in a ball mill of Frisch. Depending on grinding time, different grinding level of the sample was obtained. The particle size distribution of grounded material was determined by electron scanning microscope BS300. The thermokinetics of reaction of grounded ilmenite was investigated in calorimeter. Reaction was initiated by pouring ilmenite to sulphuric acid. After initiation, reaction begins simultaneously followed by the temperature rise inside the calorimetric vessel. After reaction, the products of reaction were analyzed by ICP and XRF spectrometers and on the base of these results was determined degree of conversion of titanium raw material, and thermal effect of reaction.

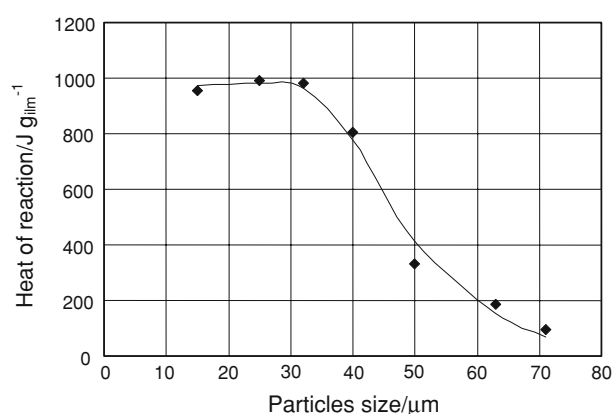
## Results

In order to determine the influence of the particle size of ilmenite on thermokinetics of reaction, ilmenite was grounded and next was separated on fractions with different particles size and reaction of sulphuric acid with every of these particles fraction was investigated. In Fig. 1 are presented the changes of thermal power of reaction of sulphuric acid with different particle size fractions of ilmenite. Presented curves of the thermal power demonstrate very strong dependence of the reaction rate on the size of ilmenite particles. In extreme cases i.e. when the diameter of particles is smaller than  $20\ \mu\text{m}$  the thermal power is big enough to expect that in these conditions, reaction can create danger of explosion, however, if particles diameter is in range  $40\text{--}63\ \mu\text{m}$  the reaction rate is so slowly that it is possible to expect that the degree of reaction completeness is on very low level.

An important parameter of reaction is the heat emitted during reaction. This parameter also depends on particle size of ilmenite and could be used to the estimation of degree of reaction completeness of titanium raw material. Investigation of particle size influence on heat emitted was realized in the same way as in previous case, grounded



**Fig. 1** Changes of thermal power in reaction of sulphuric acid with ilmenite for different particles size

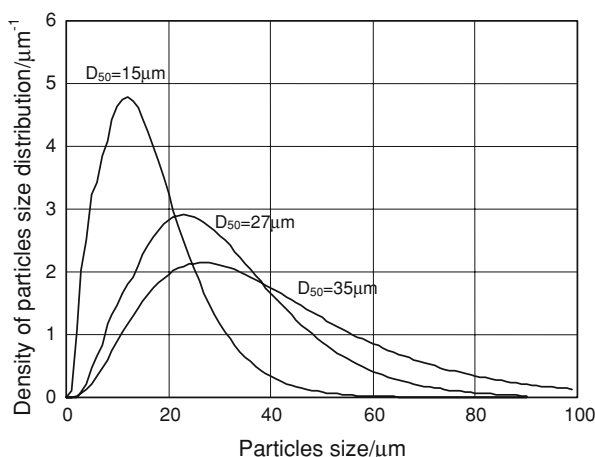


**Fig. 2** Changes of heat emitted during reaction in dependence on the size of the fraction of ilmenite particles

ilmenite was divided in very narrow fractions of particle size and for every of these fractions heat of reaction was investigated. Results of measurement were presented in Fig. 2. On the graph is clearly visible the changes of the heat of the reaction. Below particles size of  $30\ \mu\text{m}$  heat of reaction is practically constant, above this value, heat of reaction is changing down to the very low level what can be result of incomplete conversion of ilmenite particles, i.e. the amount of the heat emitted is insufficient for supporting the run of the reaction.

In the result of the grinding process we are obtaining particles about different dimensions. As was mentioned earlier, size of particles or shape of density of particles sizes distribution is very important parameter in reaction. Therefore is so important to know the shape of density distribution of the particle size in the result of the grinding process.

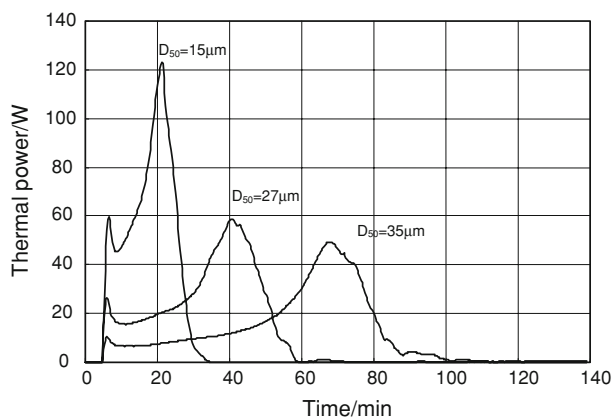
Density of particles size distribution was measured for three samples of ilmenite with different degree of grinding. To measurements was used the scanning microscope



**Fig. 3** Density of particles size distribution samples of ilmenite after grinding

BS300 with appropriate software. Results of the measurement were presented in Fig. 3. Obtained curves of density of particles size distribution are asymmetrical and they differ from the curve of the normal distribution. For each of this samples were determined also values of  $D_{50}$  (where  $D_{50}$  is a size of the sieve on which remain 50% of examined sample). Obtained values  $D_{50}$  of respective samples were as follow, 15, 27 and 35  $\mu\text{m}$ .

In Fig. 4 were presented curves of the thermal power obtained in reaction with sulphuric acid of respective samples of ilmenite only grounded (each sample with different time of grinding) with density of particles size distribution presented in Fig. 3. Differences between curves are relatively large, but much smaller than in the case presented in Fig. 1. Presented results confirm the very strong influence of the particles size on the rate of the reaction. For this reason an attempt of mathematical description of the dependence between reaction rate and particle size of the raw material was undertaken.



**Fig. 4** Changes of thermal power in reaction of ilmenite with different density of particle size distribution

**Theory**

In calorimeter in case of reaction ilmenite with sulphuric acid, emitted heat is partly accumulated in calorimetric system (what influence on reaction rate) and partly flows to the environment. Equation of the heat flow balance takes the following form in this case [13]:

$$W(t) = \frac{dQ}{dt} = \Delta H_r \frac{d\alpha}{dt} = C \frac{dT}{dt} + G(T(t) - T_0) \tag{1}$$

where  $W$  is the thermal power (W),  $Q$  heat amount generated during reaction (J),  $\Delta H_r$  heat of reaction (J),  $C$  heat capacity of calorimetric system ( $\text{J K}^{-1}$ ),  $G$  coefficient of heat losses ( $\text{J s}^{-1} \text{K}^{-1}$ ).

Very important element of this balance is the kinetics equation of reaction  $d\alpha/dt$ . In case of heterogeneous systems, such as the mixture of ilmenite with sulphuric acid, the kinetics of reaction depends mainly from the size of interfacial surface. In theoretical considerations was assumed, that the particles of solid substance have spherical shape with diameter  $D$ . Reaction will run on surface of sphere. Assuming that the products of reaction dissolve, the diameter of particle in reaction will decrease. It was also assumed that the concentration of sulphuric acid in reaction is constant, because of large excess of acid. Similarly the concentration of the products of reaction will be constant in reaction, also from the reason of large excess of sulfuric acid. On the basis of these assumptions, we can find that the rate of reaction depends only from the surface area of solid substance and we can write [2]

$$d\alpha/dt = k S \tag{2}$$

where  $\alpha = \frac{m_p}{m_0}$ ;  $m_p$  reacted mass after time  $t$  (g),  $m_0$  initial mass of substrate (g),  $S$  the current surface of solid ( $\text{m}^2$ ).

For the case when, all particles have the spherical shape and are in the same size, it is possible to use equation, the same as in contracting volume model [2, 11]:

$$d\alpha/dt = k S_0 (1 - \alpha)^{2/3} \tag{3}$$

The above equation in approximate way describes the rate of reaction. The simplicity is main advantage of this equation. However in this equation, particle size distribution is not taken into consideration.

Solid phase used in reactions is the most often finely ground and particles of solid are different in dimensions and shape. Distribution of particles size could be describing by different functions of mass or quantitative distribution.

Let's consider the function of quantitative distribution. Let's assume set of spherical particles, the total number of particles in sample is  $n_t$ , and quantity distribution of particles size is described by function  $z = f(D)$ . Surface of narrow fraction of particles from range of dimensions  $D_i + \Delta D$  will be

$$S_i = n_i f(D_i) \pi D_i^2 \Delta D. \tag{4}$$

Surface of total set of particles will be

$$S_t = n_t \pi \sum_i D_i^2 f(D_i) \Delta D \tag{5}$$

when  $\Delta D \rightarrow 0$  we obtain

$$S_t = n_t \pi \int_{D_0}^{D_{max}} D^2 f(D) dD. \tag{6}$$

In case, when we have mass distribution of particles size, number of particles of narrow fraction of dimensions range  $D_i + \Delta D$  will be

$$n_i = \frac{M_i}{\frac{1}{6} \pi D_i^3 \rho} \tag{7}$$

where  $M_i$  is mass of fraction of particles (g).

However the surface of this particles faction will be

$$S_i = \frac{6M_i f(D) \Delta D}{D_i \rho}. \tag{8}$$

Surface of total set of particles will be described by

$$S_t = \frac{6M_t}{\rho} \int_{D_0}^{D_{max}} \frac{f(D)}{D} dD \tag{9}$$

where  $M_t$  is the total mass of sample set of particles (g),  $\rho$  is the density ( $\text{g m}^{-3}$ ).

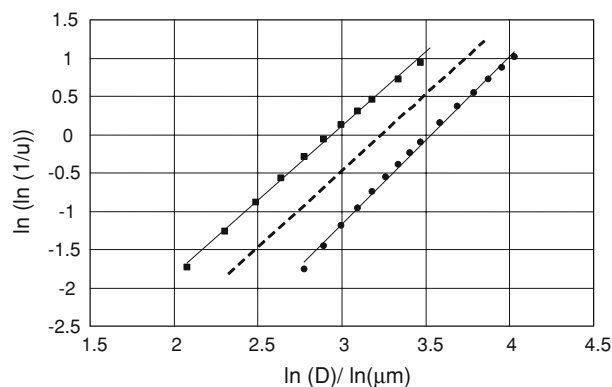
We obtained equivalent equations to estimating the surface of powder materials on basis of method of measurement density of particles size distribution. To calculate the surface area of solid on the basis of this equations is necessary the function of particles size distribution.

Powdery materials formed in natural way, e.g. by crystallization, sublimation etc., show symmetrical curves of particles size distribution. Particles size distribution of these materials can be in many cases described by Gauss equation of normal distribution.

Many samples of particles have the asymmetrical size distribution, especially such materials which were crushed. In these cases the maximum of density distribution curve, is shifted in direction of smaller particles. Such samples can be described by lognormal function or Rosin–Rammler function [12], proposed for mass distribution of samples received as a result of grinding

$$u(D) = \exp \left[ - \left( \frac{D}{D_p} \right)^n \right]. \tag{10}$$

For description the density of particles size distribution equation (10) takes the form:



**Fig. 5** Estimating value of the  $n$  parameter in Eq. 11. Dashed line is presenting values calculated from the Eq. 5, for  $n = 2$

$$f(D) = \frac{n}{D_p} \left( \frac{D}{D_p} \right)^{n-1} \exp \left[ - \left( \frac{D}{D_p} \right)^n \right] \tag{11}$$

where  $D_p$  is the characteristic dimension of particle,  $n$  is the parameter of equableness of particle size distribution.

Value of the parameter  $n$  can be estimated by double finding the logarithm of the Eq. 10. In this way in the coordinate system  $\ln(\ln(1/u(D)))$  and  $\ln(D)$  we will obtain a straight line. The value of parameter  $n$  can be determined from the slope of this straight line. Presented on the graph (Fig. 5) results of measurements for two samples of grinded material is practically parallel to a straight line obtained from the Eq. 10 for  $n = 2$ . Also in many different cases value of this parameter is approximately equal 2.

In reaction the size of particles changes, and consequently changes the size of interfacial surface. It is possible to assume that in reaction the shape of function of density of particle size distribution not change, however changes the size of particles. In the beginning of reaction disappear the smallest particles, however the diameters of remaining particles of sample decrease about  $\Delta D$ . Such run of process will appear in all steps of reaction to the moment when the diameter of the largest particles will so decrease that in next step of reaction completely disappear.

Therefore after time  $t$  from beginning of the reaction, density of particles size distribution in case of the Eq. 11 for  $n = 2$  will be in the form

$$f(D) = \frac{2}{D_p} \left( \frac{D + \Delta D}{D_p} \right) \exp \left[ - \left( \frac{D + \Delta D}{D_p} \right)^2 \right]. \tag{12}$$

Parameter of  $\Delta D$  is the function of degree of conversion and for case of particles with spherical shape (different shapes of particles fulfils this equation also [13]) we can write

$$\Delta D = D_{\max} \left[ 1 - (1 - \alpha)^{\frac{1}{3}} \right]. \tag{13}$$

Substituting Eqs. 6, 12 and 13 to 2, integrating and transforming we obtain

$$\frac{d\alpha}{dt} = k_r \left\{ \left[ D_z (1 - (1 - \alpha)^{\frac{1}{3}})^2 + 1 \right] \times \exp \left[ -D_z (1 - (1 - \alpha)^{\frac{1}{3}})^2 \right] - (D_z + 1) \exp(-D_z) \right\} \tag{14}$$

where

$$k_r = k_0 \exp \left( -\frac{E}{RT} \right) n_1 \pi D_p^2 \tag{15}$$

$$D_z = \left( \frac{D_{\max}}{D_p} \right)^2. \tag{16}$$

This is the kinetic equation taking into account the quantitatively density distribution of particles and equation of Rosin–Rammler.

Slightly different equation we receive in case when we use mass density distribution of particles. The same as previously, substituting Eqs. 9, 12 and 13 to 2, integrating and transforming we obtain

$$\frac{d\alpha}{dt} = k_r \left\{ \operatorname{erf}(D_k) - \operatorname{erf} \left[ D_k \left( 1 - (1 - \alpha)^{\frac{1}{3}} \right) \right] \right\} \tag{17}$$

where

$$k_r = k_0 \exp \left( -\frac{E}{RT} \right) \frac{6M_t \sqrt{\pi}}{\rho D_p} \tag{18}$$

$$D_k = \frac{D_{\max}}{D_p}. \tag{19}$$

Similar considerations we can make in case of other density distribution of particles e.g. the lognormal or the equation Rosin–Rammler with *n*th parameter, however in these cases only the numerical solution is possible.

The received equations (14) and (17) have a large meaning from practical point of view, because they take into account the particle size distribution in reaction and consequently gives the possibility of better description of the process.

Obtained equations have been verified on the base of experimental data. In Fig. 6 was presented the temperature changes in calorimetric vessel during reaction of Norwegian ilmenite with sulphuric acid and curve calculated from heat balance equation (1) with kinetic equation (17). How it is visible on graph, differences between experimental and calculated curves are very small. The only differences are visible on the beginning of the reaction, where initiating of the process is characterized with somewhat larger rise of

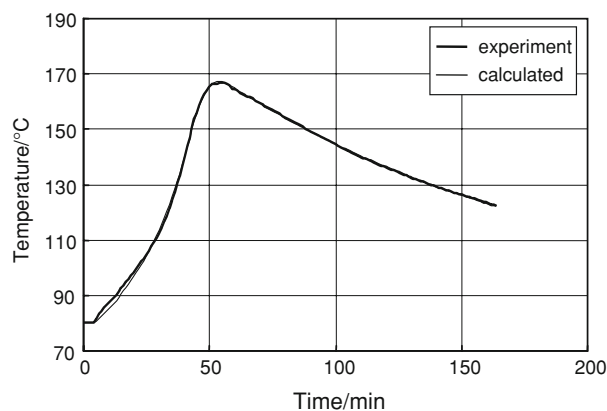


Fig. 6 Temperature changes in reaction of ilmenite with sulphuric acid

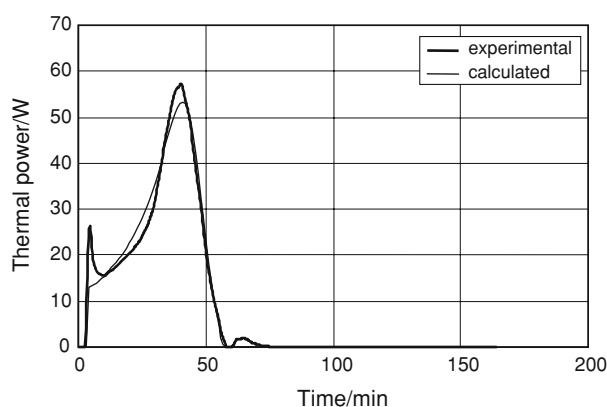


Fig. 7 Thermal power changes in reaction of ilmenite with sulphuric acid

temperature (this is better visible on curve of thermal power changes, Fig. 7).

In Fig. 7 is presented the changes of thermal power during reaction and curve calculated from Eqs. 1 and 17. In this case are visible larger differences, which appears in the moment of initiating of reaction, where on experimental curve, impulse of thermal power is visible.

Calculation results of thermal power obtained from balance equation (1) and kinetic equations (14), (17) and from the contacting volume model (3) (all particles are in the same diameter) were compared with experimental data. As comparison parameter determination coefficient ( $R^2$ ) was used. The results of calculations were presented in Table 1.

Presented in Table 1 results show that the degree of fitting of thermal power calculated with using both kinetic equations (14) and (17), are considerably better, then results obtained from the model of contracting volume equation (3).

**Table 1** Results of calculations

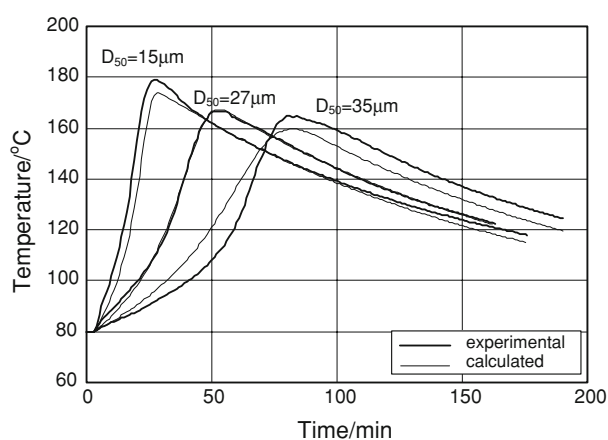
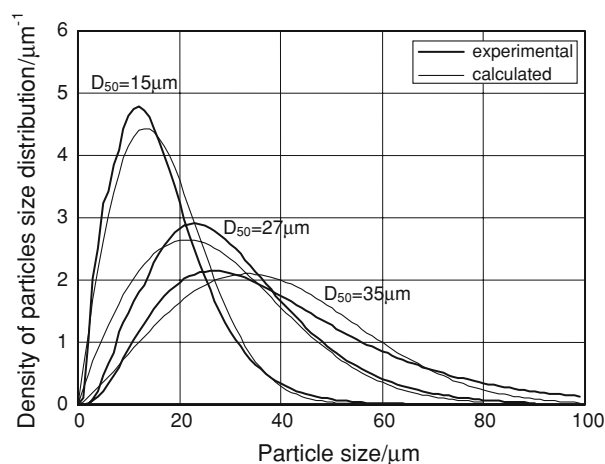
Model	$R^2$
Contracting volume (3)	0.959
Eq. 14	0.975
Eq. 17	0.982

The presented model can be used also for prediction of the run of reaction for different initial conditions (densities of particles sizes distribution). On the basis of the results obtained for the reaction ilmenite with the particles sizes distribution  $D_{50} = 27 \mu\text{m}$  with sulphuric acid, a rate of reaction for the particle sizes distribution  $D_{50} 15$  and  $35 \mu\text{m}$  was predicted. Results of calculation with experimental data were presented in Fig. 8 in the form of temperature changes for the particles sizes distribution  $D_{50} 15$  and  $35 \mu\text{m}$ .

In Fig. 8 are visible the differences between experimentally and predicted curves. These differences are not large, especially in the first case ( $D_{50} = 15 \mu\text{m}$ ), a little bit bigger differences are observed in the second case ( $D_{50} = 35 \mu\text{m}$ ), however both shape and location of curves are close to the experimental curves.

In case when we have the set of particles for which the  $n$  parameter in the Rosin–Rammler equation is  $n \neq 2$ , solution of kinetic equation is more complicated and possible mainly with numerical methods. Using equation in this form it is possible to determined parameters  $D_p$  and  $n$  in the Rosin–Rammler equation (11) on the basis of calorimetric measurement of reaction and in consequence determining the shape of the density of the particle size distribution.

Parameters for equation of the density of the particle size distribution (11) can be estimate in the following way. Combining the Eqs. 9 and 12 we will obtain:

**Fig. 8** Temperature changes in reaction of ilmenite with different particle sizes distribution with sulphuric acid and predicted from Eq. 17**Fig. 9** Density of particles size distribution determined by microscopic method and calculated on the base of calorimetric data

$$\frac{dx}{dt} = k \frac{6M_t n}{\rho D_p^n} \int_{D_0}^{D_{\max}} (D + \Delta D)^{n-2} \exp \left[ - \left( \frac{D + \Delta D}{D_p} \right)^n \right] dD \quad (20)$$

where  $\Delta D$  is determined by Eq. 13.

The solution of Eq. 20 requires applying of numerical methods and complicated calculations.

Results of such calculations on the basis of calorimetric measurements of reactions of the sulphuric acid with ilmenite with particle size distribution  $D_{50} = 15 \mu\text{m}$ ,  $D_{50} = 27 \mu\text{m}$  and  $D_{50} = 35 \mu\text{m}$  was presented in Fig. 9, together with curves presenting densities of the particle size distribution obtained by microscopic method. As can be seen on the graph, differences between calculations results on the basis of calorimetric measurements and obtained from microscopic method are not large and curves are close to each other. Bigger differences are being observed for the density of the particle size distribution  $D_{50} = 35 \mu\text{m}$ , especially in the shape of curve.

Estimated value of the parameter  $n$  in the equation Rosin–Rammler (11) on the basis of these calculations for the particle size distribution  $D_{50} = 15 \mu\text{m}$ ,  $D_{50} = 27 \mu\text{m}$  and  $D_{50} = 35 \mu\text{m}$  was respectively 1.965, 1.916 and 2.21. Results of calculation of this parameter are approximately  $n = 2$ , what is confirming earlier accepted assumption. The largest difference is appearing in the last case, for particles size distribution with shortest time of grinding.

Kinetic equations (14) and (17) and (20) can also be applied in thermal analysis in gas–solid system. In isothermal conditions and in case when the reaction rate depends from the size of interfacial surface (processes of mass transport do not influence on the reaction rate), function  $g(x)$  in the case of the Eq. 17 will be in the form:



$$g(\alpha) = \int \frac{d\alpha}{\operatorname{erf}(D_z) - \operatorname{erf}\left[D_z\left(1 - (1 - \alpha)^{\frac{1}{3}}\right)\right]}. \quad (21)$$

Only numerical methods can be used to solve this equation. Similarly only numerical methods can be used also in cases of the non-linear and linear change of the temperature. This complicates computational process but increasing computation time is not significant.

## Conclusions

Presented results of measurements demonstrating very strong influence of particles sizes of ilmenite on the thermokinetics of the reaction with sulphuric acid. Size of ilmenite particles also influence on the thermal effect obtained in the reaction, which is related with degree of transformation.

Samples of ilmenite, after grinding demonstrating the asymmetrical distribution of the particles sizes. Depending on the shape of density particle sizes distribution, different thermokinetics curves in reaction are obtained.

The knowledge about influence of this parameter plays important role in determination of the safe and effective run of reaction. By changing this parameter of reaction, is possible to operate and control the run of reaction.

Presented model of the kinetics of reaction ilmenite with sulphuric acid takes into consideration particles size distribution with equation of density of particles sizes distribution Rosin–Rammler. Obtained agreement between experimental and calculated results is satisfactory. Accepted assumption for parameter  $n = 2$  in the Rosin–Rammler equation was confirmed with experimental results.

Kinetic equations (14) and (17) can be applied in thermal analysis (under condition that the reaction rate depends only from the size of interfacial surface), however is necessary using numerical methods what the computation time is extending.

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