Influence of diffusion on the reaction of sulfuric acid with ilmenites

Maciej Jabłoński, Krzysztof Lubkowski* 몓 , Elwira Wróblewska 몓

West Pomeranian University of Technology Szczecin, Faculty of Chemical Technology and Engineering, Department of Organic and Physical Chemistry, Al. Piastów 42, 71-065 Szczecin, Poland

Abstract

* Corresponding author:

e-mail: krzysztof.lubkowski@zut.edu.pl

Presented at 24th Polish Conference of Chemical and Process Engineering, 13–16 June 2023, Szczecin, Poland.

Article info:

Received: 10 May 2023 Revised: 4 July 2023 Accepted: 14 July 2023 The reaction of ilmenite raw materials with sulfuric acid has been investigated to find out the influence of diffusion processes on the course of this reaction. Three different laboratory methods were used to initiate the reaction: mixing ilmenite with 83–85% sulfuric acid at a temperature of 80 $^{\circ}$ C, mixing ilmenite with 90% sulfuric acid at temperatures of 20–40 $^{\circ}$ C and adding water, and mixing ilmenite with water and adding 95% sulfuric acid. Changes of thermal power during the process (thermokinetics) were studied with the use of calorimetry. It was found that diffusion processes play an important role when the reaction is initiated by mixing ilmenite with water followed by the addition of sulfuric acid and are less important when the reaction is initiated by mixing ilmenite with concentrated sulfuric acid followed by the addition of water. To explain the influence of diffusion processes on the reaction, the model calculations based on mass and heat balance equations were involved. Model calculations showed that the diffusion and mass transport processes are so fast that the reaction kinetics is mainly influenced by the reaction on the surface of ilmenite particles. The adopted model of calculations showed a very good agreement with experimental results.

Keywords

titanium dioxide pigments, ilmenites, thermokinetics, diffusion

1. INTRODUCTION

The group of colorants includes pigments and dyes. Pigments are powdered, insoluble or sparingly soluble solid substances of natural or synthetic origin (mainly inorganic), the action of which is based on the ability to selectively absorb, reflect and/or scatter light. After dispersion in a carrier or binder, pigments retain their crystalline structure, unlike dyes, which are usually easily soluble organic substances. Among the inorganic pigments, the most important and widespread are titanium dioxide pigments, commonly known as titanium white (Blakey and Hall, 1988; Winkler, 2003). Due to the unique optical properties, titanium dioxide pigments are widely used in the production of coatings (paints, varnishes, lacquers), plastics, paper and in many other industrial branches (Blakey and Hall, 1988; Winkler, 2003).

In 2021, the global demand for titanium dioxide pigments reached 7.4 million Mg, worth approximately 23 billion USD, with a production capacity of 8.4 million Mg, produced in 70 industrial plants, including 50 in China (The Chemours Company, 2022; SNS Insider, 2022). The seven largest producers account for 56% of the 2021 world production of titanium dioxide pigments and their share in the production is as follows: Chemours – 14.4%, Tronox – 12.8%, Lomon Billions – 10.7%, Venator – 7.2%, Kronos – 6.3%, Ineos – 2.9%, ISK – 2.0% (The Chemours Company, 2022; SNS Insider, 2022). The share of other Chinese producers is about 36%, while 8% of titanium white is produced by small regional manufac-

turers (The Chemours Company, 2022; SNS Insider, 2022). There are currently about 400 grades of titanium white in the world trade, differing in production technology, crystal-lographic form, properties and area of application.

Titanium dioxide pigments are produced on an industrial scale with the use of two technologies: the sulphate method, where titanium dioxide is precipitated from a solution of titanyl sulphate, and the chloride method, where gaseous titanium chloride is oxidized to titanium dioxide with pure oxygen at high temperatures (Blakey and Hall, 1988; Winkler, 2003). The sulphate method has been used for the production of titanium white since 1919 (Blakey and Hall, 1988) and with this method about 54% of the pigment is produced (Winkler, 2003).

The first step in the production of titanium dioxide pigments using the sulphate method is the reaction of titanium-bearing minerals with sulfuric acid (Blakey and Hall, 1988; Gázquez et al., 2009; Mantero et al., 2013; Winkler, 2003). The reaction is of great practical and technological importance because it affects the efficiency of obtaining the final product and its quality. Ilmenite ores (mainly FeTiO₃ with TiO₂ content of 43–65%) and/or titanium-iron slags (metallurgically enriched ilmenite ores with TiO₂ content of 70–80%) are treated with concentrated sulphuric acid (80–95%). The reaction is highly exothermic, takes place in a corrosive environment at high temperature and is accompanied by significant gas emission. Due to the risk of uncontrolled increase of the



reaction rate, leading to thermal instability with the threat of a real thermal explosion (Liang et al., 2005; Parapari et al., 2016), this reaction belongs to the group of hazard reactions (Urben, 2006; Jabłoński et al., 2021b; Johnson et al., 2003). When determining the safety of a hazard type reaction, it is very useful to study changes in thermal power during the process (thermokinetics) with the use of various types of calorimeters (Ding et al., 2019; Duh et al., 1996; Hany et al., 2010; Jabłoński, 2008; Jabłoński et al., 2021a; Leung et al., 1986; Ortín et al., 1987; Zheng et al., 2020). It has been shown that the thermal effect and thermokinetics of sulfuric acid reaction with titanium raw materials strongly depend on such parameters as initial concentration of sulphuric acid (Jabłoński and Tylutka, 2016), reaction initiation temperature (Przepiera et al., 1993), particle size of titanium raw material (Jabłoński, 2009) and elemental and phase composition of titanium raw materials (Jabłoński et al., 2012). Incorrect selection of the initial reaction parameters, on the one hand, is associated with the aforementioned risk of a thermal explosion with potential deaths (Liang et al., 2005; Lin et al., 2016; Moreno et al., 2015; Parapari et al., 2016), while on the other hand, it may lead to incomplete reaction of the reaction mixture, which results in measurable economic losses.

When TiO₂ pigment is produced by the sulphate route, some amounts of decomposition sludges (ilmenite muds) as waste are also obtained. Experimental data and industry information show that the conversion degree of ilmenites is 92–95%. Decomposition sludges may contain, depending on the type of raw materials used, about 38–50% of TiO₂.

In the technological process, the initiation of the reaction is carried out in two ways. The first way is to mix concentrated sulfuric acid with ilmenite and then add water to the mixture. After adding water, the temperature of the reaction mixture rises as a result of the release of heat of dilution. Raising the temperature of the mixture initiates the reaction. During the reaction, thermal energy is released, which causes a further increase of temperature and acceleration of the reaction until the maximum temperature is reached. The concentration of sulfuric acid on the surface of the raw material grain is initially high, and after dilution it is reduced to the level at which the reaction is initiated. The time after which the concentration decreases is related to the process of diffusion of sulfuric acid in water and the mixing processes.

The second method of initiating the reaction relies on heating the mixture of sulfuric acid and ilmenite with steam. During heating the mixture to the initiation temperature, water vapour condenses and thus changes the concentration of sulfuric acid. The diffusion and mixing processes also determine the concentration of sulfuric acid on the grain surface in this case.

The rate and efficiency of the reaction are also affected by the transport of sulfuric acid to the reaction surface as well as the flow of reaction products into the solution. Since some of the reaction products go into the solution, while the rest forms a porous structure, diffusion processes may also play an important role in this case.

The main objective of the presented research was to explain the influence of diffusion processes on the reaction of sulfuric acid with titanium raw materials. Laboratory experiments and appropriate models based on mass and heat balance equations were used to achieve the purpose of the work. To our best knowledge, diffusion processes during the reaction of ilmenites with sulfuric acid have not been so far investigated and analyzed in literature sources.

2. EXPERIMENTAL

Ilmenite with an elemental composition determined by the X-ray fluorescence analysis, thermogravimetric measurements (TiO₂ - 44.4%, FeO - 34.8%, Fe₂O₃ - 11.6%, MgO - 4.1%) (Jabłoński, 2009) and with a phase composition determined by the X-ray absorption, diffraction and fluorescence measurements (ilmenite FeTiO₃ - 74.5%, hematite Fe₂O₃ - 11.6% and geikielite MgTiO₃ - 7.9%) (Jabłoński et al., 2012) was used in the experiments.

Calorimetric measurements were performed in a selfconstructed, non-isothermal and non-adiabatic calorimeter (Jabłoński, 2008; Jabłoński et al., 2021a), equipped with a calorimeter vessel with a capacity of 0.6 dm³, an electric heater, a stirrer, a temperature sensor, a dispenser and a safety valve. The calorimetric vessel was placed in a thermostatic jacket. During the reaction, the temperature inside the calorimetric vessel was recorded. Changes in temperature during the reaction constituted the basic information about the thermokinetics of the investigated process. The calorimetric vessel parameters were as follows: time constant – 257.5 min, heat transfer coefficient – 0.098 J·K⁻¹·s⁻¹. The mass of ilmenite sample used in the study was about 100 g, while the mass of sulfuric acid was in the range from 200 g to 400 g, depending on the concentration of the acid.

In the laboratory studies, the reaction was initiated in three different ways. The first method (*method I*) involved mixing ilmenite with sulfuric acid with an initial concentration of 83–85% at a temperature of 80 °C. The acid was placed in a calorimeter vessel, heated and after reaching thermal equilibrium at 80 °C, the reaction was initiated by pouring 100 g of ilmenite into sulfuric acid. The second method (*method II*) consisted in mixing ilmenite with sulfuric acid with a concentration of about 90% at temperatures 20–40 °C (depending on the final acid concentration) and adding such an amount of water that the acid concentration after dilution was at a level suitable to initiate the reaction mixture to rise to a level allowing the reaction to start. In the next experiment, ilmenite was mixed with an appropriate amount of water, not

with sulfuric acid as before (*method III*). The mixture prepared in this way was thermostated at 50 $^{\circ}$ C and then the reaction was initiated by adding sulfuric acid with a concentration of 95% (the amount of water was chosen so that the final concentration was the same as in the previous experiment).

In the presented research, elemental composition of decomposition sludges was analysed with the use of a PW 1480 sequential wave dispersive X-ray fluorescent spectrometer (Philips, Amsterdam, Netherlands), equipped with an X-ray tube with an Rh-type anode.

3. RESULTS

Figure 1a shows temperature changes of the reaction mixture during the reaction of ilmenite with sulfuric acid, which was initiated by mixing ilmenite with sulfuric acid at a temperature of $80 \,^{\circ}$ C (*method I*). After mixing the reactants, a slight increase in temperature is observed. With the course of the reaction, there is a slow increase in temperature at the beginning followed by a much faster rise in temperature until the maximum value is reached (170 $^{\circ}$ C after 80 minutes). After reaching the maximum, when the substrates are depleted, the amount of released reaction heat is so small that heat losses to the environment prevail and the temperature drops.

Changes of thermal power during the reaction of ilmenite with sulfuric acid initiated by the first method are shown in Fig. 1b. The rate of thermal power change is an important piece of information concerning the kinetics of the tested reaction. Several characteristic reaction steps are noticeable in this graph. At the initiation of the reaction, a peak associated with a rapid increase in thermal power appears. It is related to the heat of wetting the surface of the ilmenite particles with sulfuric acid (Jabłoński, 2010). Further, a slower increase of the rate of reaction heat evolution is observed until the maximum value is reached (around 60 W), which indicates the highest rate of reaction at a given moment. Then, a decrease of the heat release rate of the reaction is observed until the substrate is exhausted and the amount of heat released is very small, which corresponds to the maximum temperature of the reaction mixture. The last stage of the process (practically a horizontal line – no heat source) is related to the cooling of the reaction mixture.

The second method of initiating the reaction (*method II*) consisted in mixing ilmenite with sulfuric acid and initiating the reaction by adding water. The temperature changes in the reaction carried out in this way are shown in Fig. 2a. A significant rise in the temperature of the reaction mixture after adding water (from $40 \,^{\circ}$ C to $80 \,^{\circ}$ C) was observed. The heat of dilution allowed to initiate the reaction, which proceeded further in a manner similar to the temperature changes shown in Fig. 1a. In turn, Fig. 2b shows the changes of thermal power in the reaction initiated in this way. A high peak of thermal power changes (around 380 W) related to the heat of dilution of sulfuric acid is visible here, followed by the release of thermal energy as a result of the ongoing reaction.

Fig. 3a shows the course of temperature changes for the reaction initiated by the addition of sulfuric acid to the mixture of ilmenite and water (*method III*). The course of temperature changes in this case is completely different than in previous experiments. When the acid is added, there is a very rapid increase in temperature in a very short time (initially to $120 \,^{\circ}$ C, then up to $190 \,^{\circ}$ C). The maximum reaction temperature is reached very quickly, followed by a fairly rapid decrease in temperature, faster than that observed in the reaction initiated by adding ilmenite into sulfuric acid. Changes of thermal power during the reaction initiated in this way are shown in Fig. 3b. At the beginning of the reaction, a high peak associated with the release of dilution heat can be observed, followed by a small thermal effect of the reaction, which can be compared with a much larger thermal effect shown in Fig. 1b.

As a result of the performed measurements it was found that the conversion of ilmenites was $\sim 96\%$ when the decomposition reaction was initiated by *method I* and *method II*, whereas it was $\sim 85\%$ in the case of *method III*.



Figure 1. Changes of temperature (a) and thermal power (b) during the reaction initiated by mixing ilmenite with sulfuric acid at a temperature of 80 $^{\circ}$ C (*method I*).



Figure 2. Changes of temperature (a) and thermal power (b) during the reaction of ilmenite with sulfuric acid initiated by the addition of water (*method II*).



Figure 3. Changes of temperature (a) and thermal power (b) during the reaction initiated by the addition of sulfuric acid to the mixture of ilmenite and water (*method III*).

3.1. Model of the reaction initiation process

Let us first consider the case of initiating the reaction by adding concentrated sulfuric acid to the mixture of ilmenite and water (method III). When sulfuric acid is introduced into the mixture, the acid diffuses into the water film surrounding each ilmenite grain. The first observed effect is the dilution of sulfuric acid and the release of dilution heat, resulting in a rapid increase in the temperature of the reaction mixture to the level of about 120 °C (Fig. 3a). Further, the temperature of the reaction mixture increases more slowly to the level of about 190 °C. Due to the lower concentration of sulfuric acid in the layer at the interface, related to the diffusion process, the reaction proceeds with much lower efficiency and a smaller thermal effect of the reaction, which is clearly visible in Fig. 3b showing changes in thermal power during the reaction. In order to check the effect of diffusion on the change of sulfuric acid concentration in the layer surrounding the ilmenite grain, the following model of the process was adopted. At the beginning of the process, after mixing ilmenite and water with sulfuric acid, each ilmenite grain is surrounded by a layer of water, over which a layer of acid is formed, which is schematically shown in Fig. 4.



Figure 4. Model of the reaction of an ilmenite particle with sulfuric acid.

In the next stage, diffusion of sulfuric acid takes place through a layer of water, and to describe changes in concentration during the diffusion process, the equation of Fick's second diffusion law (1) can be used, which relates the rate of concentration change at a given point with the spatial change of concentration at that point:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \tag{1}$$

where: t - time, c - concentration, x - reaction coordinate, D - diffusion coefficient. When the diffusion coefficient does not depend on the position, we get

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{2}$$

For the case where the sulfuric acid is initially above the surface of the water film, the initial and boundary conditions are as follows: for t = 0 and x = 0, $n = n_o$, $n_o = \text{const.}$

Under these conditions, the solution to Equation (2) has the following form:

$$c(x,t) = \frac{n_o}{S(\pi Dt)^{1/2}} \exp\left(\frac{-x^2}{4Dt}\right)$$
(3)

where: S – initial contact surface of acid and water.

Changes in the concentration of sulfuric acid depending on time at temperatures of 20 °C and 80 °C, for which the diffusion coefficients are $1.73 \cdot 10^{-5}$ cm²/s and $2.7 \cdot 10^{-4}$ cm²/s, respectively (Perry and Chilton, 1973), and at a water layer thickness of 1 mm, are shown in Fig. 5.



Figure 5. Changes of sulfuric acid concentration over time on the surface of the ilmenite particle at temperatures of $20\,^\circ$ C and $80\,^\circ$ C with a water layer thickness of 1 mm.

Taking into account the data presented in Fig. 5, it can be concluded that the maximum concentration of sulfuric acid on the surface of the ilmenite particle is reached after about 3 minutes at 20 °C, and after about 15 seconds at 80 °C. On the other hand, the value of a homogeneous concentration in the entire film is reached after a much longer time. The presented concentration distributions in the film located on the surface of the ilmenite particle at different temperatures indicates that the diffusion processes play an important role in the reaction initiated with sulfuric acid.

In the reaction of ilmenite with sulfuric acid initiated by the addition of water, we are dealing with a completely different situation. When water is introduced into the mixture of sulfuric acid and ilmenite, the heat of dilution is released and the reaction is initiated. Each ilmenite particle is surrounded by highly concentrated sulfuric acid at the beginning of the reaction. It can be assumed that after water is introduced, it diffuses into an acid layer surrounding the ilmenite particle. In this case, the concentration difference at the surface of the particle is much smaller than in the previous case, as it varies from 96% to about 85%. This results in a much faster equalization of concentrations on the surface of the particle, especially at higher temperatures, and it can be assumed that the time to reach the optimal concentration is negligibly short.

3.2. Model of the reaction at the interface

In heterogeneous systems, such as a mixture of sulfuric acid and ilmenite, the kinetics of the reaction depends on the size of the interfacial surface, sulfuric acid concentration and temperature. In addition, mass transport to and from the interface can also have a significant impact. Let us consider the above processes. In order to simplify the considerations, let us assume that a single ilmenite particle has the shape of a sphere with radius r. The reaction taking place in this system will be a reaction at the interface, i.e. on the surface of the sphere. As a result of the reaction, the particle diameter will decrease. The products formed during the reaction partially dissolve, and the undissolved residues will form a porous structure, not an obstacle to mass transport processes. The following steps can be distinguished in such a reaction:

- the flow of substrates from the depth of the fluid towards the outer surface of the solid (external diffusion),
- chemical reaction on the surface of a solid,
- the flow of products from the outer surface of the solid into the fluid.

With such assumptions, the following mass and enthalpy system of equations can be written for the reaction of ilmenite with sulfuric acid:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = D\left[\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right] + k_o \exp\left(-\frac{E}{RT}\right)c^n \tag{4}$$

$$\rho c_s \frac{\partial T}{\partial t} = \lambda \left[\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right] + \Delta H_r \rho k_o \exp\left(-\frac{E}{RT}\right) c^n \quad (5)$$

where: D – diffusion coefficient, r – ilmenite particle radius, k_0 – preexponential coefficient, E – activation energy, ρ – density, c_s – specific heat, ΔH_r – enthalpy of the reaction, λ – thermal conductivity coefficient.

The above system of Equations (4), (5) can be solved with the following initial and boundary conditions:

$$c(r,0) = c_0(r) \qquad T(r,0) = T_0(r) \qquad r = 0$$

$$\frac{\mathrm{d}c}{\mathrm{d}r} = 0 \qquad \frac{\mathrm{d}T}{\mathrm{d}r} = 0 \qquad (6)$$

To check the assumptions made, the above system of Equations (4), (5) was solved using semi-differential method of lines. As a result of the calculations, the characteristics of the concentration distribution inside the reacting particle were obtained and they are shown in Fig. 6. Calculations carried

out for a particle with the largest diameter of 0.2 mm indicate that the equalization of concentrations occurs practically after one second, which compared to the total reaction time is negligibly small.



Figure 6. Distribution of sulfuric acid concentrations in a reacting ilmenite particle with a diameter of 0.2 mm.

Let us now consider the mass transport of products and reactants to and from the reaction zone. The mass stream of substrates flowing into the reaction zone is proportional to the concentration difference:

$$N_s = k_s \left(c_s - c_{sf} \right) \tag{7}$$

where: N_s – mass stream of substrates, c_{sf} – substrate concentration at the interface, c_s – substrate concentration in the solution, k_s – coefficient of proportionality of the mass stream to the difference in substrate concentrations.

A similar equation can be written for the reaction products:

$$N_{p} = k_{pr} \left(c_{pf} - c_{p} \right) \tag{8}$$

where: N_p – mass stream of products, c_{pf} – product concentration at the interface, c_p – product concentration in the solution, k_p – coefficient of proportionality of the mass stream to the difference in product concentrations.

In the case of the ongoing reaction, it can be assumed that due to the large excess of sulfuric acid, its concentration remains constant during the process. Due to the large excess of sulfuric acid, the concentration of the reaction products also remains constant. It follows that the mass fluxes flowing into and out of the reaction zone are quite large and will have a constant value.

This leads to the conclusion that the reaction rate is determined by the reaction kinetics at the surface of the particle. The following equation can be used to describe the kinetics of the process:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_o \exp\left(-\frac{E}{RT}\right) \cdot S \tag{9}$$

where: α – conversion, S – solid surface.

In constructing the kinetic model, we assume that all particles have the same size and shape, the enthalpy of the reaction is constant and does not depend on temperature, the thermal conductivity of the reaction mass is high enough so that the temperature is the same in the entire sample at a given moment, and that the specific heat of the reaction mass is constant and does not depend on the temperature (Jabłoński and Przepiera, 2001). Therefore, the mass and heat balance for the entire reaction in the calorimeter, taking into account heat losses to the environment, the surface of the solid and the degree of conversion, will take the form of the following system of equations:

$$C\frac{\mathrm{d}T}{\mathrm{d}t} + G\left(T(t) - T_0\right) = \Delta H_r \frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{10}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{11}$$

where: C – heat capacity, G – heat loss coefficient.

Using Equation (9) we get:

$$C\frac{\mathrm{d}T}{\mathrm{d}t} = \Delta H_r k_o \exp\left(-\frac{E}{RT}\right) S - G\left(T(t) - T_0\right) \quad (12)$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_o \exp\left(-\frac{E}{RT}\right) S \tag{13}$$

In the case of particles of various shapes (sphere, cylinder, etc.), an equation can be used (Jabłoński and Przepiera, 2001) that takes into account the relationship between the current surface area S and the degree of conversion α in the following form:

$$S = S_0 (1 - \alpha)^{2/3}$$
 (14)

Substituting Equation (14) into the system of Equations (12), (13), we get:

$$C\frac{\mathrm{d}T}{\mathrm{d}t} = \Delta H_r k_o \exp\left(-\frac{E}{RT}\right) S_0 (1-\alpha)^{2/3} - G\left(T(t) - T_0\right)$$
(15)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_o \exp\left(-\frac{E}{RT}\right) S_0 (1-\alpha)^{2/3} \tag{16}$$

The system of Equations (15), (16) can be solved with numerical methods for the initial conditions:

$$T(0) = T_0, \qquad \alpha(0) = 0$$
 (17)

As a solution to this system of equations, the changes of conversion, temperature and interfacial area as a function of time are obtained. Obtaining this information experimentally is very difficult, and in some cases even impossible.

The correctness of the presented model was tested on experimental results for the reaction of ilmenite with sulfuric acid. Temperature changes during the experiment together with the curve determined on the basis of the system of Equations (15), (16) are shown in Fig. 7.



Figure 7. Changes of temperature during the reaction of ilmenite with sulfuric acid and calculated from the system of Equations (15), (16).

Both curves coincide, and the occurring differences are small, which proves a good fit of the kinetic model to the experimental data. It can therefore be concluded that the model takes into account the most important processes occurring during the reaction.

Using the system of Equations (15), (16) it is also possible to calculate changes in the degree of ilmenite conversion depending on time. The results of these calculations are shown in Fig. 8. The maximum value of the degree of conversion practically coincides with the maximum temperature reached during the reaction, which indicates that the entire mass of the substrate is reacted in the main stage of the process.



Figure 8. Changes in the degree of conversion during the reaction of ilmenite with sulfuric acid, calculated on the basis of the system of Equations (15), (16).

Figure 9 shows the dependence of the reaction temperature on the degree of conversion. The shape of the graph is close to linear, which confirms the simple correlation between the temperature and the degree of conversion.

Figure 10 shows changes of thermal power during the tested reaction, comparing the experimental data with the model obtained by solving the system of Equations (15), (16). Although the curve obtained on the basis of experimental data is more irregular for obvious reasons, the similar shape of



Figure 9. Dependence of temperature on the degree of conversion during the reaction of ilmenite with sulfuric acid, calculated on the basis of the system of Equations (15), (16).



Figure 10. Changes in thermal power during the reaction of ilmenite with sulfuric acid, determined experimentally and calculated on the basis of the model equations.

both curves confirms the correctness of the adopted model.

The presented model can also be used to recalculate the temperature course of the reaction system with other initial parameters. Since the system of equations includes a parameter related to the initial surface of the substrate, it is possible to recalculate the course of temperature changes for other initial values of the surface, i.e. for other narrow particle size fractions that will meet the condition of the same size of all particles.

4. CONCLUSIONS

Based on the conducted experiments, it was found that diffusion processes play an important role in initiating the reaction by mixing ilmenite with water and then adding sulfuric acid. It was noticed that the diffusion processes are less important in the case of initiating the reaction with the addition of water to ilmenite mixed with concentrated sulfuric acid. The conducted experiments and model calculations show that it is most advantageous to initiate the reaction by mixing ilmenite with sulfuric acid at the optimum concentration for a given reaction and heating the reaction mixture. In the reaction of sulfuric acid with ilmenite, the diffusion and mass transport processes are so fast that the reaction kinetics is mainly influenced by the reaction on the surface of the molecule. The adopted model of calculations taking into account this type of assumption shows a very good agreement with the experiment. The actual course of temperature changes is relatively well described by the above model. The model did not take into account other very important factors such as the distribution of substrate grain diameters, irregular shape of molecules, the occurrence of diffusion phenomena and mass transport resistance. An additional advantage of the model is its ability to estimate the degree of conversion based on changes of temperature during the reaction.

REFERENCES

- Blakey R.R., Hall J.E., 1988. Titanium dioxide, In: Lewis P.A. (Ed.), *Pigment handbook*. 2nd edition, John Wiley & Sons Inc., New York.
- Ding J., Yu L., Wang J., Xu Q., Ye S., 2019. A symmetric dualchannel accelerating rate calorimeter with the varying thermal inertia consideration. *Thermochim. Acta*, 678, 178304. DOI: 10.1016/j.tca.2019.178304.
- Duh Y.S., Hsu C.C., Kao C.S., Yu S.W., 1996. Applications of reaction calorimetry in reaction kinetics and thermal hazard evaluation. *Thermochim. Acta*, 285, 67–79. DOI: 10.1016/0040-6031(96)02899-7.
- Gázquez M.J., Bolívar J.P., García-Tenorio R., Vaca F., 2009. Physicochemical characterization of raw materials and coproducts from the titanium dioxide industry. *J. Hazard. Mater.*, 166, 1429–1440. DOI: 10.1016/j.jhazmat.2008.12.067.
- Hany C., Lebrun H., Pradere C., Toutain J., Batsale J.-Ch., 2010. Thermal analysis of chemical reaction with a continuous microfluidic calorimeter. *Chem. Eng. J.*, 160, 814–822. DOI: 10.1016/j.cej.2010.02.048.
- Jabłoński M, 2010. Investigation of thermal power of reaction of titanium slag with sulphuric acid. *Cent. Eur. J. Chem.* 8, 149–154. DOI: 10.2478/s11532-009-0127-7.
- Jabłoński M., 2008. Investigation of reaction products of sulphuric acid with ilmenite. *J. Therm. Anal. Calorim.*, 93, 717– 720. DOI: 10.1007/s10973-008-9134-8.
- Jabłoński M., 2009. Influence of particle size distribution on thermokinetics of ilmenite with sulphuric acid reaction. *J. Therm. Anal. Calorim.*, 96, 971–977. DOI: 10.1007/s10973-009-0048-x.
- Jabłoński M., Lawniczak-Jabłońska K., Klepka M.T., 2012. Investigation of phase composition of ilmenites and influence of this parameter on thermokinetics of reaction with sulphuric acid. *J. Therm. Anal. Calorim.*, 109, 1379–1385. DOI: 10.1007/s10973-011-2136-y.
- Jabłoński M., Lubkowski K., Tylutka S., Ściążko A., 2021a. Heat effects in the reaction of sulfuric acid with ilmenites influenced by initial temperature and acid concentration. *Pol. J. Chem. Technol.*, 23, 37–42. DOI: 10.2478/pjct-2021-0028.
- Jabłoński M., Lubkowski K., Tylutka S., Ściążko A., 2021b. The influence of sulphur addition on the hazard-type reaction of ilmenite ores with sulfuric acid. *Pol. J. Chem. Technol.*, 23, 17–23. DOI: 10.2478/pjct-2021-0025.

- Jabłoński M., Przepiera A., 2001. Kinetic model for the reaction of ilmenite with sulphuric acid. *J. Therm. Anal. Calorim.*, 65, 583–590. DOI: 10.1023/A:1012405826498.
- Jabłoński M., Tylutka S., 2016. The influence of initial concentration of sulfuric acid on the degree of leaching of the main elements of ilmenite raw materials. *J. Therm. Anal. Calorim.*, 124, 355–361. DOI: 10.1007/s10973-015-5114-y.
- Johnson R.W., Rudy S.W., Unwin S.D., 2003. *Essential practices for managing chemical reactivity hazards*. American Institute of Chemical Engineers, New York, New York. DOI: 10.1002/9780470925300.
- Leung J.C., Fauske H.K., Fisher H.G., 1986. Thermal runaway reactions in a low thermal inertia apparatus. *Thermochim. Acta*, 104, 13–29. DOI: 10.1016/0040-6031(86)85180-2.
- Liang B., Li C., Zhang C., Zhang Y., 2005. Leaching kinetics of Panzhihua ilmenite in sulfuric acid. *Hydrometallurgy*, 76, 173–179. DOI: 10.1016/j.hydromet.2004.10.006.
- Lin C.P., Li J.S., Tseng J.M., Mannan M.S., 2016. Thermal runaway reaction for highly exothermic material in safe storage temperature. *J. Loss Prev. Process Ind.*, 40, 259–265. DOI: 10.1016/j.jlp.2016.01.006.
- Mantero J., Gazquez M.J., Bolivar J.P., García-Tenorio R., Vaca F., 2013. Radioactive characterization of the main materials involved in the titanium dioxide production process and their environmental radiological impact. *J. Environ. Radioact.*, 120, 26–32. DOI: 10.1016/j.jenvrad.2013.01.002.
- Moreno V.C., Kanes R., Wilday J., Véchot L., 2015. Modeling of the venting of an untempered system under runaway conditions. *J. Loss Prev. Process Ind.*, 36, 171–182. DOI: 10.1016/j.jlp.2015.04.016.
- Ortín J., Torra V., Tachoire H., 1987. Thermal power measurements in a differential-heat-conduction-scanning calorimeter at low temperature-scanning rates. *Thermochim. Acta*, 121, 333– 342. DOI: 10.1016/0040-6031(87)80183-1.
- Parapari P.S., Irannajad M., Mehdilo A., 2016. Modification of ilmenite surface properties by superficial dissolution method. *Miner. Eng.*, 92, 160–167. DOI: 10.1016/j.mineng. 2016.03.016.
- Perry R.H., Chilton C.H., 1973. *Chemical Engineers' Handbook*. Fifth Edition, McGraw-Hill, New York.
- Przepiera A., Jabłoński M., Wiśniewski M., 1993. Study of kinetics of reaction of titanium raw materials with sulphuric acid. *J. Therm. Anal.*, 40, 1341–1345. DOI: 10.1007/BF02546898.
- SNS Insider, 2022. *Titanium dioxide market size & share analysis report*. (Report Code: SNS/C&M/1734), June 2022. Available at: https://www.snsinsider.com/reports/titanium-dioxidemarket-1734.
- The Chemours Company, 2022. *The Chemours Company 2021* annual report (Form 10-K). February 17, 2022.
- Urben P.G. (Ed.), 2006. *Bretherick's handbook of reactive chemical hazards*. 7th edition, Academic Press, Amsterdam.
- Winkler J., 2003. *Titanium dioxide*. Vincentz Network, Hannover, 2003.
- Zheng Y., Zhang C., Liu H., 2020. The determination of isobaric heat capacities of liquid by the new flow calorimeter. *Thermochim. Acta*, 690, 178644. DOI: 10.1016/j.tca.2020.178644.