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Investigation of thermal power of reaction of titanium slag with sulphuric acid

Research Article

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Abstract: Enriched titanium raw materials with high titanium content called titanium slags are received by the electrothermal reduction of ilmenite. Titanium slags are most frequently used in the titanium dioxide industry. The reaction of titanium slags with sulphuric acid is strongly exothermic and creates danger of thermal explosion. Kinetics of this reaction depends on the parameters such as temperature of initiation, sulphuric acid concentration and dimension of particles of titanium slag. The reaction of titanium slag with sulphuric acid was investigated at non-isothermal conditions in a special construction calorimeter. The observed thermal power changes in the calorimeter ("calorimeter run"), are the basis for estimation of reaction kinetics. A proposed model describing the thermal power changes and taking into account the moment of initiation of reaction is presented. The calorimetric investigations showed, that reaction rate of titanium slags with sulphuric acid depends on initial temperature of reaction, size of particles of titanium raw material and sulphuric acid concentration.

Keywords: *Thermokinetics • Calorimetric investigations • Titanium slag*

1. Introduction

The last years in production of titanium pigments by the sulphate method is changing the raw material used from ilmenites to enriched titanium materials called as titanium slags, with titanium content in range of 70- 90% TiO_2. The difference in content of TiO_2 in ilmenite and titanium slag is large, because in the case of ilmenite the content of TiO_2 is in the range 40 - 60%. So large difference in composition of titanium raw materials has influence on the conditions of reaction.

The composition of titanium slags is different and the content of titanium dioxide and the remaining chemical elements is dependent on the composition of the initial raw material, and the way of enrichment. The most frequent method for obtaining titanium slags is using electrothermal reduction of ilmenites.

As in the case of ilmenite, in the process of TiO_2 production by the sulphate method, reaction of titanium slag with sulphuric acid is the first step [1,2]. This process is highly exothermic and should be properly adjusted to avoid uncontrolled reaction. Conditions of titanium slag with sulphuric acid reaction are quite different from reaction of ilmenite with sulphuric acid and knowledge about thermokinetics of this reaction has large influence on efficiency, safety and the quality of products.

2. Experimental procedure

The QIT titanium slag (QIT – Fer et Titane Inc., Quebec, Canada) was considered in this study as the raw material. The composition of titanium slag determined by XRF method (Philips PW1480) was the following: TiO_2 - 78.6%, FeO - 10.2%, MgO - 3.2% and SiO_2 - 3.7%.

The phase composition of titanium slag was investigated by X-ray diffraction (XRD) (Philips PW1710). The diffractogram is presented in Fig. 1. The analysis of these results shows that the probable phases present are

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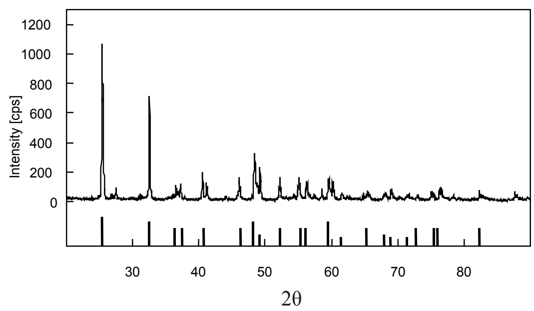

Figure 1. X-Ray pattern of titanium slag with iron titanium oxide $FeTi_5O_{10}$ pattern.

pseudobrookite Fe_2TiO_5, ferropseudobrookite $FeTi_2O_5$, iron titanium oxide $FeTi_5O_{10}$, titanium oxide Ti_3O_5, magnesium titanium oxide $MgTi_2O_5$ and appears also not large admixture of rutile. All mentioned compounds with exception of rutile, have the pseudobrookite structure and therefore it is difficult to indicate presence of determined phases on the basis of XRD.

Contents of iron(II) as well as of titanium(III) in the sample of the slag were determined by analyses according to the description included in the monograph [5]. The following results were obtained from the analyses: titanium(III) (Ti_2O_3) – 14.6% and iron(II) (FeO) – 10.1%. It is shown that in the case of iron, practically the total amount of Fe has an oxidation number of II. Confirmations of these results are derivatograph investigations of the slag sample presented in the paper [6].

Assuming that the main phases in the slag are ferropseudobrookite $FeTi_2O_5$, titanium pentoxide Ti_3O_5, magnesium titanium oxide $MgTi_2O_5$ and titanium dioxide TiO_2, it is possible to estimate the content of each compound on the basis of analyses results of titanium and iron oxidation number. The results of these calculations were presented in Fig. 2.

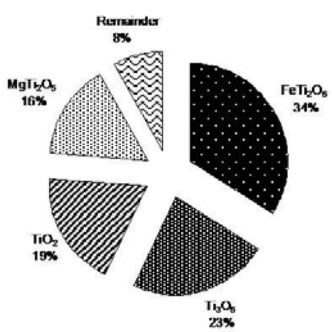

Figure 2. Estimated phase composition of titanium slag.

Thermokinetic investigation of reaction of titanium slag with sulphuric acid was realized in a special construction calorimeter. The constructed calorimeter consists of calorimetric vessel equipped with heater, temperature sensor Pt100, stirrer and batcher. The calorimetric vessel was also equipped with a safety valve enabling venting the excess of gases evolved during the violent reaction. This apparatus was described in detail previously [3].

The measurements were realized in the following way. Sample of the slag was dried and next grounded to obtain assumed degree of granulation. The degree of granulation was determined by the electron scanning microscope BS300.

The sample of slag was placed in the batcher and next the sulphuric acid was poured into calorimetric vessel. After obtaining thermal equilibrium, reaction was initiated by pouring the slag into calorimetric vessel. In this moment, reaction started inside calorimetric vessel and at the same time a raise of temperature was observed. After reaching the maximum of temperature which was the final stage of the reaction, temperature decreased. The end of the reaction was when the thermal power generated in the process was close to zero.

3. Results and discusion

The thermokinetic investigations were realized for different initial conditions. The influence of initial temperature of reaction, the concentration of sulphuric acid and the size of particles on rate of reaction were investigated.

In Fig. 3 are presented the results of measurements realized for initial temperatures of reaction range 110°C to 150°C. Presented results indicate, that the influence of initial temperature is very essential. The increase maximum value of the thermal power is relatively fast and the change of initial temperature of reaction mixture about 10°, practically doubles value of the maximum of thermal power.

Fig. 3 shows that, at initial temperature of reaction 150°C the maximum of thermal power achieves value about 250 W. This value of thermal power can be interpreted as very high probability of thermal explosion in industrial conditions.

On Fig. 4 are presented results of measurements of the reaction of QIT titanium slag with sulphuric acid for different initial concentrations of sulphuric acid. Influence of this parameter on reaction is also very essential, but its nature is completely different. There is a clearly visible difference in reaction rate with sulphuric acid at

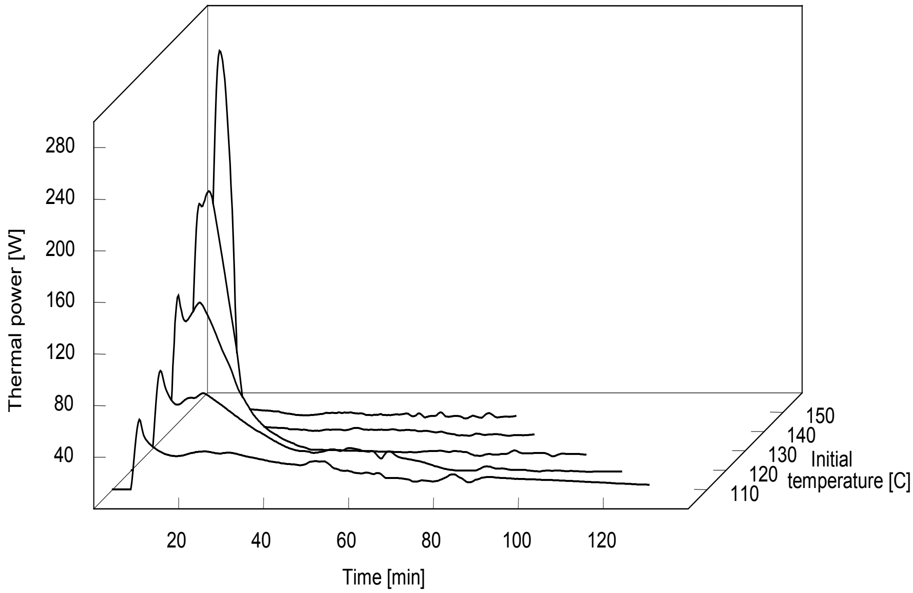

Figure 3. Thermal power changes at reaction of titanium slag with sulphuric acid at different initial temperatures (sulphuric acid concentration – 92%, particle size D_{50}=21 μm).

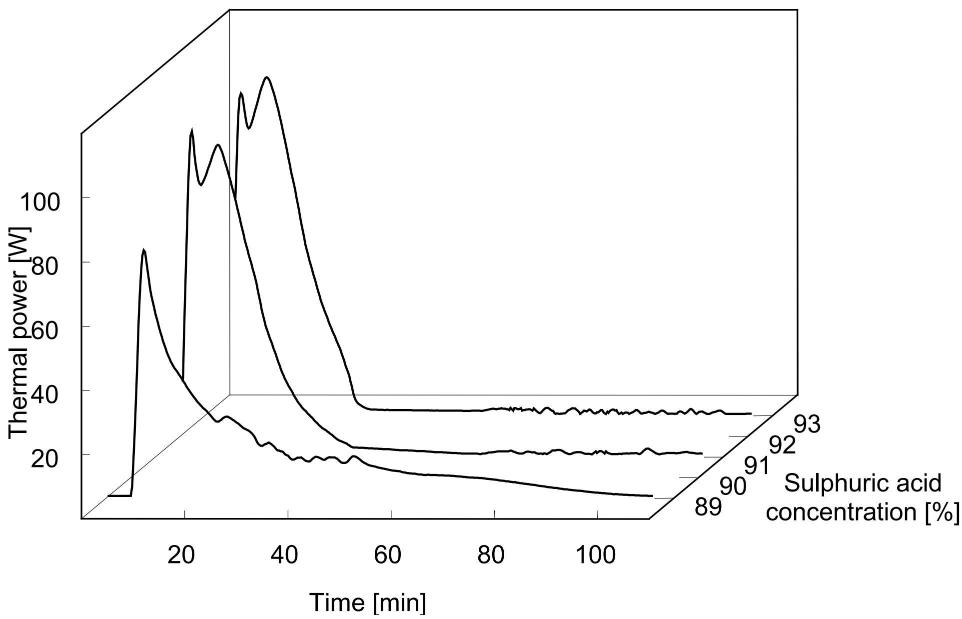

Figure 4. Thermal power changes at reaction of titanium slag with sulphuric acid at different concentration (initial temperature – 130°C, particle size D_{50}=21 μm).

concentration 89%, and acids at concentrations 91% and 93%. In case of reaction with an acid at concentration 89%, only one maximum appears which is related to the initiation of the reaction. In reactions with acid at concentrations 91% and 93% we see two maxima on the thermal power curve. In the range of concentrations of sulphuric acid 89% to 91%, influence on rate of reaction is very sharp, however in range of concentrations 91% and 93% reactions rates are similar.

In Fig. 5 the influence of different size of slag particles on thermokinetics of reaction are presented. Parameter d_{50} was chosen for determination of particles size of titanium slag, which is defined as the dimension of sieve, through which 50% of the raw materials are passed through a sieve. The raw material was ground in a Fritsch ball mill. Presented thermokinetics curves on Fig. 5, show influence of this parameter on reaction rate. It appears, that as the particle size decreases, the reaction rate increases.

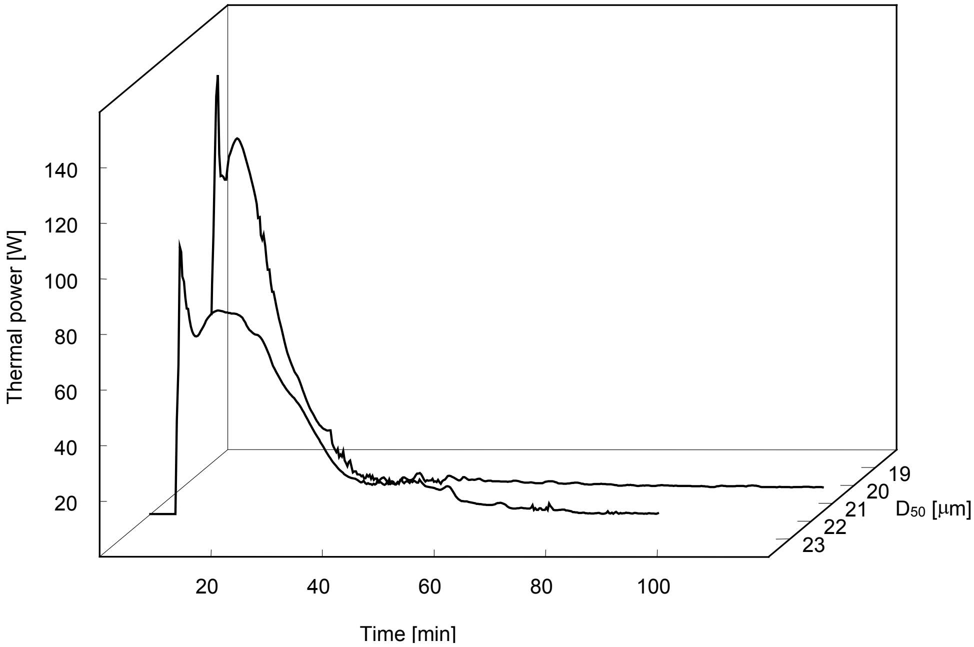

Figure 5. Thermal power changes at reaction of titanium slag with sulphuric acid at different particles size (initial temperature – 130°C, sulphuric acid concentration – 92%).

The results presented above show the essential influence of the initial temperature of the reaction, initial concentration of the sulphuric acid as well as size of particles of titanium slag on rate of reaction.

These investigations show that the most optimal initial temperature of the reaction is temperature from the range 130 – 140°C. Next investigation of the influence of the sulphuric acid concentration on the arising of thermal power show that it is possible to apply sulphuric acid in the range of concentrations of 91-93%. The particles size of titanium slag should be included in a range of D_{50} value 20–21 µm. Determination of more exact conditions of the reaction are dependent on such additional parameters as efficiency of the reaction. For analysis of optimal conditions also a model of the reaction is helpful.

At the beginning of the curve of thermal power changes especially at low initial temperatures of the reaction, clearly visible is the sharp increase of the thermal power, in the shape of characteristic peak. In the next part of the curve appears a second maximum, which increase with the initial temperatures, gradually overlapping with the first peak. The first peak of thermal power on the curve is related with the moment of initiation of the reaction, *i.e.* when the mixing of reacting substances (titanium slag with sulphuric acid) takes place. The second maximum on the curve is related to maximum of reaction rate. This value is essential for kinetics parameter estimation. For estimating kinetic parameters it is possible to apply the set of equations, which is a result of the heat and mass balances of the process in the calorimeter [3].

$$W(t) = \Delta H_r \frac{d\alpha}{dt} = C\frac{dT}{dt} + GT(t) \qquad (1)$$

where

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)(1-\alpha)^{2/3} \qquad (2)$$

where: W – thermal power, α - degree of transformation, A - preexponencial coefficient, E - activation energy, C - thermal capacity of parts of calorimeter and investigated substances, ΔH_r – heat of reaction, G-coefficient of heat losses.

This set of equations was obtained on the basis of the reaction model which was constructed under assumption, that products of reaction dissolve partly creating a porous structure which is not a barrier for processes of mass transport. Additional assumptions of the kinetic model are as follows, all particles are of identical dimension and shape (spherical), enthalpy of reaction is constant, the coefficient of 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 the temperature.

In heterogeneous systems interfacial surface plays an essential role. The rate of reaction depends mainly on the interfacial surface and is closely connected with the degree of transformation. For spherical particles the rate of reaction is described by Eq. 2 (different shapes of particles also fulfill this equation) [3].

However this set of equations is not describing changes of thermal power exactly especially in initial period of reaction where on the experimental curve the first maximum is appearing. As a result of calculations using Eq. 1 we obtain only one maximum and therefore differences between experimental and calculated curves are large enough in the initial period.

As it was mentioned above the first peak on the curve of thermal power is related with the moment of initiating the reaction, *i.e.,* of mixing of the reagents. It is possible to assume, that the appearing thermal effect during mixing reagents is related with covering the surface of the solid by liquid Consequently it is possible to describe the rate of this process with the kinetic equation used in the process of adsorption, where it is assumed that the rate of the process of covering of the surface is proportional to the part of surface not occupied [4]:

$$\frac{d\theta}{dt} = k_z(1-\theta) \qquad (3)$$

where, θ - is the degree of covering of the surface, k_z - is the proportion coefficient.

It is reasonable to assume, that this process, is occurring in adiabatic conditions, therefore, the amount of emitted heat will be proportional to the degree of covering of the surface.

$$Q/Q_z = \theta \qquad (4)$$

where, Q_z – total heat of immersion
So we obtain

$$\frac{dQ}{dt} = k_z(Q_z - Q) \qquad (5)$$

Assuming, that specific heats of the calorimeter components and substrates do not depend on temperature, we obtain

$$\frac{dT}{dt} = k_z(T_z - T) \qquad (6)$$

After integration this differential equation we obtain a function of the form

$$T = T_z - \Delta T \exp(-k_z t) \qquad (7)$$

where, $\Delta T = T_z - T_0$
Finally, the equation of the energy balance takes the form

$$C\frac{dT}{dt} = \Delta H_r \frac{d\alpha}{dt} + \frac{dQ}{dt} - GT(t) \qquad (8)$$

Eq. 8 can be used for estimating the value of the heat of immersion. Calculated on the basis of the Eq. 8 the heat of immersion in the reaction of titanium slag with sulphuric acid at concentration 93% and at temperature 130°C, was 27 J g^{-1}. The total thermal effect of this reaction was 855 J g^{-1}. Fig. 6 shows experimental and calculated thermal power. Differences between the experimental and calculated curve in the initial period are relatively small. Considerably big differences arise near the maximum of the rate of the reaction, where in the case of the Eq. 8 lower values are obtained.

Calculated value heat of immersion was compared with value determined in direct calorimetric measurement. To perform this measurements it is necessary to eliminate thermal effects of reaction. Heat of immersion was measured at low temperature, because reaction is running so slowly that the main thermal effect in the measurement is the heat of immersion. The average value of the heat of immersion measured at 25°C in the calorimeter was 24.9 J g^{-1}.

Heat of immersion is not large, however it is significant for practical use. When the reaction is initiated, the thermal effect influences acceleration of the reaction rate, what is advantageous in the lower temperature of initiation. However, if the reaction is being initiated at relatively high temperature, the thermal effect can excessively accelerate the reaction, and can in an extreme case cause thermal explosion. In such case, mixing raw material with sulphuric acid at lower temperatures and then heating reactionary mixture to the higher temperature, in which initiation of reaction following, is more advantageous.

4. Conclusion

The results of investigations of reaction of titanium slag with sulphuric acid in calorimetric system are the source of essential information of thermal effects of this reaction. Particularly important are measurements of thermal power changes of reaction, because these

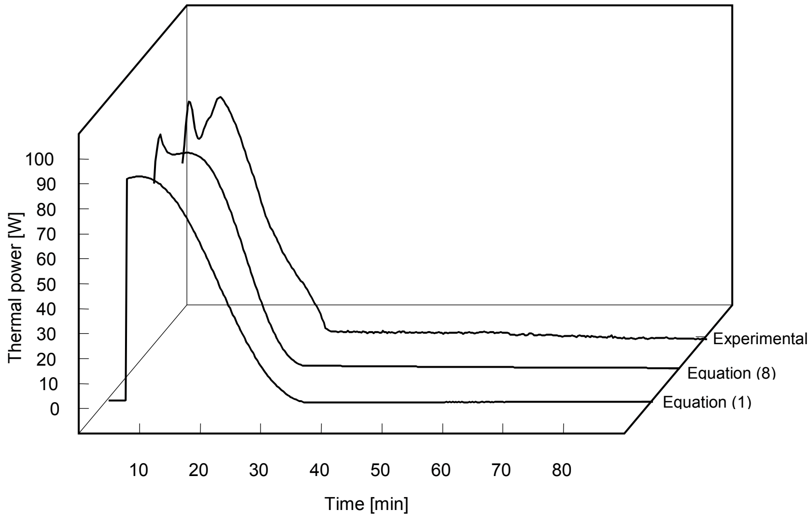

Figure 6. Thermal power changes during reaction of titanium slag with sulphuric acid obtained experimentally and calculated from Eqs. 1 and 8.

measurements are the base to estimate the kinetics of the process. The results of investigations show a very large influence on reaction rate of the sulphuric acid with titanium slag following parameters, the initial temperature of the reaction, initial concentration of the sulphuric acid and the particle size of raw material.

On the basis of these investigations and presented model, it is possible to determine the optimal conditions for the titanium slag with sulphuric acid reaction.

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