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HAZARD IN REACTION OF TITANIUM RAW MATERIALS WITH SULPHURIC ACID

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The reaction of ilmenite titanium raw material with sulphuric acid was investigated in 'hazard' type calorimetric system. The investigations show the essential influence of initial temperature, particle size distribution and concentration of sulphuric acid on rate and heat power of reaction and determine the limits of safety of the process and also its efficiency.

Keywords: *calorimetry, hazard, ilmenite, safety*

Introduction

Series of incidents in which the thermal explosions occurred on different stages of technological process are well-known in chemical industry. This phenomena can be studied by thermal analysis and calorimetry [1–3]. The main reason of these incidents is chemical reactivity of reactants. The effect of these incidents were large material losses, and in some cases even dead and injury to people [4]. These cases illustrate how serious attention should be focused on conditions in which given process run and how essential is knowledge on this subject.

It was estimated that 20% of explosions or uncontrolled reactions in technological processes was caused by ignoring the effect of heat accumulation in reaction mixture. The analysis of history of incidents leads to the conclusion, that in many cases the source of problems was the lack of knowledge about chemical reactivity of the process, its thermodynamics and in consequence incorrect control of reactor [5].

The production of titanium pigments (TiO_2) from raw materials containing titanium is the important industrial technology. Titanium dioxide has increasing application as white pigment in different branches of industry.

One of the first and simultaneously one of the most important stages of technological process of the titanium dioxide production, by the sulphate method which have influence on efficiency as well as safety of production, is the digestion reaction of titanium raw material with sulphuric acid.

The reaction of grounded raw material with sulphuric acid is carried out as a batch process. At the first stage the mixture of raw material and sulphuric acid is prepared. Then the mixture is introduced into reactor. At this moment is very important to choose right initial parameters of reaction in order to avoid uncontrolled process.

The reaction of titanium raw material with sulphuric acid is initiated by heating the reaction mixture. When exothermic reaction starts, the temperature of mixture in a few minutes increases to about 200°C. Water formed in reaction is ejected out from reactor as a vapour.

The composition and properties of titanium raw material have large influence on its reaction with sulphuric acid.

Each kind of titanium raw material requires proper selection of the process parameters for digestion, which are achieved mainly by experimental investigation.

Ilmenites and titanium slags are used as a raw material in sulphate technology of titanium dioxide production. Ilmenite is mineral with metallic gloss and black or grey colour. It shows weak magnetical properties, what is sometimes used in processes of its enrichment.

The chemical composition of titanium raw materials depends on place of their origins. Main differences are in content of trace and accompanying elements.

Enriched raw materials, with high titanium content, called titanium slags are more frequently used in industry. Titanium slag is received by electrothermal reduction of ilmenite.

Experimental

In order to estimate the range of safe run of reaction and eliminate the risk of thermal explosion the calorimetric technique was used. Calorimetry enables the direct determination of reaction thermal effects as well as its kinetics.

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The reaction of sulphuric acid and titanium raw materials is strongly exothermic. Except of heat emitted during reaction, vapours and gases can be also emitted and in extreme situations we can expect the danger of thermal explosion, what creates difficulties in investigations of this type of reaction. The strongly corroding environment and high temperature of reaction are additional problems.

The preliminary investigative experiences have shown, that for determination of thermal effects of strongly exothermic reactions with possibility of thermal explosion, in aggressive environment of sulphuric acid and in high temperatures, most favourable is to use the 'hazard' type calorimeter, which can be adapted to work in the temperature range from 25 to 300°C.

The constructed calorimeter consist of calorimetric vessel equipped with heater, temperature sensor Pt100, stirrer and batcher. Calorimetric vessel was also equipped with safety valve enabling venting the excess of gases evolved during violent reaction. This apparatus in detail was described previously [6].

The reaction in calorimeter was initiated by mixing of reactants. Calorimetric vessel for that purpose was equipped in batcher having special construction. This calorimeter enables investigation of reaction in temperatures range from 25 to 300°C.

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 following TiO_2 – 44.4%, FeO – 34.8%, Fe_2O_3 – 11.6%, MgO – 4.1% and SiO_2 – 2.1%.

The sample of ilmenite before measurement was dried and ground. The particle size distribution of ground material was determined by sieve analysis and electron scanning microscope Tesla BS300. The sample of ilmenite was placed in batcher, while sulphuric acid was placed in calorimetric vessel. When thermal equilibrium in calorimetric system was attained, reaction was initiated by introducing ilmenite to calorimetric vessel.

After reaction the mixture was cooled down and the products of reaction were dissolved in water and analysed using ICP and XRF spectrometry. The analysis of solid product of reaction was carried out using X-ray diffractometry. Results of this investigation show high amorphy of the sample and the received diffractogram pattern was very close to hydrated iron sulfate.

The average specific heat of products of reaction was determined in 'drop' calorimeter. This method investigation of average specific heat is close to the apparatus described in paper of Świętosławski and Zielenkiewicz [7]. The average specific heat of products of reaction was in the range of 1.07 to 1.5 J g^{-1} K^{-1} in dependence from the composition of reactionary mixture.

On the base of results was calculated the degree of conversion of titanium raw material, which is defined as ratio of the titanium amount dissolved to the total titanium amount in digested sample.

Results and discussion

The aim of calorimetric investigations was to find influence, such parameters as the initial concentration of sulphuric acid, initial temperature of reaction and particles size distribution of titanium raw material on rate and thermal effect of reaction of sulphuric acid with titanium raw material. These parameters on the basis of preliminary measurements show that they have essential influence not only on rate of reaction and safety of, but also on efficiency of the process.

As the first parameter of investigation was select the initial temperature of reactionary mixture. The first effects of reaction were observed in temperature 60°C. However rate of reaction in this temperature was very low. The curves of thermal power of reaction in calorimeter for initial temperatures from 70 to 90°C are shown on Fig. 1. With increase of initial temperature is observed increase of thermal power rate of reaction. At the beginning on the curve of thermal power is observed the sharp increase, what is related with initiation of reaction.

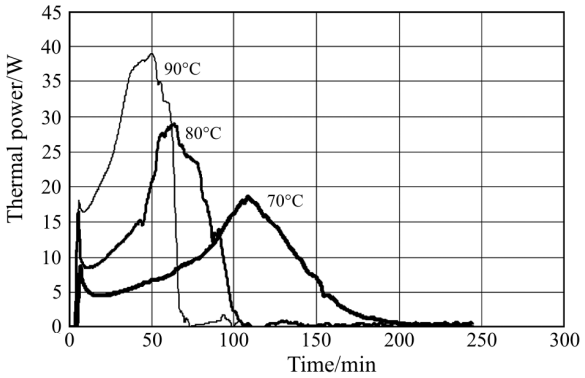

Fig. 1 Thermal power at reaction of Norwegian ilmenite with sulphuric acid at different initial temperatures

The same large influence on reaction rate as the initial temperature is observed also for particle size of titanium raw material. Presented below experimental results was realized as follow. Titanium raw material was ground and next separated on different fractions of particles size and reaction of sulphuric acid with every of these particles fraction were investigated. In Fig. 2 is presented the changes of thermal power of reaction of sulphuric acid with different particle size fractions of ilmenite. This results show, that rate of reaction of ilmenite particles with smaller sizes is more and more greater. If the particles size fraction is

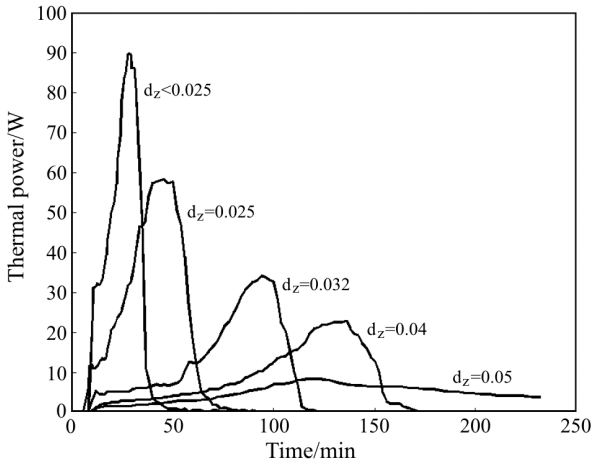

Fig. 2 Thermal power at reaction of ilmenite with sulphuric acid at different particles sizes (mm)

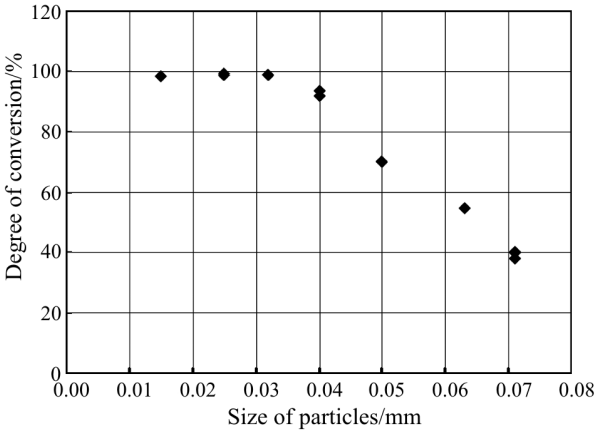

Fig. 3 Degree of conversion in dependence of ilmenite particle size fraction

below 0.025 mm, then the thermal power is enough large to expect, that in these conditions reaction can create danger of explosion.

In Fig. 3 is presented obtained degree of conversion in dependence from the fraction of particle size. On this graph is visible, that above the fraction of particles with diameter 0.04 mm follows decrease of degree of conversion. This shows the influence of the particle size not only on thermokinetics, but also on the efficiency of the reaction.

In this calorimetric system was determined also the thermal effect of the reaction of ilmenite with different concentration of sulphuric acid and results are presented in Fig. 4. As we see on this graph in the range of concentrations of sulphuric acid 83 to 93%

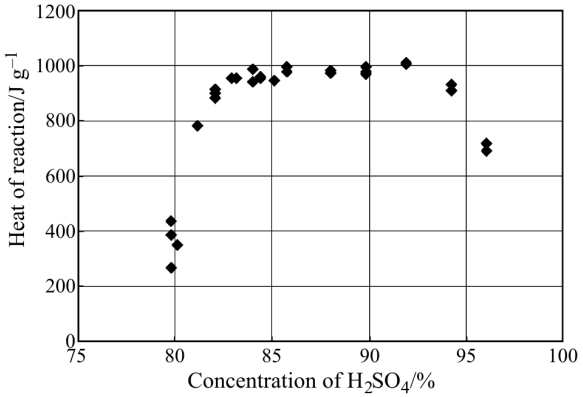

Fig. 4 Influence concentration of sulphuric acid on heat of reaction

thermal effect is not depended from concentration and the average value of the thermal effect for this range is about 980 J g^{-1}. Above and below this range of concentrations we observe the decrease of the thermal effect, what suggest that in these concentrations generated quantity of heat is not sufficient to the more effective run of the reaction.

The realized investigations show large influence of the initial sulphuric acid concentration and the initial temperature of reaction as well as particle size distribution of titanium raw material on kinetics as well as thermal effect of the reaction. The knowledge about influence of these parameters plays important role in determination of the safe and effective run of reaction. By changing initial parameters of reaction it is possible to operate and control the run of reaction.

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