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INVESTIGATION OF REACTION PRODUCTS OF SULPHURIC ACID WITH ILMENITE

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The reaction of sulphuric acid with titanium raw materials runs violently with simultaneous emission of gases. Such run of reaction creates danger of explosion. This process is very complicated from the reason of complexity of reactions and variety of compounds in reaction mixture. To determine safe conditions of reaction with high efficiency, it is necessary to investigate phase composition products of reaction.

Products of reaction were investigated by using X-ray diffraction. However reaction products show high amorphy and this is the reason of difficulties to determine all phases. For this reason also was used additional method – ‘drop’ calorimeter. This method is used for determination of average specific heat of liquid or solid samples. In this case, this method was used for verification of phase composition of products of reaction.

On the basis of investigation the phase composition of reaction product is following: titanyl sulfate, iron(III) sulfate, monohydrated iron(II) sulfate, magnesium sulfate and unreacted remainders of ilmenite and magnesium silicate.

Keywords: *average specific heat, ilmenite, phase composition, products of reaction*

Introduction

Reaction of the sulphuric acid with ilmenite is the first step in sulphuric technology of the titanium pigments production. The reaction of the sulphuric acid with titanium raw materials runs violently with simultaneous emission of large amounts of heat and gases. It is very important for a such selection of the reaction conditions, to run safety with maximum efficiency. Thermokinetics of ilmenite with the sulphuric acid reaction and conditions in which reaction is running were an object of previous study [1–3].

Knowledge about compounds which are present in products of reaction are important from efficiency point of view. So analysis of products of reaction is important because on this base we are able to modify conditions of the process to run safe with maximum efficiency.

For phase analysis very often thermal analysis is used in combination with X-ray diffractometry (XRD) [4–6].

Investigation of reaction products of ilmenite with sulphuric acid is particularly difficult from the reason of presence strongly corroding environment.

Experimental

Ilmenite is a raw material which contain such main elements as iron, titanium or magnesium. Composition of ilmenite is depending on the place of its origin. In this investigation the Norvegian ilmenite was used. The elemental composition of this ilmenite determined by X-ray fluorescence spectrometer XRF was as follows: TiO_2 – 44.4%, FeO – 34.8%, Fe_2O_3 – 11.6%, MgO – 4.1% and SiO_2 – 2.1% [2]. In mineral ilmenite presence of such phases as ilmenite $FeTiO_3$, hematite Fe_2O_3 and enstatite $MgSiO_3$ was found [7].

Reaction product were received from reaction of ilmenite with sulphuric acid in specially constructed calorimeter described elsewhere [2, 3].

The concentration of the sulphuric acid and dimension of ilmenite particles applied in the reaction were selected in an optimal way from the efficiency as well as the rate of the reaction point of view on the basis of previous study [3]. Initial concentration of sulphuric acid in the reaction was 85% and the ilmenite particles size D_{50} was about 22 μm. To the reaction was used double excess of sulphuric acid. Since the reaction was strongly exothermic, released heat caused a strong rise temperature of reactionary mixture. Therefore products of reaction were cooled for next analysis.

Results and discussion

As first method for phase investigation of the reaction products X-ray diffraction was used. The measure-

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ments was realized on diffractometer Philips PW1710 equipped with the X-ray tube with the copper anode. Measurement result of sample of reaction products was presented on Fig. 1. Obtained diffraction results show high amorphy which was a reason of difficulties in the identification of phases appearing in the sample. However analysis of diffraction results shows that the presence of iron(II) sulphate monohydrate in the sample was the most probable compound. Other compounds where difficult to identify.

In order to identify remaining phases, the sample of reaction products was heated to the temperature of 1000°C. The sample of reaction products was placed in the open type crucible and heated with 5 K min^{-1} heating rate. The changes of the sample mass together with increase of temperature was presented in Fig. 2.

Initial loss of mass visible on the curve is probably related with removing water from the sample. In the range of temperatures 300 to 700°C mass changes is not observed. Just above the temperature at 700°C sharp loss of mass of the sample is appearing. This transformation is probably related with emission of sulphur oxides. Occurring transformations, were investigated also by the X-ray diffraction. The samples were also heated in the range of temperature 100 to 1000°C and analyzed by diffractometer. Results of investigation were presented as three dimensional plot of diffraction patterns in Fig. 3.

This plot shows that the sample is amorphous to temperature at 300°C. Above this temperature are visible new phases which are identified as probable compounds iron(II) sulphate and titanyl sulphate. Above temperature at 700°C begins new transformation where appears pseudobrookite and rutile.

In order to identify remaining phases, the sample of products of the reaction was dissolved in the water. Solution was filtered and the received filter cake was dried and analysed in the X-ray diffractometer. Results of the measurement were presented in Fig. 4. This diffraction pattern shows the presence of magnesium silicate (enstatite) $MgSiO_3$ and ilmenite $FeTiO_3$. Presence of ilmenite and magnesium silicate in filter cake shows that not all quantity of this phase reacts with sulphuric acid. Remaining phases from the reason of amorphousness of the sample were difficult to identify.

The filter cake was heated to the temperature at 800°C and was analysed on diffractometer (Fig. 5).

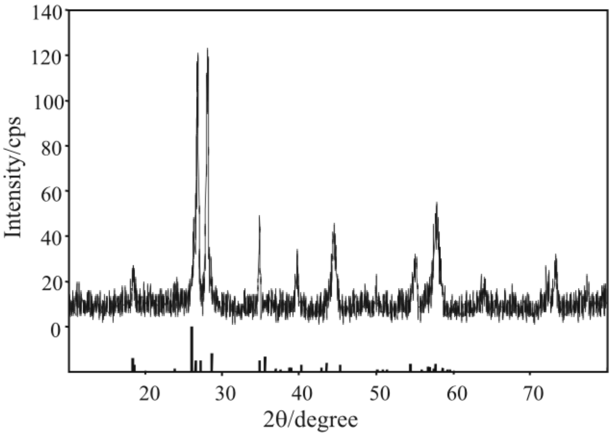

Fig. 1 Diffraction pattern of products of reaction of Norwegian ilmenite with sulphuric acid, with the $FeSO_4$ H_2O pattern

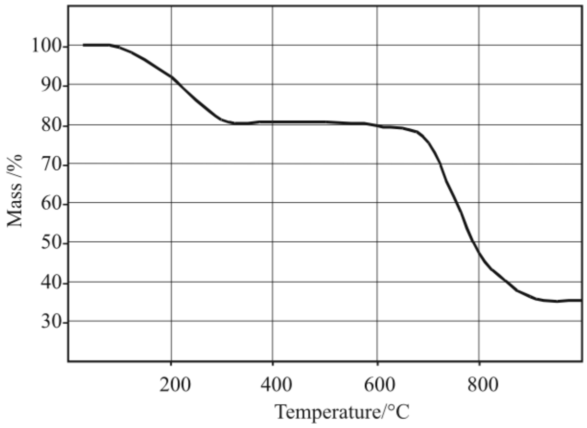

Fig. 2 Changes mass of heated sample

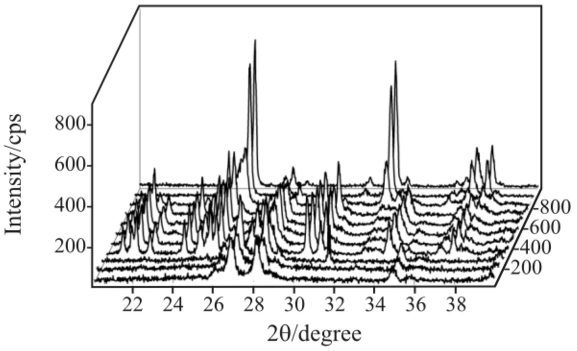

Fig. 3 Three dimensional plot of diffraction patterns of products of reaction of Norwegian ilmenite with sulphuric acid calcined at different temperatures

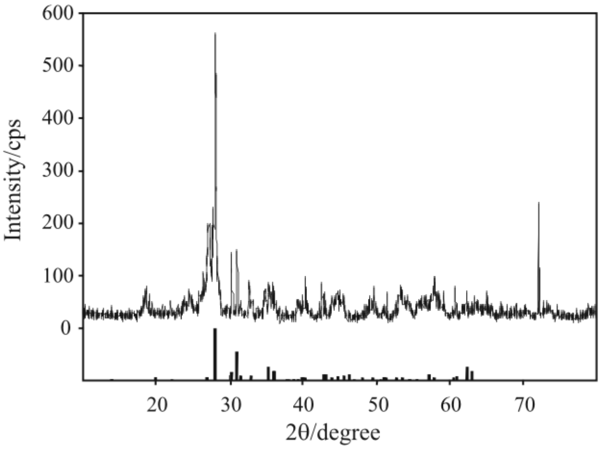

Fig. 4 Diffraction pattern of the filter cake with the $MgSiO_3$ pattern

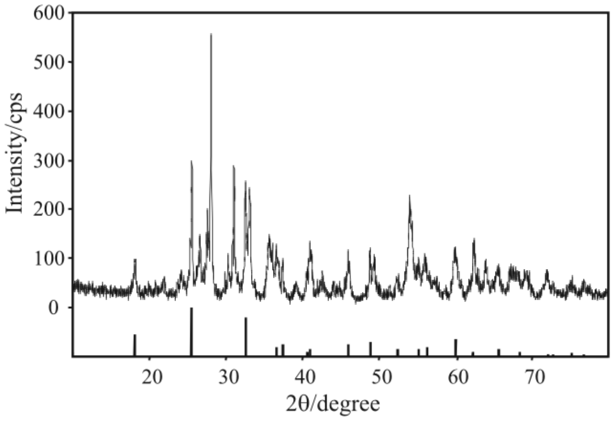

Fig. 5 Diffraction pattern of calcined filter cake at 800°C with the pseudobrookite pattern

Results of investigation shows presence of magnesium silicate (enstatite) – $MgSiO_3$, pseudobrookite – Fe_2TiO_5, and rutile – TiO_2. Pseudobrookite and rutile, are a result of transformation of ilmenite, what was described earlier [8].

In the initial raw material ilmenite, except of $FeTiO_3$ and $MgSiO_3$ also haematite Fe_2O_3 is appearing [7]. However in products of the reaction as well as in the filter cake compounds containing iron(III) was not found. It is probably resulted the amorphousness of these compounds. If the samples are heated, the iron(II) is changing to the iron(III), and as the result of this transformation pseudobrookite appears. This phase was found in calcined samples of the reaction products and in the calcined filter cake.

Investigation of reaction products by X-ray diffraction method shows such phases as iron(II) sulphate monohydrate, titanil sulphate and unreacted remainders of ilmenite and magnesium silicate.

It is very difficult to determined all phases presented in the sample of products reaction by X-ray diffraction method. On the basis of X-ray diffraction results it was assumed that during reaction ilmenite with sulphuric acid appeared presented below chemical reaction [2]:

$$TiO_2+H_2SO_4 \rightarrow TiOSO_4+H_2O$$

$$Fe_2O_3+3H_2SO_4 \rightarrow Fe_2(SO_4)_3+3H_2O$$

$$FeO+H_2SO_4 \rightarrow FeSO_4+H_2O$$

$$MgO+H_2SO_4 \rightarrow MgSO_4+H_2O$$

So it was assumed that in products of reaction appearing titanil sulphate, iron(II) sulphate monohydrate, iron(III) sulphate, magnesium sulphate and unreacted remainders of ilmenite and magnesium silicate. Except mentioned compounds in the reaction mixture also water and sulphuric acid will appear.

For the verification of the composition of products of reaction, measurement of the average specific heat was used. This experimental value was compared with the value of specific heat of each component of reaction mixture data [9, 10].

It was assumed that the specific heat of components not dependent from temperature, except of specific heat of aqueous sulphuric acid solution. This dependence was assumed as linear.

To measure of average specific heat of reaction mixture was used ‘drop’ calorimeter. Large advantage of this method is the possibility of measurement specific heat of liquid or solid samples and resistance of this apparatus on very strongly corroding environment. This method of investigation of average specific heat is close to apparatus described in paper of Świętosławski and Zielenkiewicz [11]. Average specific heat of each mixture was determined by ‘drop’ calorimeter method in range of temperatures 20 to 100°C.

The composition of examined samples of the reaction products changes in wide range and was dependent from the kind and the amount of the titanium raw material and the amount and concentration of the sulphuric acid used to the reaction. Measured values of the average specific heat changed in the range from 1.07 to 1.5 kJ kg^{-1} K^{-1} depending on composition of reactionary mixture.

Obtained experimental data were compared with the values of specific heat calculated on the basis of composition of reactionary mixture. Received difference between the experimental and calculated value of the specific heat expressed as standard deviation was 3.6%. This value of standard deviation shows relatively good fitting calculated and experimental values what is presented in Fig. 6.

Good agreement of experimental and calculated results confirmed assumption of composition and the kind of compounds appearing in reaction products. Comparatively good agreement of experimental and

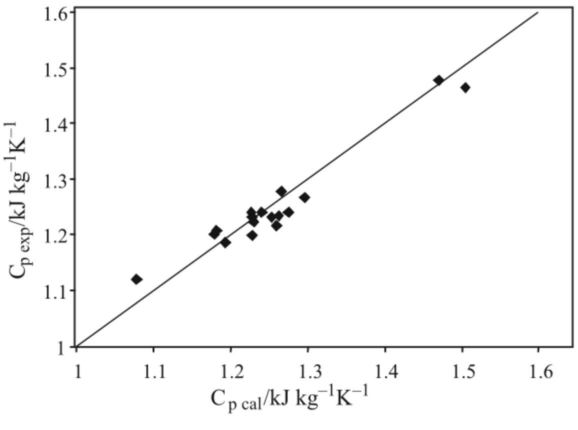

Fig. 6 Comparison experimental and calculated value of the specific heat

calculated results shows also that specific heat of salts and oxides depends very weakly from temperatures in contrary to specific heat of sulphuric acid in the range of temperatures 20 to 100°C.

Conclusions

Determination of the phase composition of the reaction products is difficult from the reason of the presence of the sulphuric acid as well as high amorphousness of the mixture.

On the basis of investigation of reaction products of ilmenite with sulpuric acid by using X-ray diffractometer and calorimetric method ‘drop’ type, was found that the most probable main phases appearing in the reaction products are titanil sulphate, iron(II) sulphate monohydrate, iron(III) sulphate, magnesium sulphate and unreacted remainders of ilmenite and magnesium silicate. Remaining minor phases are difficult to identify from the reason of high amorphousness of products of the reaction and low concentration.

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