

The influence of admixtures on the course of hydrolysis of titanyl sulfate

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The study focused on the question how admixtures, such as iron(II), iron(III), magnesium and aluminium salts influence the degree of TiOSO_4 conversion to hydrated titanium dioxide (HTD). Titanyl sulfate solution, an intermediate product in the industrial preparation of titanium dioxide pigments by sulfate route was used. The admixtures were added to the solution and their concentration was gradually changed. It was found that hydrolysis clearly depended on Fe(II) and Fe(III) concentrations. The higher the concentration of iron(II) (up to 5 wt %) in the solution was, the higher conversion degree was achieved. A reverse relationship was observed concerning the influence of iron(III) introduced up to 1.5 wt %. The constant rates of both phases of titanyl sulfate hydrolysis (including the formation of an intermediate colloidal TiO_2 and final products) depended on iron(II) and iron(III) content in the solution. The concentration of other constituents did not influence hydrolysis in the investigated part of the process (up to 2.6 wt % of Mg and up to 0.3 wt % of Al). However, the size of primary particles of the obtained $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ did not depend on the content of the above-mentioned constituents in the solution.

Keywords: hydrate titanium dioxide, hydrolysis, titanyl sulfate, admixtures.

INTRODUCTION

Titanium dioxide is the most widely produced white pigment, used in paints, plastics, rubber, paper, as well as in ceramic, cosmetic and textile industries. Among inorganic pigments it plays a major role due to its unique property of being able to effectively diffuse visible light. TiO_2 is completely non-toxic and chemically and thermally stable, it does not lose its pigment properties during the process of manufacturing of a final product. The paint and coatings industry alone uses an estimated 2.31 million tons of titanium dioxide annually out of a total of 4.05 million tons produced worldwide¹⁻³.

TiO_2 is manufactured by two methods. The older one is the sulfate process. It is based on the decomposition of titanium-containing raw material by sulfuric acid and the hydrolysis of titanyl sulfate. The other method is the chloride process. The latter process is associated with the chlorination of titanium dioxide or its concentrate and the oxidation of TiCl_4 ⁴⁻⁸.

The production of TiO_2 by sulfate method requires natural or synthetic rutile, ilmenite and titanium slags. Titanium slags are made from ilmenite by the chemical reduction of its iron oxide content. For technological and economical reasons a mixture of these raw materials is usually used. A complex composition of raw materials and their admixtures can negatively affect TiOSO_4 hydrolysis and the resulting properties of the product. Mineral rutile (TiO_2 content, reaching 94–96 wt %) is a natural form of titanium dioxide. The main admixtures found in rutile are iron, as well as chromium and vanadium compounds⁹. Synthetic rutile is produced from ilmenite and is often introduced to improved slags as enriched ilmenite¹⁰. The theoretical chemical formula of ilmenite is FeTiO_3 (TiO_2 content reaching 45–60 wt %). The most commonly found admixture of this mineral is silicon dioxide¹¹. Chemical composition of titanium slag produced from different raw materials changes only slightly. Titanium oxide comprises the main part of titanium slag. Titanium slag often contains solid solutions with complete miscibility $(\text{Mg,Fe,Mn})\text{O} \cdot \text{TiO}_2\text{--Ti}_2\text{O}_3$, where silicate phase, or sometimes even Ti_2O_3 can be present. High-grade tita-

anium slag contains 70–85 wt % of TiO_2 ⁶. Table 1 presents the compositions of titanium containing raw materials used for the production of titanium dioxide^{6,7}.

Table 1. The mean composition of titanium-containing raw materials

Component	Raw materials (wt %)		
	Ilmenite	Titanium slag	Rutile
TiO_2	51.8	72.0	96.0
FeO	23.8	23.0	—
Fe_2O_3	16.0	—	0.70
SiO_2	0.80	1.20	1.00
Al_2O_3	1.00	3.30	0.15
MgO	0.15	0.60	—
MnO	1.50	—	0.02
V_2O_5	0.20	—	0.50
Cr_2O_3	0.10	—	0.27

The admixtures found in significant quantities in titanium containing raw materials are iron(II), iron(III), silicon, aluminum and magnesium. SiO_2 found in raw materials is completely removed during the clarifying process (i.e. in the sulfate process of white pigment production). In spite of clarifying and filtration, other constituents are still found in titanyl sulfate liquor in smaller, but still substantial quantities. The admixtures affect the course of the hydrolysis of titanyl sulfate and the purity of the hydrated titanium dioxide, which is the product of the reaction. The admixtures are located inside TiO_2 grains, which makes it impossible to remove by washing them out while preparing the hydrated titanium dioxide for calcination. Not only do admixtures change titanium dioxide's colour, but they also affect its photoactivity and its physical and chemical properties⁹. Hydrolysis of titanium sulfate compounds is a complex physiochemical process and it is one of the most important stages in producing titanium dioxide. It is crucial for obtaining the desired properties of the final product¹². In industrial practice there are two ways to conduct the hydrolysis process: Blumenfeld and Macklenburg's methods^{13,14}. In the former method nuclei are produced in the whole mass of

solution which undergoes hydrolysis through appropriate dilution and keeping the solution at its boiling point. In the latter method nuclei are formed separately and they are added to the solution undergoing hydrolysis. The $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ particles are precipitated by the addition of sodium hydroxide to TiOSO_4 . Though the hydrolysis process has been used for over eighty years very little is known about the mechanisms of the particle formation process. There are many presumable mechanisms which can occur during TiO_2 precipitation^{15, 16}. The primary size enlargement mechanisms are nucleation and growth, while agglomeration, aggregation, and breakage are usually defined as secondary mechanisms. Each mechanism can occur in several ways, subject to the type of system and environment within the precipitator.

There are many other ways (besides Blumenfeld and Mecklenburg methods) to obtain titanium dioxide by hydrothermal hydrolysis from acidic aqueous TiOSO_4 solution but the final material has photocatalytic and not pigment properties^{15, 17, 18}.

There are many factors which can affect the hydrolysis process: temperature, TiOSO_4 , free H_2SO_4 , Fe^{2+} and Fe^{3+} concentrations, nuclei, stirrer speed or even the solution storage time before hydrolysis^{6, 12, 19 - 22}.

The content of iron(II) and iron(III) in the solution used for hydrolysis has a principal influence on the process and the properties of the product. Iron(II) affects the kinetics of hydrolysis. This can be explained by shifting the reaction equilibrium of sulfate metatitanic acid conversion into sulfate orthotitanic acid, because of sulfate orthotitanic acid reacting with iron(II) sulfate. A reverse phenomenon can be observed in the presence of Fe^{3+} , when the amount of sulfate metatitanic acid increases and hydrolysis is inhibited¹².

In the work of Juho-Pertti²² the influence of high Fe(II) content on titanium dioxide precipitation from titanyl sulfate solution (314 – 224 g TiO_2/dm^3 , 0 – 0.53 weight ratio $\text{Fe(II)}/\text{TiO}_2$, constant ratio $\text{H}_2\text{SO}_4(\text{act.})$ to TiO_2) was shown. It was found that the higher Fe(II) content was in the solution the slower the so-called gray stage of the hydrolysis was established (the gray color of the solution). It was symptomatic for the base liquor that the higher iron(II) concentration was, the lower was the concentration of titanium dioxide in the solution, the higher was the total sulfate content and the relative reactivity factor of the liquors was changed. When this factor was high, the precipitation proceeded fast because the colloidal titanium dioxide was a precipitation initiator. The delay in the gray stage can be also a consequence reaction between titanium sulfate and iron(II) sulfate in sulfuric acid solutions to form yellow complexes. A complex formation could also decrease the amount of polycondensable titanium dioxide and the aggregate.

The aim of this work was to study the fundamental aspects of HTD synthesis by hydrothermal hydrolysis of titanyl sulfate solutions, which is also important for improving this stage in the synthesis of pigment titanium dioxide. We investigated the course of titanyl sulfate hydrolysis depending on the concentration of admixtures (i.e. Fe^{2+} , Fe^{3+} , Mg^{2+} and Al^{3+}) found in the starting solution. These are the main admixtures

found in titanyl sulfate solution produced in sulfate process, in which a mixture of ilmenite and titanium slag is the raw materials.

EXPERIMENTAL SECTION

An industrial acidic aqueous titanyl sulfate solution was used in the study. The liquor is highly viscous and dark brown in colour. This solution was called „black leaching liquor”.

The physicochemical properties of titanium liquor i.e. titanyl sulfate solution depend both on the kind of the raw material used and the successive stages of its production. The main constituents of hydrolyzed titanyl sulfate are TiOSO_4 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$ and many other compounds which are derived from titanyl raw materials¹². In sulfate titanyl solutions there is a complex system of phases equilibrium, which is additionally complicated by such phenomena as dissociation, hydrolysis, complexing, hydration, association or even polymerization. An important property of industrial solutions of titanyl sulfates is their stability, which is a measure of their tendency to undergo hydrolysis. For the good quality liquors this tendency amounts to 600 – 700 (the total amount of cm^3 of water added to 1 cm^3 of the investigated solution)^{6, 20}. The factors which affect the stability of a solution are its acidity, titanyl sulfate concentration, the kind of admixtures found in it as well as the temperature. Titanyl sulfate solutions produced in industrial installations are not stable while being stored even at ambient temperature. Their susceptibility to hydrolysis gradually increases. It is explained by an uncontrolled and very slow hydrolysis of titanyl sulfate taking place in the conditions in which a solution is stored. A formation of even small amounts of colloidal TiO_2 becomes during the process of real hydrolysis an inducing factor that speeds up the process of hydrated titanium dioxide precipitation. Therefore, the experiments were carried out on fresh solutions of titanium liquor obtained from industrial installations at various periods of time. The solutions varied to some extent as for their content of various constituents and their stability. Owing to these differences the results from successive experiments can only be compared within one series of experiments. The stability of titanium liquor solutions used in all the series of experiments amounted to 650 – 700. The liquor's density and its mean composition are shown in Table 2.

The hydrothermal hydrolysis of titanyl sulfate was carried out with the use of the Blumenfeld method (a dilution of the solution and increasing the temperature up to the boiling point). An appropriate amount of concentrated titanyl sulfate solution and one of the investigated admixtures was introduced into a dropper, while at the same time an appropriate amount of water was introduced into the glass-reactor (designated volume 500 cm^3), depending on the initial TiOSO_4 concentration in the solution. The water and titanium liquor were heated up to the temperature of 96°C. When they reached the desired temperature, the liquor was dropped in for 20 min, while at the same time the temperature was increased to 102°C. After the dropping-in was over the reaction mix-

Table 2. The mean content of constituents found in industrial titanyl sulfate solution

Density	Component (wt %)										
	Main		Trace								
(g/cm^3)	TiOSO_4	free H_2SO_4	Fe	Mg	AL	V	Mn	P	Cr	K	Si
1.59	30	11.5	3.98	0.082	0.078	0.068	0.057	0.042	0.017	0.007	0.003

ture was heated for 20 min to the so-called first boiling point, i.e. to 107 – 109°C (dependent on the concentrations of TiOSO_4 and free H_2SO_4). The solution was kept at this temperature for the whole time of the process, i.e. for 180 min under rotation 960 rpm. The boiling point of the reaction mixture was assumed to be the start of hydrolysis (0 min). That was the starting point of defining titanyl sulfate hydrolysis degree.

The conversion degree of titanyl sulfate (α) into hydrated titanium dioxide was calculated from the equation:

$$\alpha = \frac{C_0 - C}{C_0} \cdot 100\% \quad (1)$$

where C_0 – initial concentration of Ti calculated as TiOSO_4 in the solution, g/dm^3 , C – concentration of Ti as TiOSO_4 in the solution after time t , g/dm^3 .

Table 3 presents the initial contents of titanyl sulfate, free sulfuric acid and the investigated admixtures found in the hydrolyzed solution in successive series of experiments. The range of admixtures content varied: 1.5 – 5 wt % of Fe^{2+} ; 0.03 – 1.5 wt % of Fe^{3+} ; 0.08 – 2.6 wt % of Mg^{2+} and 0.07 – 0.3 wt % of Al^{3+} . The investigated constituents were introduced into titanium liquor in the form of sulfates. TiOSO_4 and free H_2SO_4 initial content in the liquor was similar and it amounted to about 380 $\text{g TiOSO}_4/\text{dm}^3$ and 175 $\text{g H}_2\text{SO}_4/\text{dm}^3$ respectively (Table 3). Fe^{2+} content in the solution amounted to 3.78 wt %. Therefore, it was necessary to lower the content of this impurity to 1.5 wt % through cooling down the solution and crystallization of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

Throughout all the course of the process, the samples of the suspension were collected after the defined periods of time. The precipitates were separated from the liquid phase (post-hydrolytic sulfuric acid) by centrifuging (20 min, 8000 r.p.m), washed with distilled water to remove free sulfuric acid, dried at ambient temperature (the so-called air-dry state), and crushed.

Kinetic experiments were conducted in order to assess the influence of Fe(II) and Fe(III) on the course of titanyl sulfate hydrolysis. A hydrolysis of acidic titanyl sulfate solution containing 380 $\text{g TiOSO}_4/\text{dm}^3$ and 182 $\text{g H}_2\text{SO}_4/\text{dm}^3$ with a variable content of both kinds of iron was performed (2.04 – 3.67 wt % of Fe^{2+} ; 0.06 – 1.5 wt % of Fe^{3+}). The water and titanium liquor were heated up to the temperature of 96 °C. When they reached the desired temperature, the liquor was dropped in for 20 min, while at the same time the temperature was increased to 102 °C. The end of the dosage of titanium liquor was assumed to be the start of hydrolysis (0 min). That was the starting point of defining titanyl sulfate hydrolysis degree. After the dropping-in was over the reaction mixture was heated for 20 min to the so-called first boiling point. The solution was kept at this temperature for the whole time of the process, i.e. for 180 min under rotation 960 rpm.

After introducing a solution of titanyl sulfate into water samples of the reaction mixture were taken according to the following procedure. The solid phase was separated from the liquid one by centrifuging (5000 r.p.m., 20 min). In the liquid phase the content of Ti calculated as titanium dioxide was determined and its content was a sum of Ti as titanium dioxide present in the form of not hydrolyzed TiOSO_4 and colloidal titanium dioxide. Next, the liquid phase separated by centrifuging was treated with concentrated hydrochloric acid, at the phase ratio 1:1 and following peptization the

colloidal TiO_2 was precipitated. The solid phase was again separated from the liquid one by centrifuging (5000 r.p.m., 20 min). In the liquid phase obtained in this way the content of Ti calculated as titanium dioxide (which was present in the form of non-reacted TiOSO_4) was determined. On the basis of the obtained results the contents of the successive forms of titanium dioxide were calculated, i.e. the contents of TiO_2 precipitated in the solid phase, colloidal TiO_2 and TiO_2 which remained in the solution in the form of TiOSO_4 .

Titanium and iron were determined in the liquid phase using a spectrometric method²³. Free sulfuric acid was determined by means of potentiometric method. The stability of titanium liquor was also determined⁶. Magnesium and aluminium were determined using ICP-AES method²⁴. The X-ray diffraction analysis was used to determine the crystallites size in the hydrated titanium dioxide samples (X'Pert PRO Philips diffractometer with $\text{CuK}\alpha$ radiation)²⁵. The crystallites average size (d_{crys}) variation was determined on the basis of Scherrer's equation:

$$d_{\text{crys}} = \frac{\lambda \cdot K}{\beta \cdot \cos \theta} \quad (2)$$

where λ is the wavelength of $\text{Cu K}\alpha$ radiation, K is the particle shape factor, β is the full width at half maximum of the intensity peak.

The variation of crystallites average size of the anatase phase was calculated from the (101) reflection of anatase. The width of the peak at half maximum was calculated taking into account the so-called instrumental broadening. This parameter was determined on the basis of the sample of coarse crystalline silicon. The particles average size of TiO_2 was determined using of a scanning electron microscope (DSM 962, Zeiss)²⁶.

RESULTS AND DISCUSSION

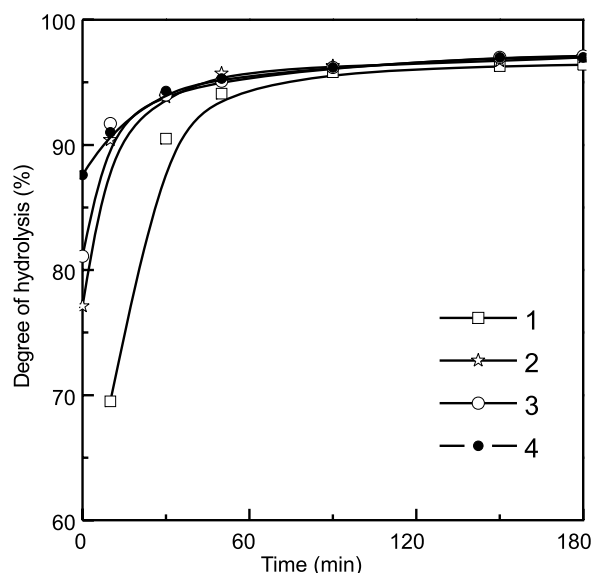
In the first series of the experiments the influence of iron(II) concentration in the hydrolyzed solution on the degree of titanyl sulfate conversion to hydrated titanium dioxide was investigated. The iron(II) content in the initial solution was 3.78 wt % (Table 3). The content of the admixture in the starting solution undergoing hydrolysis was equal to 1.5 wt %, 4 wt %, and 5 wt % respectively in the successive series of the experiments. It was found that the concentration of a given investigated constituent in the solution affected the degree of titanyl sulfate conversion mainly at the initial stage of hydrolysis (Figure 1). The higher iron(II) concentration was, the higher conversion degree was obtained.

In the experiment in which iron(II) initial concentration in the solution was 5 wt % the hydrolysis degree at the reaction mixture boiling point was approximately 90%. The lowest conversion degree, at this stage of the process (<70%) was observed in the experiment, in which Fe^{2+} concentration in the solution amounted to 1.5 wt %. After 60 min, the degree of hydrolysis was almost the same irrespective of iron(II) content in the solution and it varied to a very small degree to the very end of the process. The final conversion degree amounted to approximately 97%.

The particle size of the obtained $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ was determined by means of a scanning electron microscope (Figure 2). No influence of iron(II) concentration in the initial solution on the product's mean particles size was recorded. A diameter of medium particles was approximately 1 μm . The

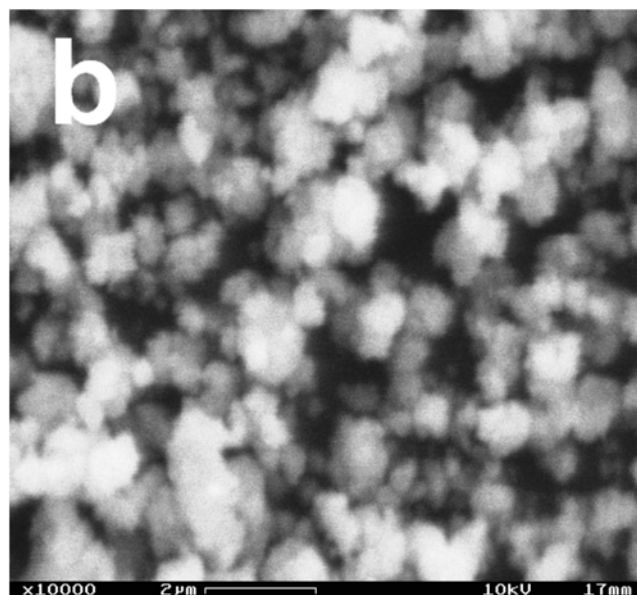
Table 3. The influence of the initial concentration of TiOSO_4 and free H_2SO_4 on their content in the post-hydrolytic sulfuric acid

Number of series	Number of experiment	Initial concentration in the solution (wt %)						Final concentration in the solution (wt %)	
		TiOSO_4	free H_2SO_4	Fe^{2+}	Fe^{3+}	Mg^{2+}	Al^{3+}	TiOSO_4	free H_2SO_4
I	1	23.63	8	1.5	0.03	0.07	0.05	1.04	24.91
	2	23.63	8	3.78	0.03	0.07	0.05	0.82	24.89
	3	23.63	8	4	0.03	0.07	0.05	0.81	24.84
	4	23.63	8	5	0.03	0.07	0.05	0.82	24.67
II	5	23.23	8.7	3.78	0.03	0.07	0.05	1.08	25.23
	6	23.23	8.7	3.78	0.3	0.07	0.05	1.50	24.5
	7	23.23	8.7	3.78	0.5	0.07	0.05	1.82	24.1
	8	23.23	8.7	3.78	1	0.07	0.05	2.32	23.8
	9	23.23	8.7	3.78	1.5	0.07	0.05	3.08	23
III	10	23.03	8.7	4.21	0.05	0.08	0.06	0.84	25.86
	11	23.03	8.7	4.21	0.05	0.9	0.06	0.76	25.12
	12	23.03	8.7	4.21	0.05	1.5	0.06	0.72	25.32
	13	23.03	8.7	4.21	0.05	2	0.06	0.78	25.46
	14	23.03	8.7	4.21	0.05	2.6	0.06	0.66	24.89
IV	15	23.43	8.4	3.96	0.05	0.06	0.07	1.14	24.96
	16	23.43	8.4	3.96	0.05	0.06	0.3	1.28	25.88

**Figure 1.** The influence of reaction time and initial concentration of Fe^{2+} in the solution on the degree of titanyl sulfate hydrolysis with the initial Fe^{2+} concentration equal to: 1 – 1.5 wt %; 2 – 3.78 wt %; 3 – 4 wt %; 4 – 5 wt %

size of the particles changed only slightly. The average size of hydrated TiO_2 crystallites ranged between 8 and 15 nm and did not depend on the content of the investigated constituents in the reaction mixture. Figure 3 shows the X-ray diffraction pattern of the precipitated hydrated titanium dioxide.

In the second series of the experiments the influence of Fe^{3+} concentration on the course of the investigated reaction was studied. In these experiments the content of iron(III) in the initial solution was 0.03 wt % (Table 3). The content of this component was increased to 0.3 wt %, 0.5 wt %, 1 wt % and 1.5 wt % respectively. The experiments showed that when the higher Fe^{3+} concentration was in the initial solution, then the lower conversion degree was achieved for the whole time of the process (Figure 4). After 30 min of the reaction the conversion degree in the solution containing 0.03 wt % of Fe^{3+} was by 20% higher than in the reaction, in which Fe^{3+} concentration was 1.5 wt %. At the end of the process (180 min) the degree of hydrolysis was 96% for the experiment with the lowest iron(III) content and 88% for the experiment with the highest concentration of the investigated constituent.

**Figure 2.** SEM images of titanium dioxide obtained in the hydrolysis of titanyl sulfate from a solution with the initial Fe^{2+} concentration equal to: a) 1.5 wt %, b) 5 wt %

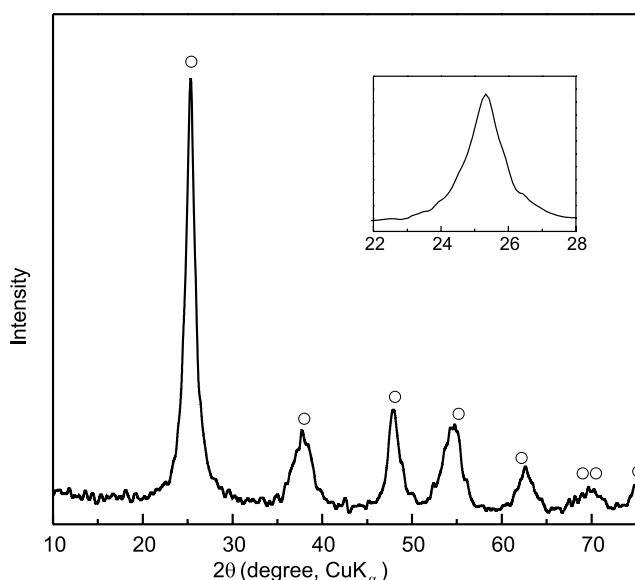


Figure 3. A sample diffraction pattern of a product of titanyl sulfate hydrolysis: anatase (O)

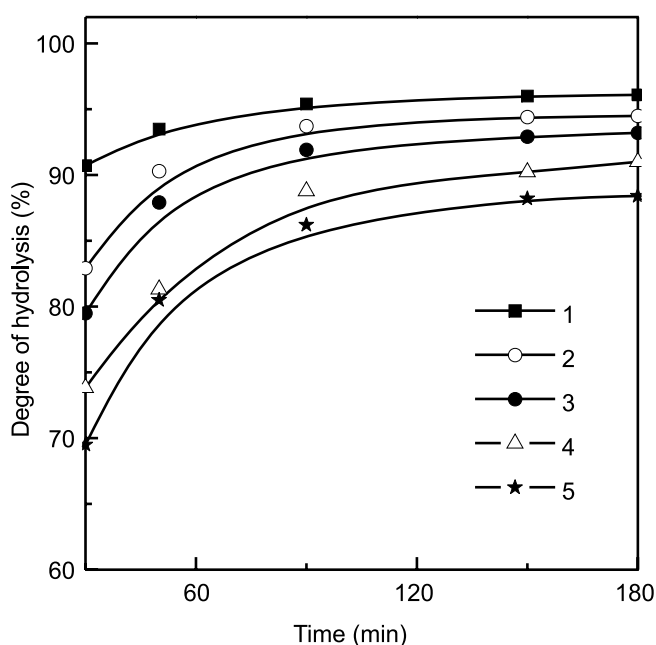


Figure 4. The influence of reaction time and initial concentration of Fe^{3+} in the solution on the degree of titanyl sulfate hydrolysis with the initial Fe^{3+} concentration equal to: 1 – 0.03 wt %; 2 – 0.3 wt %; 3 – 0.5 wt %; 4 – 1 wt %; 5 – 1.5 wt %

It was found that Fe^{3+} concentration does not affect the average diameter of the particles of hydrated titanium dioxide. Nevertheless, no unequivocal influence of iron(III) on the mean size of the crystallites of the obtained product was observed. The average size of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ crystallites ranged between 11 to 15 nm.

In the following series of the experiments the influence of Mg^{2+} concentration in the initial solution was investigated on the course of TiOSO_4 hydrolysis. The content of this admixture in the starting solution was 0.08 wt % (Table 3). The content of Mg^{2+} varied from 0.08 wt % to 0.9 wt %, 1.5 wt %, 2 wt % and 2.6 wt %. After having carried out a series of experiments it was found that the changes in magnesium concentration did not influence the hydrolysis of titanyl sulfate (Table 4). All the experiments carried out at the same titanyl sulfate solution yielded almost the same degree of hydrolysis. At the beginning of the process (after 30 min) the degree

amounted to approximately 95% and later it changed only slightly until the end of the reaction. The final hydrolysis degree reached 97%.

Table 4. The influence of reaction time and initial concentration of magnesium in the solution on the degree of titanyl sulfate hydrolysis

Time (min)	Degree of hydrolysis (%)				
	Mg^{2+} (wt %)				
	0.08	0.9	1.5	2	2.6
0	89.2	91.8	–	–	–
10	94	94.7	92.3	93.2	–
30	94.2	95.4	95.1	94.9	95.4
50	94.5	96.2	96.6	94.9	97
90	96.6	97	96.8	96.9	97.4
150	96.8	97.1	97.2	96.9	97.4
180	96.9	97.2	97.3	97	97.5

On the basis of the carried out investigations it was found that magnesium concentration in the starting solution did not affect the mean size of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ particles which was around $0.5 \mu\text{m}$. The experiments also showed that the higher content of the investigated constituent, the larger were the aggregates of hydrated titanium dioxide (Figure 5). It was found that the mean size of the crystallites of HTD ranged from 7 to 9 nm and that their size did not depend on the initial magnesium content in the reaction mixture.

In the last series of the experiments the influence of Al^{3+} in the initial solution on the course of titanyl sulfate hydrolysis was investigated. The content of the component in the subsequent attempts was 0.07 wt % and 0.3 wt % (the content in the initial solution was 0.07 wt % – Table 3). On the basis of the carried out experiments it was found that an estimated four-fold change in Al^{3+} concentration in the reaction mixture had no influence on the process of hydrolysis (Table 5). In both experiments the conversion degree both at the beginning and at the end of the process was similar and it amounted to 87% (after 10 min) and 96% (after 180 min), respectively. It turned out that it was impossible to determine the influence of aluminium on TiOSO_4 hydrolysis for a higher content of this impurity (0.5 wt %). In the samples of the suspension collected during the process a significant presence of colloidal phase was confirmed. It was impossible to separate the phase during centrifuging.

It was also found that Al^{3+} content did not influence the mean size of the particles of the product (Figure 6). No influence of aluminium concentration on the mean size of crystallites of the product (which ranged from 8 to 10 nm.) was found.

Table 5. The influence of reaction time and initial concentration of aluminum in the solution on the degree of titanyl sulfate hydrolysis

Time (min)	Degree of hydrolysis (%)	
	Al^{3+} (wt %)	
	0.07	0.3
0	–	–
10	86.5	87.8
30	92.3	91.7
50	93.8	93.1
90	95.2	94.7
150	95.7	95.1
180	96	95.3

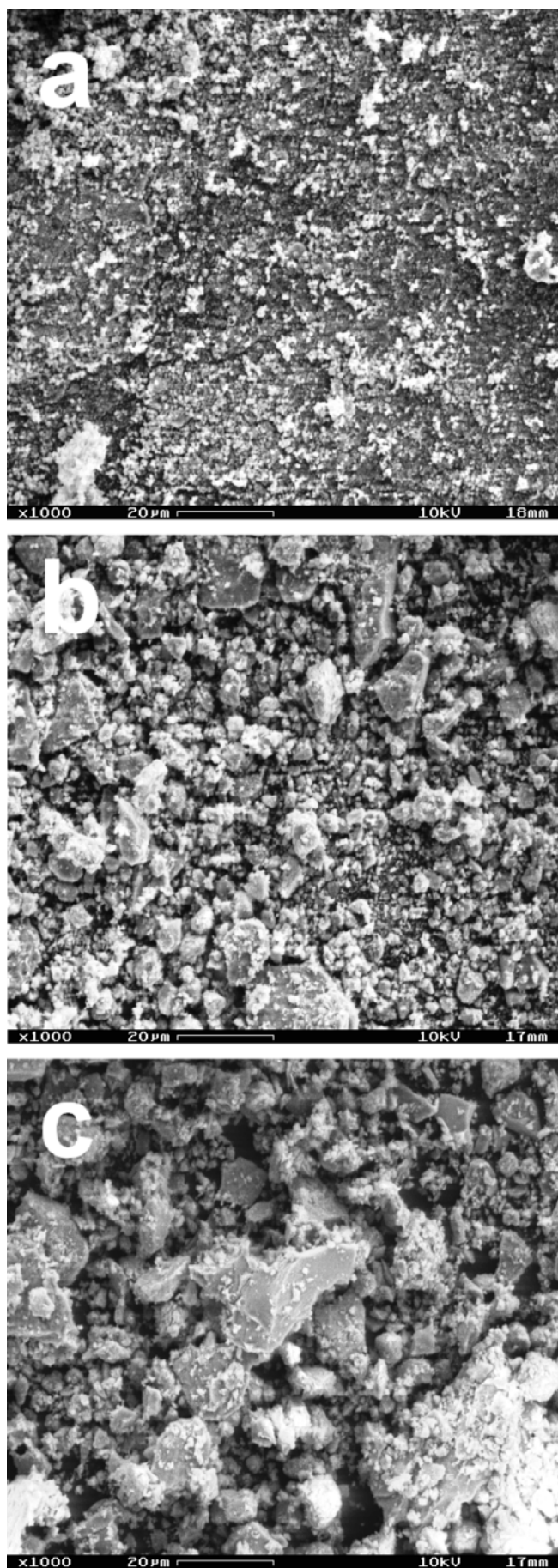
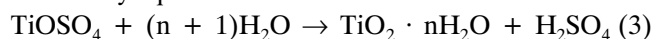
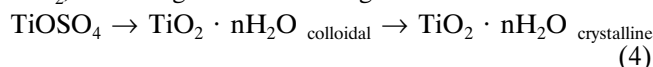


Figure 5. SEM images of titanium dioxide obtained in the hydrolysis of titanil sulfate from a solution with the initial Mg^{2+} concentration equal to: a) 0.08 wt %, b) 1.5 wt %, c) 2 wt %

Titanil sulfate hydrolysis can be presented in the form of a summary equation:



The process yields an intermediate product, i.e. colloidal TiO_2 , according to the following formula¹⁷:



Following on from that in $TiOSO_4$ hydrolysis kinetics investigations it was assumed that the process proceeds according to the scheme of the consecutive reaction²⁷:



where substance B is the intermediate product in the process of obtaining substance C from substance A, k_1 and k_2 are the constant rates of both reaction.

In the reactions of this type the conversion rate of substance A (r_A) to substance C is defined by the speed of the slowest stage of process. It was assumed that at the beginning of the reaction ($\tau = 0$) only substance A with c_A^0 concentration was present. Additionally, it was assumed that both partial reactions are of the first order.

The rate of a reactant's loss A (r_A) was defined with the following equation:

$$r_A = \frac{dc_A}{d\tau} = -k_1 c_A \quad (6)$$

from which it follows that

$$c_A = c_A^0 e^{-k_1 \tau} \quad (7)$$

where $c_A^0 = c_{TiOSO_4}^0$ is the initial concentration of titanil sulphate as TiO_2 [g/dm³], $c_A = c_{TiOSO_4}$ is the concentration of titanil sulphate as TiO_2 after time τ [g/dm³], τ is the time [min.]

The time of B (r_B) formation can be given as:

$$r_B = \frac{dc_B}{d\tau} = k_1 c_A - k_2 c_B \quad (8)$$

By substituting into the equation momentary concentrations C_A (equation 7) the changes of B concentration in time were defined with the following equation:

$$\frac{dc_B}{d\tau} = k_1 c_A^0 e^{-k_1 \tau} - k_2 c_B \quad (9)$$

This is a differential equation of 1st order. After its integration we obtain:

$$c_B = c_A^0 \frac{k_1}{k_2 - k_1} (e^{-k_1 \tau} - e^{-k_2 \tau}) \quad (10)$$

where $c_B = c_{TiO_2(\text{colloidal})}$ is the concentration of colloidal titanium dioxide after time τ [g/dm³].

The rate of C formation is expressed with the following equation:

$$r_C = \frac{dc_C}{d\tau} = k_2 c_B \quad (11)$$

When we have instantaneous values of concentrations A and B, concentration C can be determined from relation:

$$c_c = c_A^0 - c_A - c_B \quad (12)$$

hence:

$$c_c = c_A^0 \left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 \tau} + \frac{k_1}{k_2 - k_1} e^{-k_2 \tau} \right) \quad (13)$$

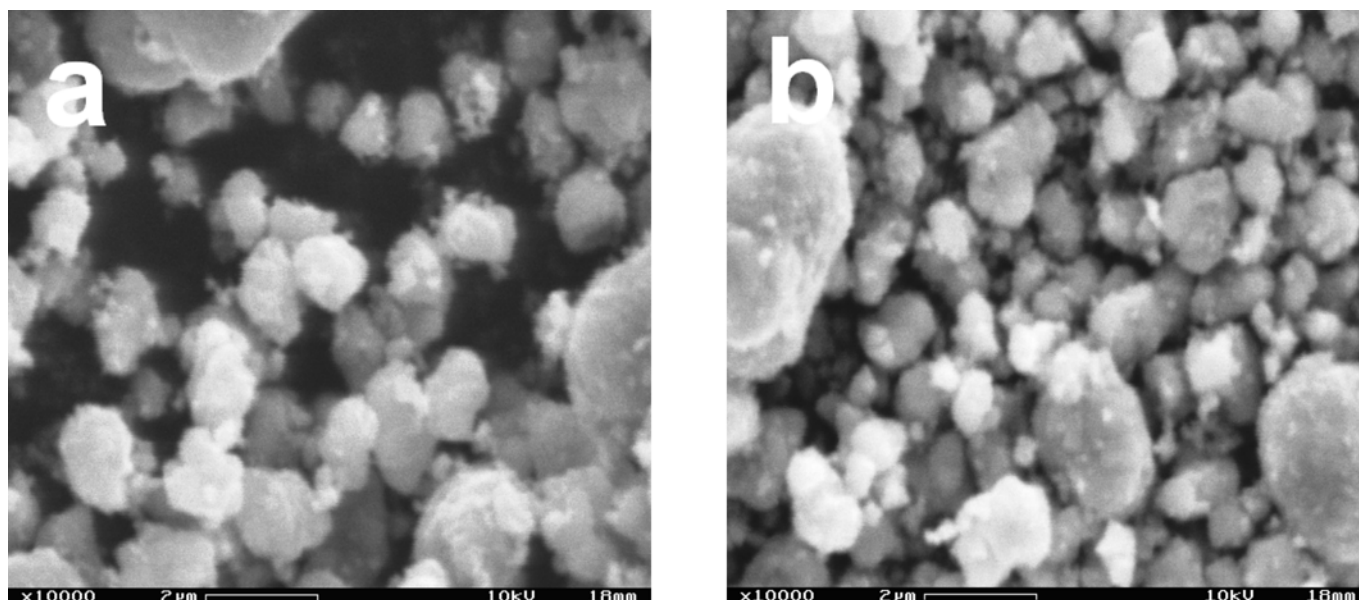


Figure 6. SEM images of titanium dioxide obtained in the hydrolysis of titanyl sulfate from a solution with the initial Al^{3+} concentration equal to: a) 0.07 wt %, b) 0.3 wt %

where $c_c = c_{\text{TiO}_2}$ is the concentration of precipitated titanium dioxide after time τ [g/dm^3]

Equations 7, 10, 13 give current concentrations of the reacting substances depending on the time in the consecutive reaction.

Figures 7 – 9 compare how the presence and amount of Fe(II) and Fe(III) in a hydrolyzed solution affect the changes in the concentration of substrate A (TiOSO_4 calculated as TiO_2), intermediate product B (colloidal TiO_2), and the final product C (precipitated $\text{TiO}_2 \cdot n\text{H}_2\text{O}$) for a consecutive reaction of the first order. The curves seen in Figure 8 show that the amount of colloidal TiO_2 at first was increasing and then it was going down. The degree of increase depended on the initial content of iron in hydrolyzed solution. The highest increase in the amount of the intermediate product was observed in the experiment, in which the initial concentrations of Fe(II) and Fe(III) were 3.67 wt % and 0.06 wt % respectively. At the same time less colloidal TiO_2 was formed when the content of Fe(II) was lowered to 2.04 wt % (0.06 wt % of Fe(III)). Even less colloidal TiO_2 was formed when the content of Fe(III) was increased to 1.5 wt % (3.67 wt % of Fe(II)). In the latter case the conversion of colloidal TiO_2 into crystalline TiO_2 was significantly slower. High content of colloidal TiO_2 in the solution was observed until the 35th minute of hydrolysis. The curves presenting a degree of TiOSO_4 conversion (Fig.7) and titanium dioxide precipitation (Fig.9) also show that the content of both forms of iron affects the rate of TiOSO_4 hydrolysis as well as the final degree of conversion.

During the experiments constant reaction rates for both stages of hydrolysis were determined (Table 6). It was found that a decrease of initial Fe(II) content by 1.63 wt % decreased the rate of colloidal TiO_2 formation by 1.6 times., but a decrease of the final product formation other affected

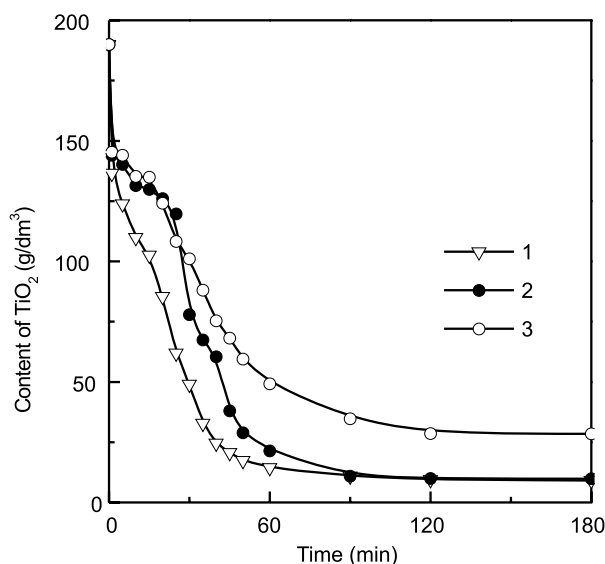


Figure 7. The influence of Fe(II) and Fe(III) contents in the hydrolyzed solution on the change of substrate's (TiOSO_4 calculated as TiO_2) concentration in time, where: 1 – Fe(II) 3.67 wt %; Fe (III) 0.06 wt %; 2 – Fe(II) 2.04 wt %; Fe (III) 0.06 wt %; 3 – Fe(II) 3.67 wt %; Fe (III) 1.5 wt %

the reaction only insignificantly. However, an increase of Fe(III) content by 1.44 wt % resulted in a significant reduction of the constant rate of both the intermediate product formation (a two-fold decrease) and the final product formation (a decrease of 1.5 times).

It can be supposed that Fe(III) catalyzes sulfate metatitanic acid formation, an acid which hydrolyzes more slowly, and that Fe(II) catalyzes sulfate orthotitanic acid formation, an acid which hydrolyzes more quickly.

Table 6. The influence of Fe(II) and Fe(III) contents on the reaction rate of titanyl sulfate hydrolysis

Content (wt %)				Reaction rate constants (min^{-1})		R^2/k_1 ($\alpha = 0.05$)	R^2/k_2 ($\alpha = 0.05$)
Fe(II)	Fe(III)	Mg	Al	k_1	k_2		
3.67	0.06	0.07	0.06	0.0477	0.1493	93.0	94.9
2.04	0.06	0.07	0.06	0.0298	0.1383	92.3	95.4
3.67	1.5	0.07	0.06	0.0223	0.1033	89.9	95.4

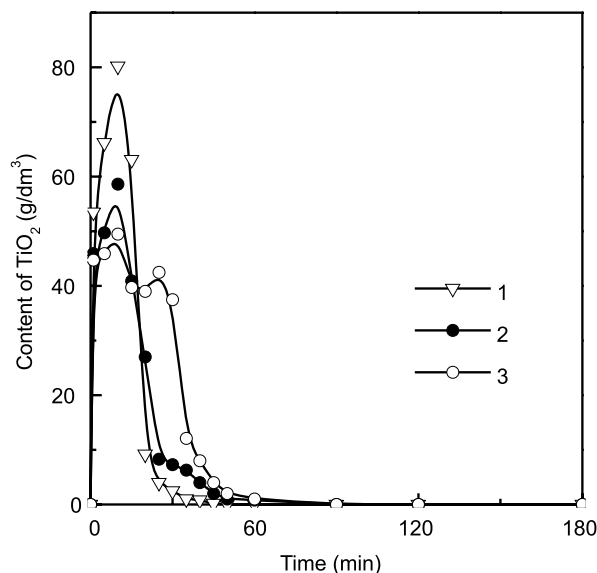


Figure 8. The influence of Fe(II) and Fe(III) contents in the hydrolyzed solution on the change of intermediate product's (colloidal TiO_2) concentration in time, where: 1 – Fe(II) 3.67 wt %; Fe (III) 0.06 wt %; 2 – Fe(II) 2.04 wt %; Fe (III) 0.06 wt %; 3 – Fe(II) 3.67 wt %; Fe (III) 1.5 wt %

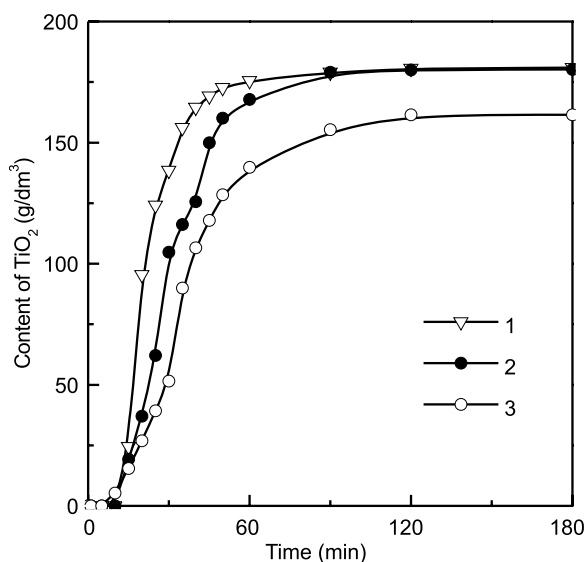


Figure 9. The influence of Fe(II) and Fe(III) contents in the hydrolyzed solution on the change of final product's (precipitated $\text{TiO}_2 \cdot n\text{H}_2\text{O}$) concentration in time, where: 1 – Fe(II) 3.67 wt %; Fe (III) 0.06 wt %; 2 – Fe(II) 2.04 wt %; Fe (III) 0.06 wt %; 3 – Fe(II) 3.67 wt %; Fe (III) 1.5 wt %

CONCLUSIONS

On the basis of the experiments it can be said that:

(1) Hydrothermal hydrolysis process depended on Fe^{2+} and Fe^{3+} concentration in the starting solution. The higher was iron(II) content, the higher degree of conversion was obtained – most of all at the initial stage of the process. The lower iron(III) content in the investigated part of the process was, the higher degree of conversion was obtained. This dependence is in agreement with the findings of other authors found in the literature on the subject^{6, 12},

(2) An increase of initial Fe(II) content in the solution led to an increase of reaction rate of both phases of titanyl sulfate hydrolysis. Conversely, an increase of Fe(III) content led to a reduction in the rate of intermediate and final products

formation. Iron at a lower oxidation degree was a catalyst of titanyl sulfate hydrolysis to hydrated titanium dioxide, whereas iron at a higher oxidation degree was an inhibitor of this conversion.

(3) Hydrolysis process did not depend on either magnesium or aluminium content in the starting solution,

(4) The mean size of primary hydrated titanium dioxide particles did not depend on admixtures content in the solution,

(5) The size of the aggregates created by hydrated titanium dioxide depended only on magnesium concentration in the starting solution, which was going to be hydrolyzed. The higher the content of this constituent was, the larger the clusters of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ particles were,

(6) The mean size of the crystallites of the hydrated titanium dioxide ranged between 8 and 16 nm. Their size did not depend either on the reaction time or on the amount of the introduced constituents into the solution in the investigated part of the process.

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