ISSN-L 2664-9969; E-ISSN 2706-5448

UDC 661:543.5
DOI: 10.15587/2706-5448.2025.335323

Viacheslav Kirnyi,
Mykola Yukhymenko

PHYSICAL AND CHEMICAL PROPERTIES OF IRON(II) SULFATE HEPTAHYDRATE AS FACTORS FOR SELECTING THE DRYING PROCESS MODE IN A FLUIDIZED BED APPARATUS

The object of the study is iron(II) sulfate heptahydrate – the main solid waste product of titanium dioxide sulfate production, the accumulation of which poses a significant environmental threat. The problematic stage of its processing is the technological stage of dehydration in a fluidized bed to a monohydrate form, for which it is important to select an acceptable hydrodynamic regime and drying regime.

Experimental studies included microscopic, sieve, pycnometric and titrimetric methods of analysis. The average equivalent particle diameter was found to be 0.50 mm, with a shape factor of 0.75. The bulk density of the material is 911 kg/m^3, and the true density is 1888 kg/m^3. The free moisture content was found to be 2.2%, and the crystallisation moisture content was 38.7%, which corresponds to the heptahydrate form of $FeSO_4 \cdot 7H_2O$. Chemical analysis showed that the mass fraction of $FeSO_4$ in the samples ranges from 48.8% to 51.7%, and the Fe^{2+} content is 18%. Free sulphuric acid is present in an amount of 0.3–1.3%.

Granulometric analysis revealed significant polydispersity of the material, in particular the presence of agglomerates and fine fractions in samples No. 1–3 of the closed storage composition of iron(II) sulfate heptahydrate. For sample No. 4, which was characterised by the most uniform particle distribution, the minimum fluidization velocity of the largest particle fraction (0.7 m/s) and the fluidization velocity (0.97 m/s) for the equivalent particle diameter of the material were calculated. It was found that particles with a diameter of less than 0.207 mm will be carried out of the boiling layer, which requires additional measures to reduce material losses. The heat transfer coefficient for particles of intermediate fractions (0.315–1.6 mm) is 77.79–349.17 W/(m^2 · K), which ensures efficient heat exchange during the drying process.

Based on the data obtained, the choice of a horizontal sectioned fluidized bed apparatus is justified. The proposed design provides for the division of the process into independent zones with individual control and regulation of the drying agent parameters (temperature and flow rate). This makes it possible to obtain a stable hydrodynamic regime for polydisperse materials and reduce the influence of mixing on the driving force of the process.

The results obtained allow predicting the behaviour of the material in the fluidized bed apparatus and calculating the fluidization and drying regimes.

Keywords: *iron(II) sulfate heptahydrate, particle size distribution, free and crystallization moisture, impurities.*

Received: 19.04.2025
Received in revised form: 18.06.2025
Accepted: 09.07.2025
Published: 29.08.2025

How to cite
Kirnyi, V., Yukhymenko, M. (2025). Physical and chemical properties of iron(II) sulfate heptahydrate as factors for selecting the drying process mode in a fluidized bed apparatus. Technology Audit and Production Reserves, 4 (3 (84)), 18–25. https://doi.org/10.15587/2706-5448.2025.335323

1. Introduction

The most popular white pigment in the world is titanium dioxide. It is mainly used because of its whiteness and inert properties. There is an annual, steady growth in the production of titanium dioxide [1, 2]. Its application areas are constantly expanding. The main consumers of titanium dioxide are such industries as paint, paper, and plastic [3]. The basic industrial methods of titanium dioxide production are chloride and sulfate [4]. The sulfate production method has a number of significant disadvantages: high energy consumption, a complex multistage scheme, and high sulfuric acid consumption. The sulfate method generates a large amount of waste: iron sulfates, diluted sulfuric acid contaminated with impurities. Given the long-term activity of global manufacturers of pigment titanium dioxide, a significant amount of solid waste has accumulated, which remains a source of environmental pollution. One of the main types of solid waste from the sulfate scheme for the production of pigment titanium dioxide is iron(II) sulfate heptahydrate (ferrous sulfate). Currently, about 1.5 million tons of ferrous sulfate waste have been accumulated in the Sumy region of Ukraine [5]. Currently, most companies operating using sulfate technology use the resulting solid waste as secondary raw materials for other industries. It should be noted that spent pickling solutions are another source of environmental pollution by ferrous sulfates [6].

Ways of utilizing ferrous sulfate are determined by the presence of a valuable component in its composition – iron. A common practice is to process ferrous heptahydrate into tetrahydrate, monohydrate or anhydrous forms. Ferrous sulfate is used in the production of: coagulants for wastewater treatment, colored pigments, nitrogen-phosphorus

sulfur-containing fertilizers. Recently, special attention has been paid to two areas of utilization of ferrous sulfate. The first is the production of animal feed additives, since iron in the divalent form is suitable for the production of hemoglobin in their early stages of development. The additive can be given in heptahydrate and monohydrate forms, but monohydrate is the best, since it is a dry product with a high iron content [7]. The second is the production of an active additive to cement for use as a reducing agent to reduce the content of water-soluble Cr(VI) [8].

The presence of a significant amount of water in ferrous sulfate crystal hydrate complicates its further use, so it must first be dehydrated. The introduction of effective and energy-saving technologies for processing ferrous sulfate into forms that have market demand is possible provided that the process of dehydration of ferrous sulfate is thoroughly studied, and optimal methods and designs of technological devices are found.

Many studies are associated with the dehydration processes of crystal hydrates, in particular of iron sulfate, which cover various drying methods and their optimization. One of the effective ways to implement an effective process of dehydration of iron sulfate is its drying in a suspended bed. Thus, studies [9] show that the use of suspended beds significantly increases the efficiency of the process due to intensive heat exchange, which reduces drying time and reduces energy costs. The process of drying crystal hydrates of iron sulfate in a fluidized bed depends on many parameters.

The final result of the process is significantly influenced by the dispersed composition and particle size of the material, the content of free and crystallization moisture, and other physicochemical properties that determine a certain place for detailed research. These parameters, among others, affect the hydrodynamics of fluidizing the material layer, the general hydrodynamic picture in the apparatus, the intensity of the evaporation process at the stages of constant and decreasing drying rates, and the uniformity of drying. The work [10] presents the results of the study of the physicochemical properties of iron sulfate obtained in clean laboratory conditions. The work [11] studies the physicochemical characteristics of the raw material and by-products of titanium dioxide production, including the analysis of the shape of the particles of heptahydrate and monohydrate of iron sulfate. The work [12] presents the results of the thermogravimetric analysis of iron sulfate particles smaller than 45 μm. The physicochemical characteristics of iron sulfate will depend on the technology of its production, especially on the stage of crystallization in the production of pigment titanium dioxide by the sulfate method. There is a lack of research that covers a comprehensive approach to studying these parameters in the context of data for convective drying in fluidized bed apparatuses.

The aim of research is to determine certain physicochemical properties of iron sulfate and their influence on the choice of drying mode in fluidized bed apparatuses.

2. Materials and Methods

2.1. Object and hypothesis of the research

The object of research is iron sulfate – the main solid waste of sulfate production of titanium dioxide, the accumulation of which poses a significant environmental threat.

The objectives of research are to determine the granulometric composition of iron sulfate, the shape factor of particles, the content of free and crystallization moisture, impurities, the influence of the granulometric composition on the hydrodynamic characteristics of the suspended layer and to justify the design of a dryer for dehydration of crystal hydrates. The hypothesis of research is that the dehydration of crystal hydrates of a polydisperse composition with a significant mass content of chemically bound crystallization moisture should be carried out in a sectioned fluidized bed apparatus. In each section of the apparatus, it is possible to organize an individual fluidizing mode and heat and mass transfer.

The assumption of research is the selection of individual indicators of the physicochemical properties of iron sulfate, which may have a more significant impact on the drying process. The simplification of the study is the selection of individual methods among a significant number of existing ones. Also, a certain simplification of the study is a certain selection of samples produced in Turkey and Ukraine, presented on the market.

2.2. Methodology for analyzing the dispersed characteristics of the material

A number of standard methods were used to analyze the dispersed characteristics of the material, in particular:

– *particle size and shape:* The structure of the material in terms of size and shape determines the dynamic characteristics of the fluidized bed, which are crucial for effective heat and mass transfer. The mass exchange surface of the particles determines the rate of water evaporation, and its reduction due to agglomeration or disruption of the layer structure leads to a decrease in the rate of dehydration. The study of granulometric characteristics allows to establish optimal gas flow supply modes and prevent local overheating of the material;

– *moisture content:* The content of free and crystallization moisture determines the further thermal behavior of the crystal hydrate. Crystallization water is a structural component of the crystal lattice of iron sulfate heptahydrate and is removed in stages through the formation of tetrahydrate and monohydrate forms. This determines the kinetics of its drying process;

– *bulk and true densities:* These parameters affect the hydrodynamics of the fluidized bed, and in addition, the true density changes significantly during structural reorganization during phase transitions, which will further determine the conditions for the deposition of particles in the fluidized bed;

– *the main components*: Sulfuric acid, Fe^{2+} ions and titanium dioxide impurities. A high content of free sulfuric acid can cause the formation of acidic solutions on the surface of the crystals, which can complicate drying. A high drying rate in an oxygen-containing environment promotes the oxidation of Fe^{2+}. Control and preservation of the content of Fe^{2+}, as a target component, is critically important.

Since the accuracy and reliability of the results are crucial for further improvement of the dehydration technology, all methods were selected taking into account their reliability and representativeness for the samples under study. All experiments were carried out taking into account the requirements of the standards governing the study of the physicochemical properties of materials. For this study, samples of a closed warehouse for the production of titanium dioxide by the sulfate method No. 1, 2, 3 and sample No. 4 (without TiO_2 content), presented on the Ukrainian market, were selected.

2.3. Microscopic analysis

The algorithm for microscopic examination of dispersed particles of iron sulfate included visual and analytical examination of samples using photofixation. The shape of the particles was determined using a POLAM-P312 microscope through analysis from several fields of view.

As regulatory documents for microscopic analysis of dispersed particles, the following were used: ISO 13322-1:2014 [13], which regulates the use of microscopic analysis to determine the size and shape of particles, ISO/DIS 9276-1 [14], which establishes standards for processing and presenting data on the dispersed composition.

The particle shape factor was determined based on measurements of the geometric dimensions of the particles as the ratio of the average cross-sectional area of the particles in three projections to the equivalent cross-sectional area of a sphere in accordance with the recommendations [15].

The use of standards ensured the accuracy and repeatability of the results. Given the ability of iron sulfate to dehydrate under the influence of light or heat, the most moderate lighting conditions were chosen to

ISSN-L 2664-9969; E-ISSN 2706-5448

minimize this effect during the analysis. The results of microscopic analysis were compared with the results of sieve analysis.

2.4. Sieve analysis

Studies to determine the granulometric composition of iron sulfate were carried out according to the standard sieve analysis method. A set of sieves with aperture sizes of 3; 2.5; 2; 1.6; 1.2; 1; 0.63; 0.315; 0.16 mm were used to analyze the dispersed composition. The study was conducted using the "wet granulometric analysis" method. This approach uses a liquid medium (in this case, 96% ethyl alcohol) to disperse particles and prevent their aggregation. This makes it more reliable for materials that are sensitive to moisture, tend to form agglomerates, or that may change size when dried during the standard procedure. The material remaining on each sieve was weighed and the content of each formed fraction in the original sample was calculated as a percentage by mass.

The equivalent diameter of the sample was determined by the formula

$$\frac{1}{d_e}=\sum_{i=1}^{k}\frac{x_i}{d_i}, \quad (1)$$

where k – number of fractions in the sieve layer, mm; x_i – weight fraction of the fraction; d_i – average diameter, mm, calculated as [16]:

– arithmetic mean

$$d_i=\frac{d_1+d_2}{2}; \quad (2)$$

– geometric mean

$$d_i=\sqrt{d_1\cdot d_2}; \quad (3)$$

– harmonic mean

$$d_i=\frac{2\cdot d_1\cdot d_2}{d_1+d_2}; \quad (4)$$

– Laschinger mean

$$d_i=\frac{d_1-d_2}{\ln(d_1)-\ln(d_2)}; \quad (5)$$

– Melor mean

$$d_i=\sqrt[3]{\frac{(d_1+d_2)\cdot(d_2^2+d_1^2)}{4}}; \quad (6)$$

– mean in the form

$$d_i=\frac{4}{5}\cdot\frac{d_2^5-d_1^5}{d_2^4-d_1^4}. \quad (7)$$

2.5. Determination of bulk and true density of dispersed material

To determine the bulk density of samples, the methods established by ISO 3923-1:2008 [17] and ISO 567:2021 [18] were used.

Bulk density is an important parameter that directly affects the hydrodynamics of the fluidized bed, as it determines the degree of particle compaction and their interaction during drying in the fluidized bed. The method consisted of using a toroidal cylinder and a pycnometer, with accurate measurement of the mass of samples in different states.

The method for determining the bulk density of iron sulfate involved the following steps. The first is sample preparation (drying iron sulfate in a drying oven at a temperature of 45°C to a constant mass to remove free moisture. The second is cooling the sample in a desiccator, filling the container (measuring cylinder) avoiding the formation of cavities and additional compaction of the material, weighing. The third is calculating the bulk density according to the formula

$$\rho_{bulk}=\frac{m}{V}, \quad (8)$$

where ρ_{bulk} – bulk density, g/cm^3; m – sample mass, g; V – cylinder volume, cm^3.

The true density was determined by the pycnometric method. It involves the use of a liquid. For iron sulfate, it is optimal to use a liquid that does not cause the dissolution of crystals (alcohol or special organic liquids). In this study, the liquid used was 96% ethyl alcohol, which well wets the particles of the studied material to displace air from the pores and cavities between the particles, and also prevents their aggregation or dissolution.

Method of determination true density of iron sulfate provided for the following stages. The first is sample preparation (drying iron sulfate in a drying oven at a temperature of 45°C to a constant mass to remove free moisture). The second is cooling the sample in a desiccator, measuring the mass of the dried sample in a pycnometer, measuring the mass of the dried sample in a pycnometer filled with 96% ethyl alcohol; control measurement of the liquid. The third is calculation of the true density according to the formula

$$\rho_{true}=\frac{m}{V_t}, \quad (9)$$

where ρ_{true} – true density, g/cm^3; m – sample mass, g; V_t – volume of the true phase of the sample, cm^3;

$$V_t=V_l-V_{emp}=\frac{(m_4-m_1)-(m_3-m_2)}{\rho_l}, \quad (10)$$

where m_1 – the mass of the empty pycnometer, g; m_2 – the mass of the pycnometer filled with the dried sample, g; m_3 – the mass of the pycnometer filled with the sample and liquid, g; m_4 – the mass of the pycnometer filled with liquid, g.

The temperature coefficient of expansion of the liquid was not taken into account when conducting these measurements, which at low temperatures can be considered acceptable for this type of analysis.

2.6. Determination of the mass fraction of moisture (free and crystallization)

The determination of the mass fraction of free and crystallization moisture was carried out in accordance with DSTU 2463-94 [19]. Free moisture was determined at a temperature of 45°C, and crystallization moisture at 135°C, which allowed separating hygroscopic moisture from that associated with the crystal lattice. Drying was carried out in a drying oven to a constant mass, weighing was performed after cooling the sample in a desiccator to avoid the influence of moisture from the air.

The mass fraction of both free and hygroscopic moisture was calculated by the formula

$$W=\frac{(m_1-m_2)\cdot 100}{m}, \quad (11)$$

where m_1 – the mass of the box with the sample before drying, g; m_2 – the mass of the box with the sample after drying, g; m is the mass of the iron sulfate sample.

The method is standard and allows to accurately estimate the moisture content of the samples, which is important for controlling the dehydration process.

2.7. Determination of the mass fraction of $FeSO_4$, Fe^{2+}, $H_2SO_{4(free)}$ and TiO_2

The purpose of this stage is to determine the mass fractions of $FeSO_4$, Fe^{2+} (ferric ions), free H_2SO_4, and TiO_2 (titanium dioxide impurity) using standard chemical methods. The methods for determining the mass fraction of $FeSO_4$and Fe^{2+} were selected from titrimetric procedures. A titration setup and standard titrant $KMnO_4$ were used for this. The titrimetric method allows for the accurate determination of the amount of Fe^{2+}, which is the main component of iron sulfate. This method is convenient because it does not require complex preliminary sample preparation and has high accuracy. This method also determines the values for $FeSO_4$, which is important for assessing the degree of dehydration and the composition of the final product.

The calculation of the mass fraction of $FeSO_4$ was carried out according to the formula

$$W_{FeSO_4} = \frac{(V - V_1)\cdot 0.01519\cdot 100}{m}, \quad (12)$$

where V – the volume of potassium permanganate solution used to titrate the analyzed solution, cm^3; V_1 – the volume of potassium permanganate solution used to titrate the control experiment, cm^3; m – the mass of the ferrous sulfate sample, g; 0.01519 – the mass of ferrous sulfate corresponding to 1 cm^3 of potassium permanganate solution with a molar concentration of exactly 0.1 mol/dm^3, g.

The principle of the method is to quantitatively determine Fe^{2+} and is carried out using the same titrimetric method (as for $FeSO_4$), since Fe^{2+} is the main component of $FeSO_4$.

The peculiarity of the method is that if the sample contains other forms of iron (for example, Fe^{3+}), they must be converted to Fe^{2+} by reduction.

2.8. Determination of free H_2SO_4

Based on the work of the authors [20], a method for determining the content of free sulfuric acid was adopted. The mass fraction of free sulfuric acid was determined using acid-base titration with NaOH as the titrant and a metallic orange indicator. The mass fraction of free H_2SO_4 was calculated using the formula

$$W_{H_2SO_4} = \frac{(V - V_1)\cdot 0.0049\cdot 250\cdot 100}{m\cdot 100}, \quad (13)$$

where V – the volume of sodium hydroxide solution used to titrate the analyzed solution, cm^3; V_1 – the volume of sodium hydroxide solution used to titrate the control experiment, cm^3; 0.0049 – the mass of sulfuric acid corresponding to 1 cm^3 of sodium hydroxide solution with a molar concentration of exactly 0.1 mol/dm^3, g; 250 – the initial volume of the analyzed solution, cm^3; m – the mass of the iron sulfate sample, g; 100 – the volume of the aliquot part of the analyzed solution taken for titration, cm^3.

This method is classic for such types of analysis and allows to obtain accurate data on the presence of free sulfuric acid in the sample, which is important for controlling the purity and composition of the product obtained after dehydration.

2.9. Determination of TiO_2 content

To determine titanium impurities in iron sulfate samples, a spectrophotometric method was used, which is extremely sensitive to the presence of titanium in the samples. This method allows for accurate measurement of TiO_2 even at low concentrations, which is important for assessing the influence of impurities on the physicochemical properties of the material. The method is based on the formation of a colored complex with hydrogen peroxide, which allows for the quantitative determination of titanium content.

2.10. Comparison of methods with analogues

The methods used meet modern standards for the analysis of powder materials and chemical compounds. Analogues of the methods used in other studies also include titrimetric and spectrophotometric methods for determining the content of $FeSO_4$ and Fe^{2+}, which confirms their effectiveness and accuracy in such studies. However, in this study, a wider set of methods was used to determine various components of the sample, which allows for comprehensive results on physicochemical properties.

One of the main problems of the presented research methodology is the stage of applying titrimetric procedures, namely: the accuracy of titrant dosing and determination of the titration endpoint, which requires high attention and experience. Another problem is the possibility of the presence of foreign impurities in the samples, such as Fe^{3+} or water-insoluble salts, which can affect the accuracy of the results. As a way to solve the problem, a stage of preliminary filtration of samples was introduced to minimize the influence of impurities to improve the accuracy of the results.

2.11. Correlation of the granulometric composition of dispersed particles with hydrodynamic and heat exchange parameters

To determine the minimum and operation fluidization velocities the universal Todes formulas were used [21]:

$$Re_{mf} = \frac{Ar}{1400 + 5.22\sqrt{Ar}}, \quad (14)$$

$$Re_f = \frac{Ar\cdot \varepsilon^{4.75}}{18 + 0.61\cdot \sqrt{Ar\cdot \varepsilon^{4.75}}}, \quad (15)$$

where Ar – the Archimedes criterion, ε – the porosity of the layer.

The formula [21] was used to determine the criterion

$$Ar = \frac{d^3(\rho_t - \rho_d)\cdot \rho_d \cdot g}{\mu^2}, \quad (16)$$

where d – the particle diameter, mm; ρ_t – the true particle density, kg/m^3; ρ_d – the density of the drying agent, kg/m^3; μ – the dynamic viscosity of the drying agent, Pa · s.

The optimal porosity of the layer was determined by the formula [21]

$$\varepsilon = 1 - 0.1923\cdot Ar^{0.06}. \quad (17)$$

From equations (14), (15), solved with respect to Reynolds numbers, it was found:

$$w_{mf} = \frac{Re_{mf}\cdot \mu}{d\cdot \rho_d}, \quad (18)$$

$$w_f = \frac{Re_f \cdot \mu}{d\cdot \rho_d}. \quad (19)$$

To determine the heat transfer coefficient, the equation used for $Re < 200$ [21] was used

$$\alpha = 1.6\cdot 10^{-2}\cdot \frac{\lambda}{d}\cdot \left(\frac{Re}{\varepsilon}\right)^{1.3} Pr^{0.33}, \quad (20)$$

where λ – the thermal conductivity of air at an average temperature, W/(m^2 · K); Pr – the Prandtl criterion.

3. Results and Discussion

3.1. Results

The results of the microscopic analysis are presented in Fig. 1.

Visualization of iron sulfate particles (Fig. 1) allowed to determine their shape. When taking samples No. 1–3 from storage sites, a fraction of settled material (agglomerates over 3 mm) was screened out.

ISSN-L 2664-9969; E-ISSN 2706-5448

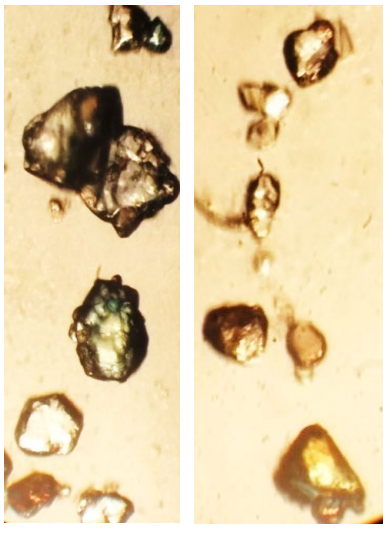

Fig. 1. Iron sulfate particles

The results of the granulometric analysis of samples No. 1–3 are shown in Fig. 2 in the form of differential curves of the granulometric composition, and sample No. 4 is shown in Fig. 3. For sample No. 4, an approximation line with an equation and a coefficient of determination is presented.

Granulometric analysis showed that samples No. 1–4 differ significantly in particle size distribution. Samples from the iron sulfate storage site, unlike sample No. 4, contain a significant amount of settled agglomerates and dust.

The values of the equivalent particle diameter of iron sulfate sample No. 4, calculated by formulas (1) and (2)–(7), are given in Table 1.

Table 1

Calculation of equivalent particle diameter

Equivalent particle diameter, d_e, mm					
by the formula (2)	by the formula (3)	by the formula (4)	by the formula (5)	by the formula (6)	by the formula (7)
0.50	0.53	0.51	0.54	0.54	0.60

For formulas (2), (6), (7) the size of the lower sieve is set to 0 mm, for formulas (3)–(5) the size of the lower sieve is set to 0.16 mm. The arithmetic mean value calculated by formulas (1)–(7) is 0.54.

For sample No. 4, the shape factor (0.75), bulk density (911 kg/m^3) and true density (1888 kg/m^3) were determined. The mass fraction of hygroscopic moisture was 2.2%, and the crystallization moisture was 38.7%. Free sulfuric acid in the samples was present in an amount of 0.3 to 1.3%.

Data on the mass fraction of $FeSO_4$ in the samples are presented in Table 2.

Table 2

Mass fraction of $FeSO_4$

Mass fraction of $FeSO_4$, %, not less			
Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4
49.9	51.7	50.9	48.8

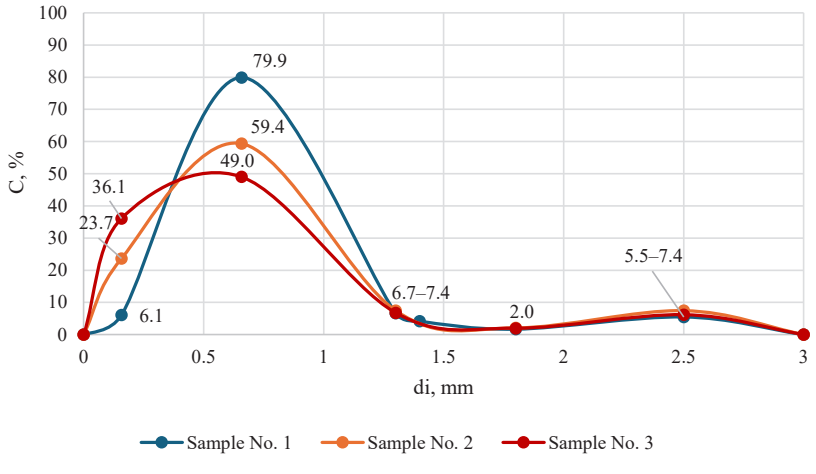

Fig. 2. Differential particle size distribution curves of samples No. 1–3

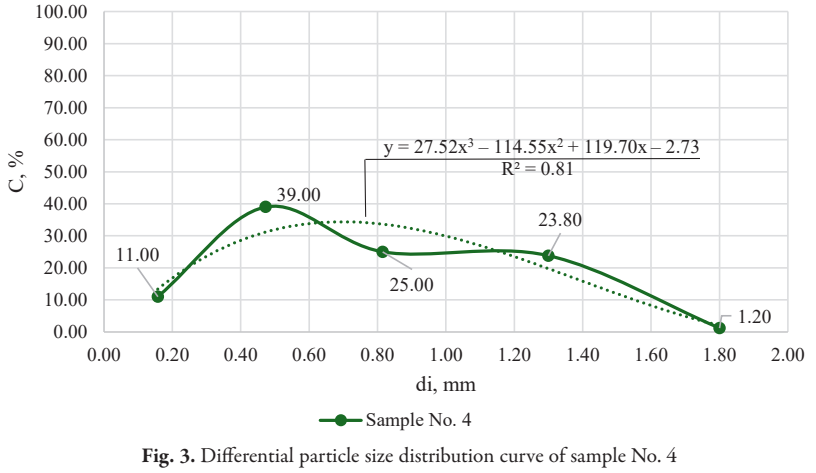

Fig. 3. Differential particle size distribution curve of sample No. 4

For sample No. 4, the calculation of hydrodynamic criteria and parameters, as well as the heat transfer coefficient, was carried out according to formulas (14)–(20) at a drying agent temperature of 110°C. The equivalent diameter was determined as the harmonic mean according to formula (1), the representative mean for the fraction according to formula (2). The results of the calculation of the minimum fluidization velocity and the velocity of floating, as well as the heat transfer coefficient for particles of intermediate fractions are presented in Table 3.

According to formula (15), the diameter of the particles d_r that will be removed from the fluidized bed was calculated. At $\varepsilon = 1$, the drying agent velocity is 0.97 m/s, determined for a diameter equivalent to 0.50 mm for a true density of 1888 kg/m^3 of iron sulfate in the heptahydrate form, $d_r = 0.207$ mm.

The results of the study confirmed that the physicochemical properties of iron sulfate heptahydrate vary depending on the particle size, dispersion composition and the presence of impurities. The most uniform composition was obtained for samples with an average particle size of 0.315–1.6 mm. The results obtained indicate a high potential of sample No. 4 of iron sulfate for further use in the study of drying processes in a fluidized bed. In sample No. 4, large particles larger than 1 mm are 25% (Table 3), so this must be taken into account during the drying process. Since the minimum fluidization and operating fluidization velocities of large and small particles are significantly different, it is advisable to represent fluidized bed dryers as a horizontally sectioned apparatus (Fig. 4).

Table 3

Results of calculations of hydrodynamic parameters and heat transfer coefficient

Sieve mesh sizes, mm	Partial residues, %	d_i, mm	$Ar \cdot 10^{-4}$	Re_{mf}	ε_{opt}	Re_w	w_{mf}, m/s	w_f, m/s	α, W/(m^2 · K)
1.6	1.2	1.8	19.757	53.11	0.60	177.30	0.70	2.35	505.50
1	23.8	1.3	7.443	26.35	0.62	109.09	0.48	2.00	349.17
0.63	25	0.815	1.834	8.70	0.65	50.55	0.26	1.48	187.94
0.315	39	0.473	0.358	2.09	0.69	18.15	0.11	0.92	77.79
< 0.315	11	0.158	0.013	0.09	0.74	1.51	0.01	0.23	7.67
Equivalent diameter, mm		0.50	0.423	2.43	0.68	20.29	0.12	0.97	85.85

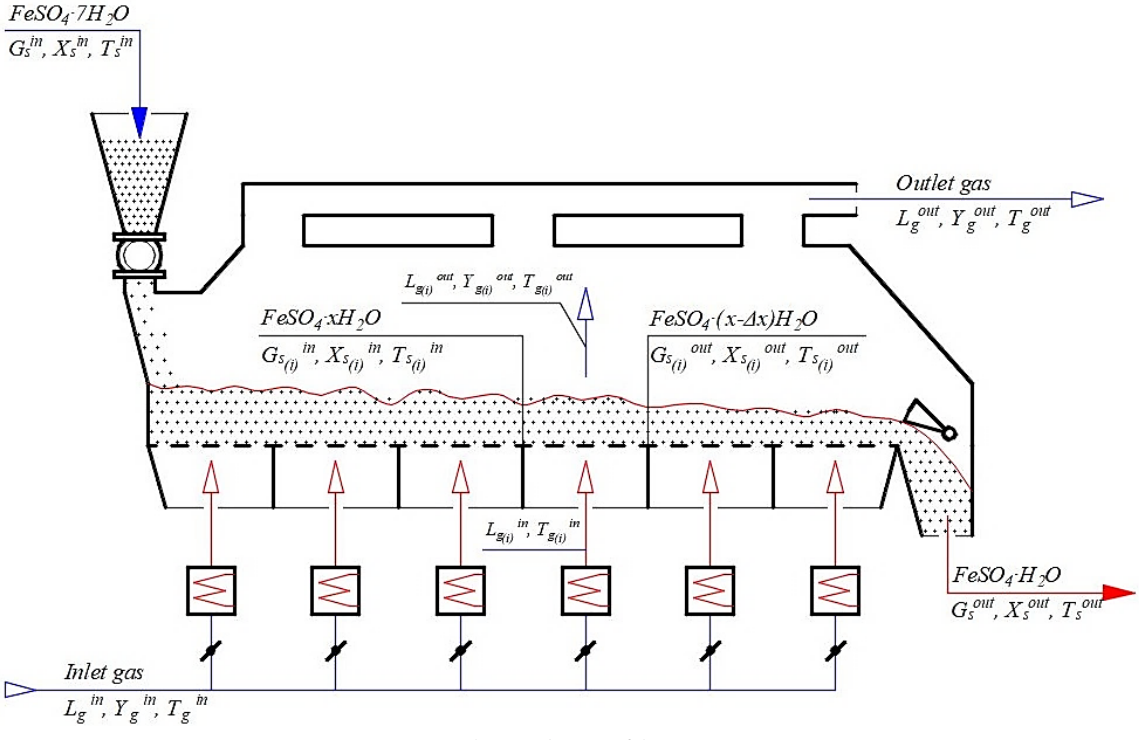

Fig. 4. Schematic diagram of the apparatus

A horizontal sectioned fluidized bed apparatus is the optimal solution for this process, as it allows for flexible control of drying parameters and prevention of undesirable phenomena. The scheme of the proposed apparatus is presented in Fig. 4.

Fig. 4 shows the flows of:

a) drying agent at the inlet (in) and outlet (out) of the apparatus and the *i*-th section: L_g, Y_g, T_g – flow rate, moisture content, temperature;

b) material at the inlet (in) and outlet (out) of the apparatus and the *i*-th section: G_s, X_s, T_s – flow rate, humidity and temperature.

3.2. Discussion

The study of the physicochemical properties of iron sulfate made it possible to obtain objective characteristics of the material, important for determining the task of organizing an effective dehydration process to the monohydrate form. The main attention was focused on the granulometric composition (Fig. 1, 2), bulk and true density, moisture content and chemical composition.

The study of the granulometric composition showed that the particle size distribution varies significantly between samples. For example, for samples No. 1–3, the main fractions were divided into relatively large (over 1 mm) and dust (up to 0.315 mm) (Fig. 1). Fluidized bed drying of samples with an uneven particle distribution will be less effective, a high proportion of fine particles should demonstrate a tendency to remove material from the fluidized bed.

The bulk and true density determined by formulas (9), (10) correlate well with the results of studies [22].

According to the measurement results, the mass fraction of hygroscopic (free) moisture was 2.2%, and the crystallization moisture was 38.7%. The latter value corresponds to the characteristic of iron sulfate common in the reference literature. Small differences in moisture content between samples may be due to storage conditions, but the high moisture content of crystalline moisture demonstrates the absence of mixtures with tetra- and monohydrate compounds in the samples.

Chemical analysis showed a stable content of $FeSO_4$ (~ 49–52%) (Table 2) in all samples. This confirms compliance with the II grade according to DSTU 2463-94 [19]. The mass fraction of Fe^{2+} (18%) indicates the absence of oxidation of iron to trivalent, which is a crucial factor for the further use of sulfate, for example, in the production of feed additives and cement additives.

The absence of TiO_2 in sample No. 4 confirms that the material is most likely a product of galvanic metal etching processes.

The values of the equivalent diameter of iron sulfate particles of sample No. 4, calculated by formulas (1) and (2)–(7), presented in Table 1, are highly similar. The minimum fluidization velocity calculated by formula (18) for the largest fraction of sample No. 4 is 0.7 m/s (Table 3), which is less than the drying agent velocity of 0.97 m/s, determined for the equivalent diameter of the material. This will prevent the deposition of large particles on the gas distribution grid of the fluidized

ISSN-L 2664-9969; E-ISSN 2706-5448

bed apparatus. The heat transfer coefficient for particles of intermediate fractions (0.315–1.6 mm) is 77.79–349.17 W/(m² · K), which ensures effective heat exchange during the drying process.

Research limitations. The results obtained revealed a significant difference in the structure of the samples in places of their long-term storage and a fresh sample. This can be crucial when designing industrial equipment for processing iron sulfate due to the uneven fluidization in the apparatus, the difference in dehydration time and the risk of channeling of the drying agent. Since iron sulfate particles have a crystalline structure, the results obtained can be extended to materials which particles have a similar nature.

On the one hand, the use of a fluidized bed has advantages: a developed contact surface of the gas and solid phases, the possibility of organizing a continuous process, high efficiency and productivity, which is due to the high intensity of convective drying in the fluidized bed. On the other hand, the fluidized bed has a number of disadvantages that limit the scope of its application: insufficient hydrodynamic stability, low permissible polydispersity index of the materials being dried, a complex hydrodynamic model. To solve the above challenges for effective dehydration of iron sulfate, it is proposed to carry out the process in a sectioned fluidized bed apparatus. This can be vertical [23] or horizontal sectioning [24]. The way to improve the model should be a model of a horizontally sectioned apparatus. In the model, the apparatus is divided into n sections, in each of which, as a result of intensive mixing of particles, both the temperature and humidity of the material are equalized. This brings the section closer to the apparatus with complete mixing of the material and complete displacement of the drying gas. Sectioning leads to a reduction in the undesirable effects of the effect of longitudinal mixing and more uniform processing of the dispersed product at the outlet of the apparatus. Therefore, the directed movement of the layer according to the model of ideal displacement of the material between the sections reduces the influence of the mixing effect on the magnitude of the driving force [25].

Practical significance. The obtained data on the physicochemical properties of iron sulfate are part of the scientific study of the drying process in a fluidized bed. In particular, taking into account the polydispersity of the material, the particle shape coefficient, density, and the content of free and crystallization moisture will allow building a drying model in a horizontal sectioned fluidized bed apparatus. Analysis of the disperse composition factor allows excluding the negative phenomena of significant particle entrainment from the apparatus with the drying agent and bed lodging. The parameters of the polydisperse granular mass of iron sulfate determined as a result of the research are an important aspect for making decisions regarding its dehydration. Prospects for further research. Solving the problem of heat transfer in a fluidized bed is complicated by the need to take into account boundary conditions. They must take into account the forces of interaction of particles moving with the flow of the medium. The description of such conditions and obtaining criterion dependencies for fluidization, heat and mass transfer between the dispersed phase and the gas flow is possible only through physical experimental studies. Therefore, the priority direction is determined to study the influence of the dispersed composition on the hydromechanical processes of fluidization particles by a drying agent, as well as the kinetics of dehydration with the analysis of the influence of temperature gradients on the rate of removal of crystallization moisture. The obtained experimental data will become the basis for the development of a CFD model of the fluidized bed, which will allow predicting the behavior of the system.

4. Conclusions

A set of physicochemical parameters of iron sulfate crucial for fluidized bed drying was determined: average equivalent particle diameter 0.5 mm, shape factor 0.75, bulk density 911 kg/m^3, true density 1888 kg/m^3, hygroscopic moisture content 2.2% and crystallization moisture content 38.7%. Chemical factors of the material were established: $FeSO_4$ content 48.8–51.7%, Fe^{2+} content at 18%, free H_2SO_4 content 0.3–1.3%. With a uniform granulometric composition, absence of agglomerates and stable chemical composition, the possibility of sample No. 4 for industrial processing without additional preparation stages was confirmed.

The influence of the dispersed composition of the material on the hydrodynamics of the process was determined. For particle diameters less than 0.207 mm, the drying agent velocity determined for an equivalent diameter of 0.5 mm leads to their entrainment and material losses. The minimum fluidization velocity of 0.7 m/s of the largest fraction is less than the hovering velocity of 0.97 m/s, which will ensure their movement along the gas distribution grid of the fluidized bed apparatus.

The choice of a horizontally sectioned material is justified. In each section, as a result of intensive mixing of the particles, the temperature and humidity of the material are equalized. Sectioning leads to a reduction in the undesirable consequences of the effect of longitudinal mixing and more uniform processing of the dispersed product at the outlet of the apparatus. The proposed design provides control and regulation of the velocity and temperature of the drying agent in individual sections, reducing the risk of particle entrainment, and the directional movement of the layer according to the model of ideal material displacement between sections reduces the influence of the mixing effect on the magnitude of the driving force.

Acknowledgments

This research work has been carried out within the project "Fulfillment of tasks of the perspective plan of development of a scientific direction "Technical sciences" Sumy State University" (State Reg. No. 0121U112684) funded by the Ministry of Education and Science of Ukraine.

Conflict of interest

The authors declare that they have no conflict of interest regarding this research, including financial, personal, authorship or other, which could affect the research and its results presented in this article.

Financing

The research was conducted without financial support.

Data availability

The manuscript has no linked data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

References

1. *Titanium dioxide market size – industry report on share, growth trends & forecasts analysis (2025–2030).* Mordor Intelligence. Available at: https://www.mordorintelligence.com/industry-reports/titanium-dioxide-market
2. *Titanium Dioxide Market size to increase by USD 6899.93 million between 2022 to 2027, market Segmentation by Application and Geography – Technavio* (2024). PR Newswire. Available at: https://www.prnewswire.com/news-releases/titanium-dioxide-market-size-to-increase-by-usd-6899-93-million-between-2022-to-2027--market-segmentation-by-application-and-geography--technavio-302089174.html
3. Das, R., Ambardekar, V., Pratim Bandyopadhyay, P.; Ali, H. M. (Ed.) (2022). Titanium Dioxide and Its Applications in Mechanical, Electrical, Optical, and Biomedical Fields. *Titanium Dioxide – Advances and Applications.* IntechOpen. https://doi.org/10.5772/intechopen.98805

4. Khaustov, V. (2023). Prospects for the development of titanium dioxide production in Ukraine. *Scientific Bulletin of International Association of Scientists. Series: Economy, Management, Security, Technologies, 2 (4)*. https://doi.org/10.56197/2786-5827/2023-2-4-2
5. Barsukova, H. V., Savchenko-Pererva, M. Y. (2021). Development of technology for obtaining a mixed coagulant from the main waste of titanium production. *Journal of Chemistry and Technologies, 28 (3)*, 289–297. https://doi.org/10.15421/082031
6. Gao, Y., Yue, T., Sun, W., He, D., Lu, C., Fu, X. (2021). Acid recovering and iron recycling from pickling waste acid by extraction and spray pyrolysis techniques. *Journal of Cleaner Production, 312*, 127747. https://doi.org/10.1016/j.jclepro.2021.127747
7. Gázquez, M. J., Contreras, M., Pérez-Moreno, S. M., Guerrero, J. L., Casas-Ruiz, M., Bolívar, J. P. (2021). A Review of the Commercial Uses of Sulphate Minerals from the Titanium Dioxide Pigment Industry: The Case of Huelva (Spain). *Minerals, 11 (6)*, 575. https://doi.org/10.3390/min11060575
8. Mončeková, M., Novotný, R., Koplík, J., Kalina, L., Bílek, V., Šoukal, F. (2016). Hexavalent Chromium Reduction by Ferrous Sulphate Heptahydrate Addition into the Portland Clinker. *Procedia Engineering, 151*, 73–79. https://doi.org/10.1016/j.proeng.2016.07.382
9. Green, D. W., Southard, M. Z. (Eds.) (2019). *Perry's chemical engineers' handbook*. McGraw-Hill Education. Available at: https://www.accessengineeringlibrary.com/content/book/9780071834087
10. Shaikh, L., Pandit, A., Ranade, V. (2013). Crystallisation of ferrous sulphate heptahydrate: Experiments and modelling. *The Canadian Journal of Chemical Engineering, 91 (1)*, 47–53. https://doi.org/10.1002/cjce.20695
11. Gázquez, M. J., Bolívar, J. P., García-Tenorio, R., Vaca, F. (2009). Physicochemical characterization of raw materials and co-products from the titanium dioxide industry. *Journal of Hazardous Materials, 166 (2-3)*, 1429–1440. https://doi.org/10.1016/j.jhazmat.2008.12.067
12. Wang, T., Debelak, K. A., Roth, J. A. (2007). Dehydration of iron (II) sulfate heptahydrate. *Thermochimica Acta, 462 (1-2)*, 89–93. https://doi.org/10.1016/j.tca.2007.07.001
13. *ISO 13322-1:2014 Particle size analysis – Image analysis methods – Part 1: Static image analysis methods* (2014). International Organization for Standardization. Available at: https://cdn.standards.iteh.ai/samples/51257/e5956ce29c644e71ad37738bd690a3cf/ISO-13322-1-2014.pdf.
14. *ISO 9276-1:1998 Representation of results of particle size analysis – Part 1: Graphical representation* (1998). International Organization for Standardization. Available at: https://cdn.standards.iteh.ai/samples/25860/7bdb509b70814f5ba4526488f14b7ba5/ISO-9276-1-1998.pdf
15. Ulusoy, U. (2023). A Review of Particle Shape Effects on Material Properties for Various Engineering Applications: From Macro to Nanoscale. *Minerals, 13 (1)*, 91. https://doi.org/10.3390/min13010091
16. Atamaniuk, V. M., Humnytskyi, Ya. M. (2013). *Naukovi osnovy filtratsiinoho sushinnia dyspersnykh materialiv*. Lviv: Vydavnytstvo Lvivskoi politekhniky, 276.
17. *ISO 3923-1:2018 Metallic powders – Determination of apparent density – Part 1: Funnel method* (2018). International Organization for Standardization. Available at: https://cdn.standards.iteh.ai/samples/69219/73e768c2dd64481eb5d96ff1c0e0a6a2/ISO-3923-1-2018.pdf
18. *ISO 567:2021 Coke – Determination of bulk density in a small container* (2021). International Organization for Standardization. Available at: https://cdn.standards.iteh.ai/samples/78697/97576b6a78994ee0b1deca87b9a59dea/ISO-567-2021.pdf
19. *DSTU 2463-94 Kuporos zaliznyi tekhnichnyi. Tekhnichni umovy (HOST 6981-94)* (1994). Derzhavnyi Standart Ukrainy. Available at: https://online.budstandart.com/ua/catalog/doc-page.html?id_doc=52579
20. Srinivasan, T. G., Vasudeva Rao, P. R. (2014). Free acidity measurement – A review. *Talanta, 118*, 162–171. https://doi.org/10.1016/j.talanta.2013.10.017
21. Davidson, J. F., Clift, R., Harrison, D. (Eds.) (1985). *Fluidization*. Academic Press, 733.
22. Tsiura, N., Kindzera, D., Huzova, I., Atamanyuk, V. (2021). Study of the kinetics of drying iron (II) sulfate heptahydrate by filtration method. *ScienceRise, 1*, 11–21. https://doi.org/10.21303/2313-8416.2021.001583
23. Yukhymenko, M., Artyukhov, A., Ostroha, R., Artyukhova, N., Krmela, J., Bocko, J. (2021). Multistage Shelf Devices with Fluidized Bed for Heat-Mass Transfer Processes: Experimental Studies and Practical Implementation. *Applied Sciences, 11 (3)*, 1159. https://doi.org/10.3390/app11031159
24. Bachmann, P., Bück, A., Tsotsas, E. (2017). Experimental investigation and correlation of the Bodenstein number in horizontal fluidized beds with internal baffles. *Powder Technology, 308*, 378–387. https://doi.org/10.1016/j.powtec.2016.11.025
25. Yukhymenko, M., Ostroha, R., Lytvynenko, A., Mikhajlovskiy, Y., Bocko, J. (2020). Cooling Process Intensification for Granular Mineral Fertilizers in a Multistage Fluidized Bed Device. In: Ivanov, V., Pavlenko, I., Liaposhchenko, O., Machado, J., Edl, M. (eds) *Advances in Design, Simulation and Manufacturing III.* DSMIE 2020. Lecture Notes in Mechanical Engineering. Springer, Cham. https://doi.org/10.1007/978-3-030-50491-5_24

✉***Viacheslav Kirnyi,*** *PhD Student, Department of Chemical Engineering, Sumy State University, Sumy, Ukraine, e-mail: v.kirnyi@pohnp.sumdu.edu.ua, ORCID: https://orcid.org/0009-0007-2168-3882*

Mykola Yukhymenko, *PhD, Associate Professor, Department of Chemical Engineering, Sumy State University, Sumy, Ukraine, ORCID: http://orcid.org/0000-0002-1405-1269*

✉*Corresponding author*