MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE NATIONAL TECHNICAL UNIVERSITY OF UKRAINE

«IGOR SIKORSKY KYIV POLYTECHNIC INSTITUTE»

I. M. Ivanenko, T. A. Dontsova, Yu. M. Fedenko

ADSORPTION, ADSORBENTS AND CATALYSTS BASED ON THEM

Approved by the Academic Council of National Technical University of Ukraine

«Igor Sikorsky Kyiv Polytechnic Institute»

as Manual for Master students of the specialty 161 «Chemical technologies and engineering»
specialization «Chemical technologies of inorganic substances and water purification»

Kyiv
Igor Sikorsky Kyiv Polytechnic Institute
2019

Reviewers: *Chygyrynets O.E.,* Dr. Sci., Prof.
Sabliy L.A., Dr. Sci., Prof.

Responsible editor *Kontsevoy A.L.,* PhD, Assoc. Prof.

The Grief is provided by the Academic Council of National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" (protocol № 11 from 09.12.2019)

Electronic educational edition

Ivanenko Iryna Mykolaivna, PhD, Assoc. Prof.
Dontsova Tetiana Anatoliivna, PhD, Assoc. Prof.
Fedenko Yurii Mykolayovich, PhD

ADSORPTION, ADSORBENTS AND CATALYSTS BASED ON THEM

Adsorption, Adsorbents and Catalysts Based on Them [Electronic resource]: Manual for Master students of the specialty 161 Chemical technologies and engineering specialization «Chemical technologies of inorganic substances and water purification» / Igor Sikorsky Kyiv Polytechnic Institute; redactors: I.M. Ivanenko, T.A. Dontsova, Yu.M. Fedenko. – Electronic text data (1 file: 3,43 Mbyte). – Kyiv : Igor Sikorsky Kyiv Polytechnic Institute, Faculty of Chemical Technology, 2019. – 256 p.

The material of this manual is set out in accordance with The Program of the discipline «Adsorption, Adsorbents and Catalysts Based on Them», covers and reveals most of the lecture material. It can have used by students at preparation to practical and laboratory classes, at performance individual and independent kinds of works, and also at preparation to control works and examination.

The tutorial contains three sections. The first section extended the technology of carbon sorbents. The second section contains the technologies of main mineral pigments, the classification and appointment of mineral pigments. The third section contains laboratory work, the purpose of which is the practical mastering of the material described in the two preceding sections.

CONTENT

INTRODUCTION

The discipline «Adsorption, Adsorbents and Catalysts Based on Them» taught in the first year of master's studies of the specialty 161 «Chemical technologies and engineering», attends to selective academic disciplines, i.e. disciplines of a free choice of students, and are profiling in the relevant curriculum.

The discipline «Adsorption, Adsorbents and Catalysts Based on Them» takes important role in formation outlook of modern specialist in specialization "Chemical technologies of inorganic substances and water purification" and is final in preparation of specialists of inorganic substances chemical technologies. Educational material of discipline «Adsorption, Adsorbents and Catalysts Based on Them» based on knowledge of normative disciplines «Applied chemistry», «Physics», «General and inorganic chemistry», «Physical chemistry», «General chemical technology», «Processes and apparatuses of chemical manufactures», «Chemical technology of inorganic substances».

The material of this manual is set out in accordance with The Program of the discipline «Adsorption, Adsorbents and Catalysts Based on Them», covers and reveals most of the lecture material. It can have used by students at preparation to practical and laboratory classes, at performance individual and independent kinds of works, and also at preparation to control works and examination.

The tutorial contains two sections. The first section extended the technology of carbon sorbents, including physical and chemical bases of adsorption, structural chemistry of activated carbon and main technologies of synthesis of carbon adsorbents. The second section contains the technologies of main mineral pigments, the classification and appointment of mineral pigments, branches of its applications, the main properties of pigments and review of raw base has been presented.

The material contributes to assimilation of material of such branches in chemical technology, as adsorbents and its producing, and also sorption processes

and its application in different branches: pigments and technologies of its obtaining (can have used for getting of metal oxides with other purpose).

CHAPTER 1 TECHNOLOGY OF CARBON SORBENTS

1.1 PHYSICOCHEMICAL BASES

1.1.1 Sorption of gases

Any technological adsorption process, no matter at what sequence it is carried – periodically or continuously, includes a row of mandatory stages, the first of all, these are adsorption and desorption. Only a comprehensive analysis of equilibrium and kinetic correlations of adsorption-desorption cycle and auxiliary stages (cooling, drying, etc.) reveals the best conditions for the whole process and recommend reasonable method of engineering calculation.

Most industrial adsorption processes are based on selective absorption of specific components of the gas-vapor mixture flow. During the absorption of gas or vapor, adsorption capacity depends on the type of sorbent, its porous structure, the nature of the substance absorbed is its partial pressure and temperature [1].

At equilibrium for the selected adsorbent-adsorbate system, amount of absorbed gas or vapor is a function of the gases/velour's partial pressure and temperature:

$$a = f(p, T). \quad (1.1)$$

Equation (1.1) is fair for all ranges of temperature, but for the characterization of adsorption processes in porous matrix, usually the dependence of adsorption capacity of the pressure at a constant temperature – the so-called «isotherm of adsorption» is used:

$$a = f(r) \text{ for } T = \text{const}. \quad (1.2)$$

In real process of the purification and separation of gases, influence of adsorption of bulk gas and other impurities, and kinetic factors may cause the need

to make adjustments in calculation of the adsorption capacity, which was initially determined by isotherms of pure components. However, in all real adsorption process, curve of thermodynamic equilibrium is the main comparative characteristics of different types of adsorbents and it determines the choice of optimal operating conditions of the process.

Simultaneously, the adsorption isotherm is a source of information about the structure of the adsorbent, adsorption heat and several other physic-chemical and technological characteristics.

C. Brunauer [1] highlighted five main types of adsorption isotherms, which are presented in Fig. 1.1. In the case of technical adsorbents, type I can be characterized as microporous adsorbents that contain virtually no transient pores. Initial bulging area of type II and IV isotherms indicate presence of macro pores with more or less substantial amount of micro pores in conjunction. Less steep initial ascent isotherm curves can be explained by mono- and multimolecular adsorption only for adsorbents with transitional porous type. Initial curved section isotherms types III and V, which are rarely found, are common for adsorbent-adsorbate systems, when interaction of molecules of adsorbate with an adsorbent much less than intermolecular interaction between adsorbate molecules, for example, caused by a presence of hydrogen bonds.

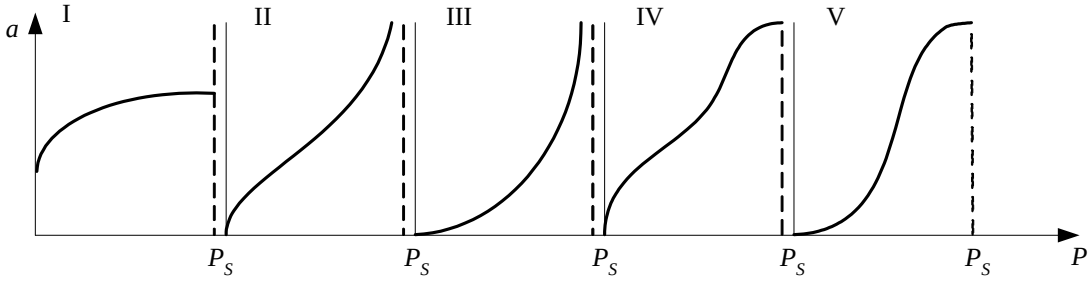


Fig. 1.1. **The main types (IV) of adsorption isotherms.**

The main difference between II to IV and III of V types is that the volume transition pore (IV and V types) in a result of capillary condensation are filled up with adsorbate earlier than relative pressure become equal 1.1. As a result, on the isotherms appears top, almost horizontal, section.

The basis of engineering calculation of almost any technological process of adsorption is the proceeding of adsorption isotherms, despite the fact, that most of them run dynamically (not statically).

Theory of monomolecular adsorption

The first fundamental equation of adsorption isotherm was Langmuir's equation. It is based on the assumption that the adsorption localized and occurs at active centers with the equal energy. They situated relatively rarely on the surface of the adsorbent. Consequently, the interaction between adsorbed molecules is absent. Each active center can adsorb only one molecule. According to this theory, with increasing of pressure, the part of solid surface, which is covered with molecules of adsorbate, increase. After reaching saturation pressure throughout the surface a monolayer of adsorbate is formed [2,3].

The ratio of filling of the surface is expressed as ratio of adsorption capacity at equilibrium pressure p to the adsorption capacity at monomolecular filling of surface a_m. The parameter a_m being called monolayer capacity. Accordingly, the equation of Langmuir's adsorption isotherm written as follows:

$$a = \frac{a_m bp}{(1+bp)}, \tag{1.3}$$

where b – a factor that takes into account the ratio of the speed of adsorption and desorption.

The equation of Langmuir covers a wide range of pressures. At the starting point of isotherm $bp<<1$, the equation takes the following form:

$$a \approx a_m bp. \quad (1.4)$$

On this site adsorption capacity increases linearly with increasing of equilibrium pressure (Henry ‘s equation). With high pressure *(bp*>>1) the surface starts to be covered by monolayer of molecules, and isotherm is parallel to the X axis:

$$a \approx a_m. \quad (1.5)$$

To simplify the use of equation (1.3), it can be transformed as follows:

$$\frac{p}{a} = \frac{1}{a_m b} + \frac{1}{a_m} p, \quad (1.6)$$

or

$$\frac{1}{a} = \frac{1}{a_m} + \frac{1}{a_m b}\frac{1}{p}. \quad (1.7)$$

The slope of the line and the segment formed by interception by the curve of the Y axis, gives information how calculate constants a_m and b. Using monolayer capacity *(*a_m, mole/g) the surface area of the adsorbent (S_{sp}, m^2/g) can be determined as:

$$S_{sp} = a_m N_A \omega_m \quad (1.8)$$

where N_A – Avogadro's number; ω_m – the area occupied by a molecule of adsorbate in a dense layer on the surface of the adsorbent.

The equation of Langmuir, and hence the method for determining the surface area can be applied to systems in which the process is not complicated by multimolecular adsorption, adsorption in micro pores and capillary condensation. To such systems can be attributed the case of adsorption of gases at temperatures above the critical on non-porous or adsorbents with large pores. Despite this limitation, the equation of Langmuir commonly used in technical adsorption.

Theory of multimolecular adsorption

A large number of adsorption systems described by isotherms type II. For these isotherms a sharp rise after reaching the relative pressure $(p/p_S)>0,2$ very common, which is associated with the formation of the second and subsequent layers of molecules that cover the molecules of the first layer.

Brunauer, Emett and Teller [4,5] in justifying theory multimolecular adsorption accepted that, despite the change in the total process model, the behavior of each adsorbed layer separately consistent with the concept Langmuir, adsorption localized and occur in the absence of interaction between the molecules of adsorbate. Each adsorbed layer generally obeys the Langmuir's equation. To create the equation of multimolecular adsorption, the authors started from the point that the rate of condensation of molecules on a clean surface is equal to the evaporation rate on the first layer. Similar assumptions made when comparing the rate of condensation in each of the previous and the evaporation rate in each subsequent layer.

Detailed analysis of equation multimolecular adsorption, called by the initial letters of the names of the authors (BET), is presented in a large number of articles and monographs. The final form of the equation is as follows:

$$a = \frac{a_m C \frac{p}{p_s}}{(1-\frac{p}{p_s})\left[1+(C-1)\frac{p}{p_s}\right]}. \qquad (1.9)$$

BET equation is fair in the range of relative pressures from 0,05 to 0,35. It is widely used to determine the specific surface of different porous bodies.

Determination of the specific surface area is usually carried out using an experimental isotherm of adsorption of standard vapor on the sample. The linear form of BET equation is used:

$$\frac{\frac{p}{p_s}}{a(1-\frac{p}{p_s})} = \frac{1}{a_m} + \frac{C-1}{a_m C}\frac{p}{p_s}. \quad (1.10)$$

Representing isotherm adsorption in the coordinates $\left(\frac{\frac{p}{p_s}}{a(1-\frac{p}{p_s})}, \frac{p}{p_s}\right)$, from the segment that is formed by the interception of the Y-axis, the value of a_m can be found and the angle of inclination of the line to the X-axis gives the value of *C* (Fig. 1.2). Specific surface area *(S_{spec})* is determined from the capacity monolayer, as described above. Constant C is directly linked to true molar heat of adsorption [19,20], which corresponds to a subtraction from heat absorption in the first layer Q_1 the molar heat of steam condensation adsorbate *λ:*

$$C = \frac{\exp(Q_1 - \lambda)}{RT}. \quad (1.11)$$

Last equation is used to calculate the value of the true heat of adsorption from experimental data. The value of the constant *C* determines the type isotherms. In the case of low value of the true heat of adsorption *(p* <2) isotherm has a concave shape (type III). If *C*>2, the isotherm gains S-shape (type II).

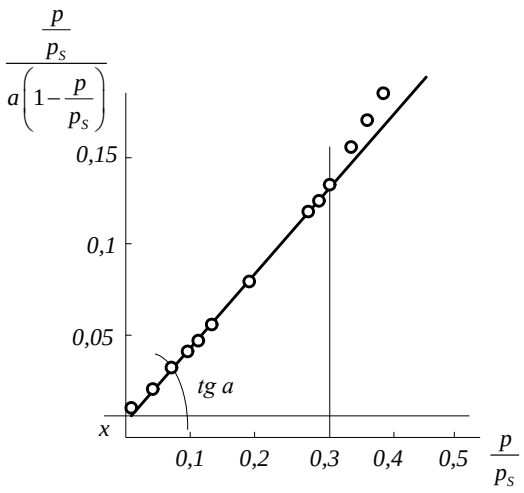


Fig. 1.2. **Graphic representation of the adsorption isotherm in BET coordinates.**

If isotherm of the investigated substance can be classified as type II (Fig. 1.1), the calculation of specific surface area can also be done using point B as the start point of inflection on the isotherm, which indicates the complete filling of monolayer when a steep climb of isotherm moves in gentle part. The value of a_m can be found by projection on the vertical axis the extension of gentle parts of the isotherm in coordinates $a - \frac{p}{p_s}$.

Calculations using two methods consistent in case of isotherms with a large slope which is typical for substances with a high heat of adsorption. Determination of B point in the case of flat isotherms (typical for substances with low heat absorption) can lead to significant errors in the evaluation of surface area.

Usually, for measurement of the specific surface area the nitrogen gas is used as adsorbate. Experiment carried out at a temperature of minus 196 °C. The size of covered area by nitrogen molecule on almost all solids is 0,162 nm^2, and packing density of molecules in the adsorbed layer equal to their packaging in a normal liquid [6,7].

The theory of volume filling of micropores

The principal difference between adsorption phenomena occurring in the micro pores or on the surface of transient pores in non-porous adsorbents requires different theoretical approaches to their description and interpretation. All theories of physical adsorption, despite their apparent physical differences, come from the same physical pattern. This physical pattern is concerned about the concept of geometric surface of phase interaction, at which the adsorption occurs with formation of one or more successive adsorption layers [8,9].

The idea of micro pores as a region of space in solids, which size is comparable with the size of adsorbed molecules, suggests that in any kind of

adsorption interactions (independently whether it is dispersion, electrostatic or other forces) that cause physical adsorption, in the whole space of micro pores the adsorption field appears. Limited adsorption space of micro pores leads to the fact that adsorbed in micro pores molecules do not form adsorption layers. Adsorption in micro pores is characterized volume filling of adsorption space. Therefore, the main geometric parameter that characterize microporous adsorbent is the volume of micro pores, not their «surface».

The concept of volume filling of micro pores results in pattern of threshold adsorption magnitude a_0 corresponding to the filling of the entire adsorption space micro pores by adsorbed molecules. Dependence a_0 from temperature is determined by the thermal coefficient of threshold absorption:

$$\alpha = -\frac{1}{a_0}\frac{da_0}{dT} = \frac{dlna_0}{dT}. \quad (1.12)$$

The coefficient is almost constant over a wide temperature range. If the threshold adsorption magnitude experimentally determined for a certain temperature T_0, then according to (1.12) thresholds adsorption a_0 for other temperature T expressed as follows:

$$a_0 = a_0^0 exp[-\alpha(T - T_0]. \quad (1.13)$$

To calculate a_0 in equation (1.13) it is necessary to know the thermal coefficient of threshold adsorption. K. Nikolaev and N. Dubinin [5,7] proposed a method for calculating the density of substance in the adsorbed state (adsorbate) for the temperature range from normal boiling temperature T_{bp} to critical T_{cr} using the physical constants of adsorbed material. This method can be used to calculate α:

$$\alpha = \frac{lg\frac{a_0^0}{a_0^*}}{0{,}434(T_{cr} - T_{bp})} = \frac{lg\frac{\rho_0^0}{\rho_0^*}}{0{,}434(T_{cr} - T_{bp})}. \quad (1.14)$$

Quite reliably calculated thresholds adsorption magnitude a_0, allows instead of adsorption magnitude a use dimensionless parameter, which expresses the degree of filling of micro pores [10,11]

$$\Theta = a/a_0. \quad (1.15)$$

The theory of volume filling of micro pores has thermodynamic origin, so to describe the adsorption equilibrium, the following thermodynamic functions like enthalpy, entropy and free energy are used. To calculate changes in these functions as a standard condition at a given temperature, we assume that the liquid phase which is in equilibrium with its saturated steam has a pressure P_S, or volatility of f_s.

The main thermodynamic function is the differential maximum performance of adsorption A, which is the free Gibbs energy of adsorption ΔG with the sign «minus»:

$$A = -\Delta G = RT \ln (p_s/p), \quad (1.16)$$

or

$$A = RT \ln (f_s/f), \quad (1.17)$$

where p – the equilibrium pressure or volatility f of the vapor at temperature T. Introduction volatility instead of pressure takes into account the imperfection of gas phase.

If adsorption is expressed in dimensionless units, then the differential work of adsorption advisable to express also in the form of dimensionless ratio, where E – the characteristic free energy of adsorption, the physical meaning of which will be mentioned below. Then the thermodynamic equation of adsorption can be represented in general form:

$$\theta = f\left(\frac{A}{E}, n\right). \quad (1.18)$$

Equation (1.18) is the distribution function of filling the micro pores on the differential work of adsorption, and E is one of the parameters of this function. Since most distribution functions in normalized form characterized by two parameters, the second of them, which is conventionally denoted by n, is in a permanent setting in the analytical expression for the function (1.18).

According to equation (1.18) we obtained equation for the so-called characteristic curve:

$$A = E\varphi\,(\theta\,,\, n). \qquad (1.19)$$

If for different vapor function φ and parameter n remain unchanged, then fair the equation:

$$\frac{A}{A_0} = \frac{E}{E_0} = \beta, \qquad (1.20)$$

i.e. characteristic curves in coordinates A-θ is affine. In other words, taken under the same values of θ *is* ratio of ordinates is constant and equal to coefficient of affinity β in the range of θ variation β in which assumptions about the immutability of function θ and sustainability of the parameter n are fair.

In the formula (1.20) A_0 and E_0 is a value for a standard pair. Good adherence of affinity conditions of characteristic curves was grounded in research of academician N. Dubinin on microporous carbon adsorbents. Also, it was shown that the development of microporous structure as a result of activation of coal within the errors of experiment do not affect the coefficient of affinity for various vapors, although the absolute values of the characteristic free energy change significantly [12,13].

Equation (1.19) shows that E=A for some filling θ_0 or characteristic point, which is defined in general case from:

$$\varphi(\theta_0, n) = 1, \qquad (1.21)$$

and at constant functions φ filling θ_0 will be the same for different vapors. The role of *n* will be discussed below. The above is the basis for experimental determination of characteristic free absorption energy by one point of adsorption isotherm, which corresponds to filling θ_0 and expressed by equation (1.21). Obviously, the absolute value of θ_0 depends on the type of function φ.

The distribution of the filling for differential molar work of adsorption is expressed as:

$$\theta = exp\left[-\left(\frac{A}{E}\right)^n\right]. \quad (1.22)$$

Analysis of many adsorption systems showed that equation (1.22) is consistent with the results of experiments with parameters *n*, which is represented by small integers.

If we put in the equation (1.22) the degree of filling through adsorption magnitude from (1.15) the following equation adsorption is obtained:

$$a = a_0 exp\left[-\left(\frac{A}{E}\right)^n\right]. \quad (1.23)$$

This equation can be represented in linear form:

$$lga = lga_0 - \frac{0.434}{E^n}A^n. \quad (1.24)$$

In the coordinate axes *(lg* a, A^n) the equation (1.24) is presented by a straight line, and intercept with the Y axis in point which is equal $lga_{0,}$ and the angular coefficient of the line is equal to $\frac{0,434}{E^n}$ (Fig. 1.3). If the exponent *n* is known, then the using graph showing linear equation (1.24), it can be easily defined threshold adsorption a_0 and the characteristic energy of absorption *E* based on one experimental adsorption isotherm. In this case, for each experimental point isotherm *(a, p)* the formula (1.16) can be used to calculate the corresponding value of the

differential molar work of adsorption in J/mol. With R = 8,32 J/mole·deg formula (1.16) takes the form:

$$A = 2{,}3 \cdot 8{,}32\ T \lg (p_s/p) = 19{,}14\ T \lg(p_s/p). \quad (1.25)$$

As already explained above, the exponent *n* in the equation of adsorption (1.23) is represented by a small integer. Almost all adsorption systems, which occurs in practice, the parameter *n* known, and its determination is not necessary. However, during the research this problem may occur. Therefore, it is useful to consider reasonable way to estimate the exponent *n* and determine the parameters a_0 and *E* of (1.24).

Usually the initial experimental adsorption isotherms determined for the temperature not to exceed the normal boiling point of adsorbate and includes a range of relative equilibrium pressures of up to decimal, in which almost completed filling of micro pores occur. Therefore, the previous value of the threshold adsorption can be obtained from the graph of isotherm by interpolation of adsorption values a_0 in the range of the high equilibrium relative pressures $\frac{p}{p_s} > 0{,}3$, where adsorption is almost constant or slightly increases with pressure. This vapor adsorption isotherm is changed for adsorption that occurs on the surface of transient pores.

Next the adsorption to the characteristic point is calculated:

$$a_x = 0{,}368\ a_0. \quad (1.26)$$

From the graph of original adsorption isotherm the equilibrium relative pressure $\frac{p_x}{p_s}$ is determined by for the characteristic points and the preliminary value of the characteristic energy of adsorption E is calculated:

$$E = 4{,}574 T lg \frac{p_x}{p_s}. \quad (1.27)$$

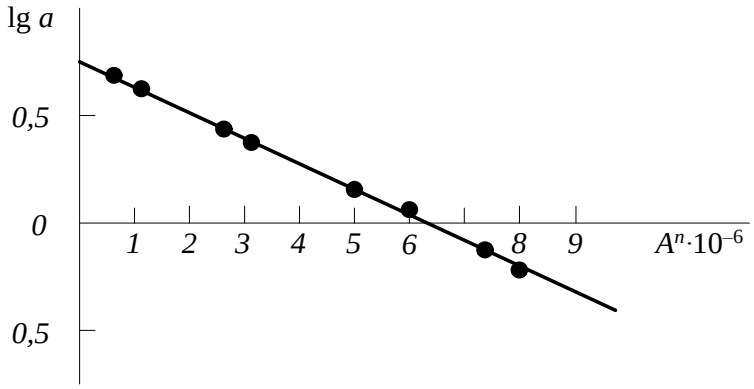


Fig. 1.3. **Adsorption isotherms in linear coordinates theories surround filling the micropores.**

Having approximate values a_0 and E the parameter n in equation (1.23) can be evaluated. After double logarithm of its left and right parts we get:

$$n = \frac{lg\left[2{,}3031 lg\frac{a_0}{a}\right]}{lg\frac{A}{E}}. \qquad (1.28)$$

Equation (1.28) allows for each point of the adsorption isotherm estimate the value of n. However, at values a close to a_0 the $lg\frac{a_0}{a}$ becomes close to zero, and determining n is unreliable. The same applies to the points isotherms that are close to the characteristic point when the $lg\frac{a_0}{a}$ in denominator approaches zero. For fillings significantly smaller than for the characteristic points θ_0, can be observed deviation from the conditions of invariance, making assessment n formula (1.28) is less reliable. Therefore, to determine n using this formula is possible even using only one point of isotherms for fillings, which are about 2 times higher than θ_0 and corresponds to the absorption of about 0,7-0,8 on a_0. The obtained value n is usually close to an integer, which is taken as a parameter n [14,15].

A specific feature of (1.24) is the deviation in the preliminary evaluation of parameter n for one to two decimals of an integer virtually has no effect on the

accuracy of a linear relationship. Relatively small changes in the parameters a_0 and E compensate such deviations. This allows for the specified determination of these parameters, representing all points of the experimental adsorption isotherms on the graph in the linear form of the equation (1.24) for evaluated integer values of the parameter n. Usually the experimental points fairly good fit to a straight line. Using the segment that is cut off on the Y-axis and the angular coefficient, the corrected value of threshold adsorption a_0^0 for the temperature $T=T_0$ (at which the initial adsorption isotherm was defined) can be calculated.

The obtained value a_0 and E for accepted integer values n are the parameters of equation (1.23) at constant temperature T_0, i.e. equation of initial adsorption isotherm. Among them, only a_0^0 depends on temperature. This dependence is expressed by equation (1.13). As mentioned above, under the conditions of temperature invariance, E and n are independent of temperature. It should be noted that because T_0 is designated normal boiling temperature of adsorbate, and a_0^0 is respective value of threshold adsorption only for calculating the thermal coefficient of thermal expansion of adsorbate α using the formula (1.14). It is easy to show that equation (1.13) a_0^0 and T_0 may represent values for $T_{bp}<T_0<T_{cr}$ at a value of α, which is defined by the formula (1.14) [16,17].

Equation (1.23) allows to calculate adsorption equilibrium of vapor at different temperatures. Suppose you want to calculate the adsorption of vapor a for a given equilibrium values of pressure p and temperature T. First, using the formula (1.25) we find the corresponding value of p and T differential molar work of adsorption:

$$A = 4{,}574\ T \ln (p_s/p), \qquad (1.29)$$

where the vapor pressure for the temperature T is taken from tables or calculated by known formulas. Threshold adsorption a_0 for the temperature T is

calculated from the equation (1.13) (see. Above). Substituting the calculated values a_0 in equation (1.23), written for ease of computation in logarithmic form

$$lga = lga_0 - 0{,}434\left(\frac{A}{E}\right)^n, \tag{1.30}$$

you can find specific adsorption a. In this way can be calculated adsorption isotherms for temperatures T that lie in the mentioned above temperature range, which is of practical interest. To increase the accuracy of calculations original experimental isotherm should be determined at temperature T_0, which is close to the average for the interval [18,19].

According to equation (1.23) and (1.13), thermal equation of adsorption can be written in the form:

$$a = a_0^0 exp\left[-\left\{\left(\frac{A}{E}\right)^n + \alpha(T - T_0)\right\}\right]. \tag{1.31}$$

In this case, the parameters of equation (1.31) is constant values of $a_0{}^0$, E and the known n. Differential molar work of adsorption A is calculated as before by formula (1.25) for given values of equilibrium pressure p and temperature T. Including the accepted values of deviation not more than 10% the magnitude of adsorption is calculated, because of (1.31) can be used in the range of fillings θ from 0,15-0,20 to 1,0. Equation (1.31) describes the adsorption only in micro pores. With significant development in microporous adsorbent volume and surface transient pores parameters $a_0{}^0$ and E get effective values if the initial experimental adsorption isotherms are not adjusted for adsorption in transient pores [19,20].

If equation (1.31) consider as thermal [19,20] equation of adsorption of standard vapor of parameters $a_0{}^0$, E_0 and n, then the equation of adsorption for another vapor following defined earlier assumptions, expressed as:

$$a = a_0^0 \frac{p^*}{p_0} exp\left[-\left\{\left(\frac{A}{\beta E_0}\right)^n + \alpha(T - T_0)\right\}\right], \tag{1.32}$$

where β affinity coefficient; $\frac{p^*}{p_0}$ – appropriate density of adsorbate; A – differential molar work adsorption and α – thermal factor limiting absorption for this pair.

The coefficient before the exponent in equation (1.32) expresses the limit adsorption at temperature T_0, which does not necessarily coincide with the same temperature for standard vapor. For some microporous adsorbents such as carbon, the coefficient of affinity can be calculated, but using the physical constants of adsorbate and standard substance. In this case, the transition from equation (1.31) to the total equation (1.32) is not accompanied by an increase in the number of constants that can be determined experimentally. They still remain two: a_0^0 and E_0, assuming exponent n known.

Defining parameters of transition pore

The main parameters of transient pores of activated carbon is the value of the volume of pores, specific surface and function of the distribution of equivalent radius. Volume of transient pores in conventional samples of activated carbon is within the range 0,02-0,10 cm^3/g. In this case, the specific surface of transient pores is in the range of 20 to 70 m^2/g. The effective range of transient pores for up distribution curves are usually stacked in the range of 4 to 20 nm. Pores of highly porous silica gel, alum gel and alum-silicate catalysts also belong to the transition type.

Volume of transient pores usually calculated from the equation:

$$V_п = W_S - V_{mic}, \quad (1.33)$$

where W_S – threshold volume of sorption space, which, in turn, is equal to:

$$W_S = a_S \cdot V_m, \quad (1.34)$$

where V_m – molar volume of adsorbed material (adsorbate); a_S – threshold absorption, which is corresponds to $\frac{p}{p_s} \approx 1$. (Defined by desiccator method in conditions of full saturation of adsorbent sample by adsorbate vapour at $\frac{p}{p_s} \approx 1$.)

For samples of activated carbon with significant volumes of transient pores formula (1.33) is not sufficiently satisfactory. A more precise calculation is necessary to introduce an amendment to the adsorbed amount of vapor on the surface of transient pores.

Then the corrected amount of transient pores V_p^* is:

$$V_p^* = W_s - (a_0 - a_{\text{п}})V_m, \tag{1.35}$$

where V_m – molar volume of adsorbate; a_0 – value of adsorption of adsorbate vapor, such as benzene or methanol at $\frac{p}{p_s} = 0{,}175$ and $\frac{p}{p_s} = 0{,}533$ respectively; a_n – value of adsorption of adsorbate vapor on the surface of transient pores prior to capillary condensation.

Calculating the value of specific surface adsorption film formed in transient pores prior to capillary condensation, is performed by A. Kiselyov equation [15].

The general thermodynamic equation of capillary condensation formulated be A.V. Kiselyov (assuming that condensed film that is formed in the primary adsorption process can be considered as liquid phase) is:

$$-\sigma' \cdot ds' = A_a \cdot da, \tag{1.36}$$

where σ' – the surface tension of adsorption film; s' – its surface; A_a – differential molar work adsorption pair; a – the amount of adsorbed substance.

Based on the study of the properties of adsorption layers is assumed that the film adsorbed substance at the start of capillary condensation has practically normal value of the surface tension of the liquid σ.

Then the equation for determining the specific surface film *s'*, which starts capillary condensation, will look like:

$$s' = \frac{1}{\sigma}\int_{a_0}^{a_s} A_a da \qquad (1.37)$$

,

where σ – surface tension of liquid, vapor of which is absorbed (for benzene σ=28,9 ergs/cm^2, for methanol σ=22,6 ergs/cm^2); a_0 – the amount of adsorbed substance at the beginning of capillary condensation; a_S – the amount of adsorbed substance at full saturation, i.e., $\frac{p}{p_s} = 1$; $A_a = RTln\frac{p_s}{p}$ – differential molar work of adsorption.

Graphically, this calculation can be represented as in Fig. 1.4.

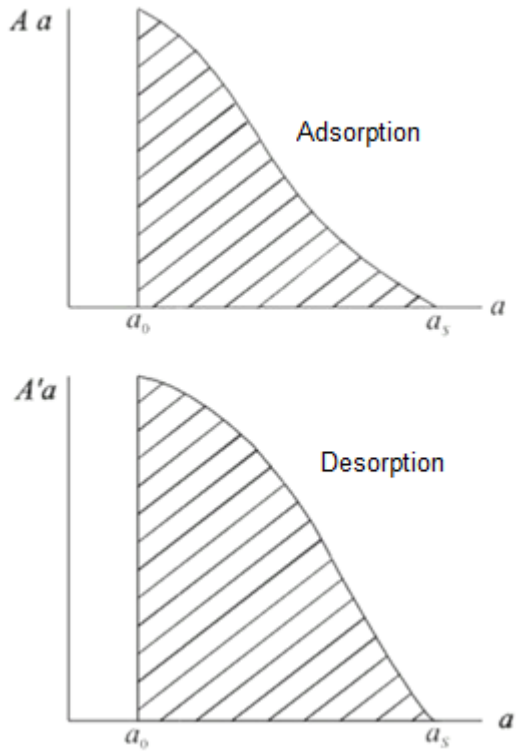


Fig. 1.4. **Graphic representation of dependence of differential molar of adsorption on the amount of adsorbed substance.**

After determination of the value of specific surface of transition pores *s'*, a value of the adsorption of adsorbate vapors in transient pores prior to capillary condensation is calculated a_n using formula:

$$a_{\text{n}} = \gamma\, s', \tag{1.38}$$

where γ – adsorption at the beginning of capillary condensation for surface unit non-porous carbon adsorbent, which has temperature of pretreatment that is close to the temperature of activated carbon. Adsorption isotherms of benzene at 20°C ($\gamma=f(h)$) for non-porous carbon adsorbent (e.g. soot) in a wide range of relative pressure ($\frac{p}{p_s} = 10^{-5\div 0,3}$)) is expressed by the empirical Freundlich equation:

$$lg\gamma = -\left(1{,}908 + 0{,}384 lg\,\frac{p}{p_s}\right). \tag{1.39}$$

After determination of a_n, you can find corrected volume $V_{\text{п}}^*$ from the equation (1.35) and V_{mic}^* as:

$$V_{mic}^* = \text{W}_\text{S} - \text{V}_\text{p}^*. \tag{1.40}$$

Calculation of the equivalent radius of transition pore and creation of integral and differential distribution curves of pore volume by equivalent radius (r_{n} , nm) are performed using the equation of Thomson-Kelvin:

$$r_{\text{п}}=\frac{2\sigma V_m 100}{2{,}3RTlg\frac{p_s}{p}}, \tag{1.41}$$

where σ – the surface tension of a liquid, a vapor of which is adsorbed; V_m – its molar volume.

Volume of transient pores V_p that corresponds to the radius obtained by the equation:

$$V_\text{p} = \alpha' \cdot V_m. \tag{1.42}$$

To calculate r_p and V_p it is necessary to have values of $\frac{p}{p_s}$ and a' which are taken from the desorption curve of adsorption isotherm hysteresis in capillary condensation ($\frac{p}{p_s} = 0{,}175 - 0{,}90$ for benzene*)*. Using obtained information the integrated structural curve *(V_n, r)* is built (Fig. 1.5), which describes the increase in the volume of pores $\Delta V_п$ with a corresponding increase of Δr. Then, if necessary, a differential curve of volume of transition pore distribution is built dependently from their equivalent radius $\left(\frac{\Delta V_п}{\Delta r}, \overline{r}\right)$ (Fig. 1.6).

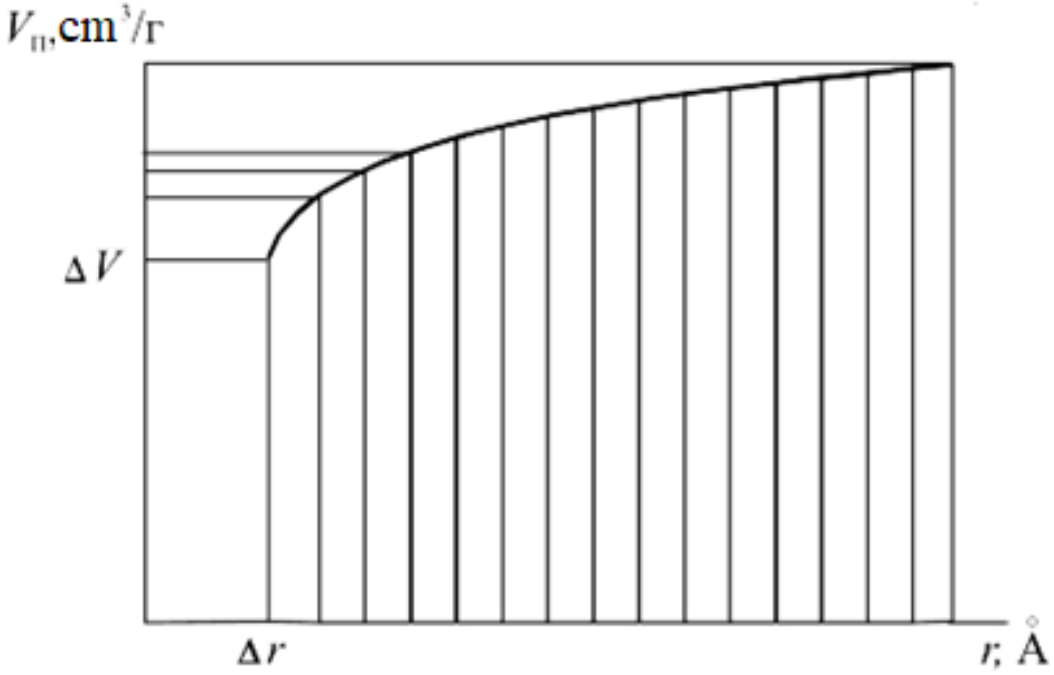


Fig. 1.5. **Graphic representation of integrated structural curve.**

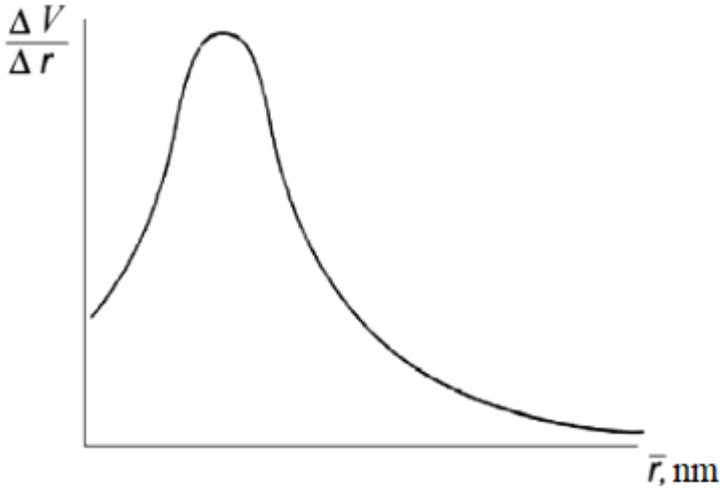


Fig. 1.6. **Graphic representation of the distribution curve number of transient pores in the equivalent radius.**

The maximum on the distribution curve indicates the radius of the pores that prevails in this adsorbent. This value r_{max} should be increased by the value of the thickness of the pre-adsorbed layer of molecules *t*.

The value of (*t*, nm) for the sorption of benzene vapor, which is accepted as the standard adsorbate on the carbon surface, can be estimated with satisfactory accuracy using different equations, such as equations adsorption (Harkins-Jura) [16]

$$t = \frac{0{,}4715}{\left(lg\frac{p_S}{p} - 0{,}035\right)^{1/2}} \quad . \tag{1.43}$$

Table 1.1. **Parameters of porous structure of activated carbon [2]**

Brand	**Volume of common pores types, cm³/g**			W_{01}, **cm³/g**	W_{02}, **cm³/g**	X_1, **nm**	X_2, **nm**
	V_{mic}	V_{mez}	V_{mac}				
SCT	0,40-0,48	0,18-0,19	0,26-0,28	0,40-0,48	—	0,54-0,57	—
SCT-1A	0,45-0,55	0,14-0,15	0,18-0,24	0,46-0,57	—	0,60-0,62	—
SCT-1B	0,42-0,50	0,15-0,17	0,18-0,22	0,43-0,59	—	0,61-0,64	—
SCT-2A	0,37-0,42	0,18-0,22	0,20-0,22	0,38-0,45	—	0,50-0,52	—
SCT-2B	0,35-0,40	0,17-0,20	0,12-0,18	0,37-0,42	—	0,54-0,55	—
SCT-3	0,37-0,46	0,06-0,09	0,25-0,32	0,37-0,46	—	0,47-0,55	—

Continuation of *Table 1.1*

SCT-3C	0,35-0,45	0,06-0,08	0,15-0,20	0,43-0,55	—	0,50-0,55	—
SCT-3U	0,37-0,42	0,24-0,28	0,21-0,24	0,39-0,43	—	0,70-0,75	—
SCT-4	0,40-0,42	0,15-0,20	0,12-0,20	0,42-0,46	—	0,59-0,60	—
SCT-6A	0,57-0,60	0,15-0,25	0,15-0,25	0,59-0,62	—	0,70-0,73	—
SCT-6B	0,55-0,61	0,17-0,28	0,15-0,30	0,57-0,60	—	0,66-0,69	—
SCT-7A	0,47-0,50	0,20-0,22	0,15-0,20	0,48-0,53	—	0,64-0,70	—
SCT-7B	0,48-0,52	0,21-0,23	0,16-0,17	0,49-0,55	—	0,66-0,72	—
SCT-7C	0,44-0,49	0,15-0,17	0,11-0,25	0,45-0,53	—	0,62-0,66	—
SCT-10	0,40-0,42	0,20-0,21	0,21-0,27	0,43-0,44	—	0,59-0,65	—
APT-1	0,43-0,45	0,15-0,20	0,12-0,30	0,44-0,47	—	0,60-0,67	—
APT-2	0,45-0,48	0,10-0,20	0,19-0,32	0,45-0,50	—	0,54-0,56	—
AG-PR	0,30-0,35	0,10-0,12	0,40-0,49	0,20-0,32	0,10-0,12	0,70-0,80	1,00-1,20
AG-OC	0,45-0,47	0,05-0,15	0,10-0,20	0,47-0,52	—	0,70-0,72	—

For nitrogen, which is more often used abroad as a standard vapor, most recommended a formula of J. de Boer:

$$t = \frac{0{,}4584}{\left(lg\frac{p_S}{p}\right)^{1/3}}, \tag{1.44}$$

then

$$r_p = r_{max} + t. \tag{1.45}$$

Parameters of porous structure of major industrial brands of carbon adsorbents for adsorption of gases and vapors are given in Table 1.1 and 1.2.

Table 1.2. **The specific geometric surface of micro pores**

Brand of carbon	***S*, m^2/g**
SCT	1200-1500
ACB	1000-1200
AG-OC	900-1000
PAU-1	2000-2500

There are the following main brands of activated carbon of this type: SCT, SCT-1, SCT-2, SCT-3, SCT-3C, SCT-3U, SCT-4, SCT-6, SCT-7, SCT-10, SCPTC,

APT, AG-PR, AG-OC, which are used for separation from air vapors of organic compounds and for the removal of gas emissions.

Activated carbon of this type is characterized by: high adsorption and holding capacity; sufficiently high mechanical strength; high activity (coal for recovery of organic solvents vapor, gasoline, ethanol, ethyl acetate, dichloroethane, etc.).

Depending on the design of the absorber (stationary, «boiling» or non-stationary layer) different requirements for fractional composition of coal are imposed.

Comparative evaluation of adsorption and strength of active carbon gas type (Table 1.3) shows almost complete identity of its adsorption characteristics by the bulk density, the volume of micro pores and the values of the time of protective action for substances that are badly and well absorbed. Domestic gas coal inferior to foreign models by strength.

***Table 1.3*. Parameters of industrial gas type activated carbon [5]**

Brand	Apparent density, kg/dm^3	Mechanical strength, %	The volume of micro-pores, cm^3/g	Duration of protective action, min	
				chloroethyl	benzene
AG-2	0,58	75	0,32	45	50
SCT-2	0,49	74	0,45	70	60
SCT-6	0,42	73	0,58	65	75
PK	0,52	-	0,30	57	55
PB	0,50	93	0,46	55	76
PC	0,56	93	0,26	52	45

1.1.2 Sorption from water solutions

Sorption of liquid solutions is more complicated than the gas-vapor mixture, so that involves the interaction of the sorbent with the substance that is absorbed and the solvent (water). It also should take into account the interaction of the solvent with adsorbate. Therefore, despite the fact that the sorption from aqueous

solutions is studied and used nearly 200 years, it has been studied much less adsorption than sorption of gas-vapor phase. In general, mechanism of adsorption from solutions in one form or another is explained by concepts, derived from the gas phase, supplementing by limiting conditions specific to the liquid phase. Differences in the approach to such a transition influence on the form and accuracy of models and calculations of sorption of water purification.

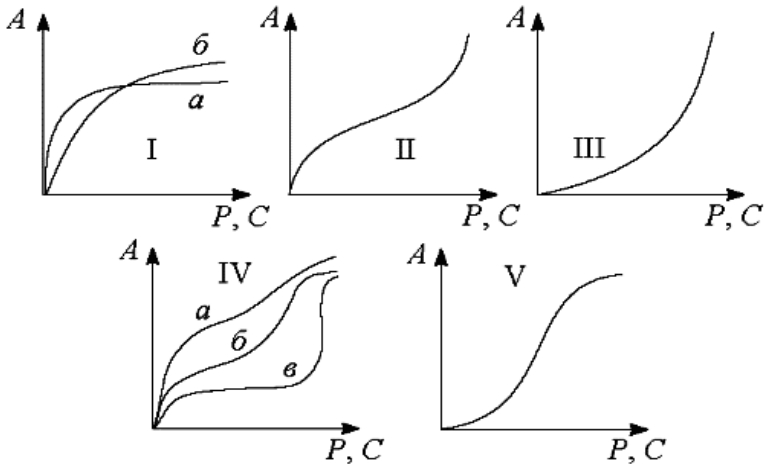


Fig. 1.7. **The classification of adsorption isotherms according to BET [19].**

Basics sorption properties of the material and the nature of sorption on it of certain substances can be obtained, as in the case of sorption process in gaseous phase, from sorption isotherms, describing the dependence of sorption capacity *A* Concentration *C* component that is absorbed and at a constant temperature: *A=f(C)* for the liquid phase. Brunauer, Emmet and Teller (BET) divided sorption isotherms into 5 main groups (Fig. 1.7). Convex plots of isotherms I, II and IV types indicate the presence of micro pores in sorbents, but also, sorbents II and IV are also macro pores. Isotherms III and V types are less common and described strong intermolecular interactions in solution. The steepness isotherms of type I characterizes the size micro pores adsorbents: a – ultra microporous, – a

microporous. Isotherm IVb correspond to transitional porous sorbent; IVc – uniformly macro porous and IVa – with a mixed structure.

The most common and complete classification of sorption isotherms of the liquid phase was given Smith (Fig. 1.8). Concave isotherm S-type is rare. Isotherms Langmuir (L-type) correspond to I and III types classification BET (Fig. 1.7).

Type H is typical for substances with high affinity (i.e., high ratio of molar volumes V_m/V_m^{cm}, where V_m and V_m^{cm} – molar volumes of investigated and standard materials), in which a large sorption capacity is achieved at very low concentrations. In case when the law of Henry is valid (type C), sorption capacity proportional to a final concentration of the solution. This is a common case in water purification, examples of which are given in Fig. 1.9. Type sorption isotherms often depends on the concentration of substances in solution. For example, sorption on soot of surfactant with a concentration of 0,1; 0,2 and 0,3 g-eq/dm^3 isotherms are shaped L2, L3 and H3 (Fig. 1.8), due to the volume association of ions in surfactant.

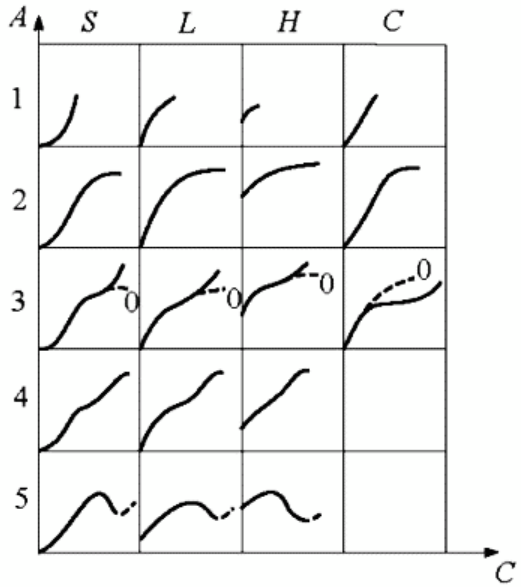
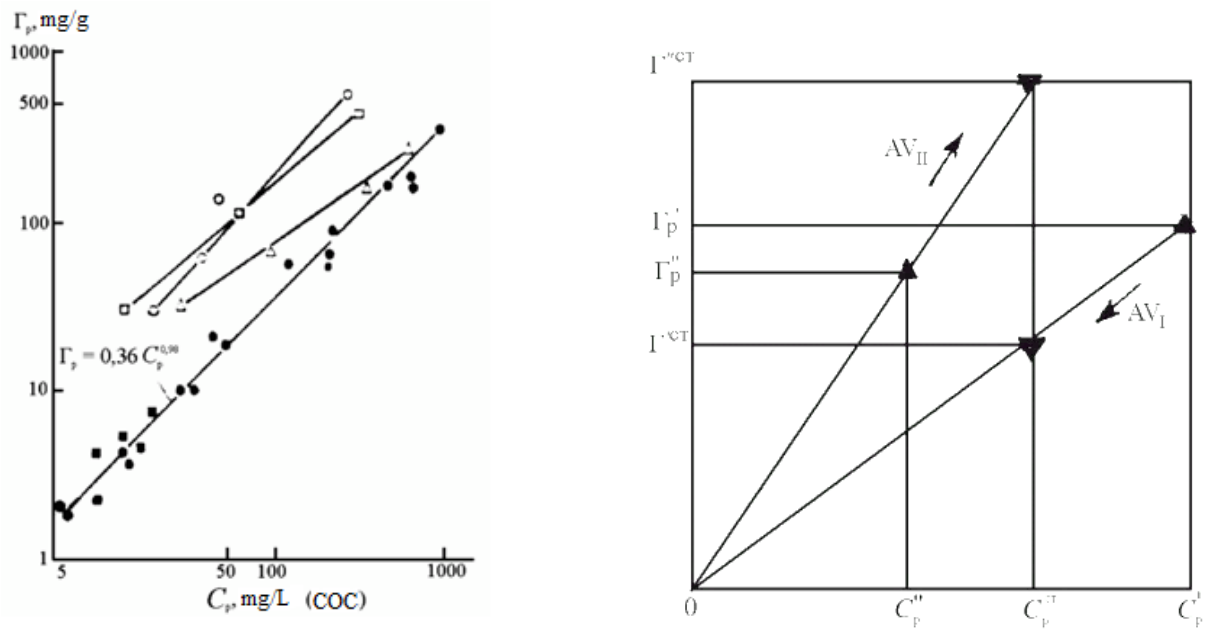


Fig. 1.8. **The classification of solutions adsorption isotherms according by Smith.**



a) b)

Fig. 1.9. **Sorption isotherms of biochemical treatment of industrial wastewater (a) and pattern for definition of sorption capacity by linear isotherms in standard conditions (B),** (Γ - excessive amount of substances absorbed in the adsorbed state): charcoal AG-3 - ● and ■; AB from lignin - ○, □ and Δ; wastewater production of synthetic rubber - ●; production of brake fluid - ■; hydrolysis plants - ○, □ and Δ; experimental points - ▲; estimated value $\Gamma_p^{ст}$ at $C_p^i = C_p^{ct}$ — ▼).

In practice, engineering studies and calculations often use a simple empirical Freundlich equation:

$$a = KC^n,$$

where K and n – constants.

Using Freundlich equation in range of average concentrations well coincides with the experimental data; isotherm is linear in coordinates (lg C, lg a). The coefficients K and n for Freundlich equation for certain substances listed in Table 1.4.

The equation of Langmuir sorption isotherms derived from molecular-kinetic theory and ideas about the monomolecular nature of the sorption. For solutions, it is:

$$a = \frac{a_m bC}{1+bC}, \tag{1.46}$$

where a_m – capacity of monolayer; b – constant; C – the concentration of the substance.

At low concentrations equation Langmuir transforms into the Henry equation:

$$a = KC \ (K = a_m b), \tag{1.47}$$

i.e. sorption capacity is directly proportional to the concentration of substances in solution. Langmuir sorption isotherms is linear in coordinates (a^{-1}, c^{-1}), which allows the graphically determine the coefficients a_m and b.

Fundamentals of adsorption thermodynamics in solutions were first formulated by Gibbs more than 100 years ago [13]. He introduced the concept of excess adsorption of Γ, i.e. excessive content of adsorbed substance in the adsorbed phase compared with its content in the solution. The magnitude of the excess adsorption can be easily determined by the formula:

$$\Gamma = (\mathrm{C}_0 - \mathrm{C}_k)\frac{V}{m}, \tag{1.48}$$

where C_0 and C_k – concentration of substances in solution before and after adsorption; V – volume of the solution; m – mass of adsorbent.

Table 1.4. **Coefficients K and n in Freundlich equation**

Substances	***K***	***n***
Amyl acetate	4,8	0,49
Aniline	25	0,32
Benzenesulfonic acid	7	0,17
Butanol	4,1	0,44
Vinyl chloride	0,37	1,09

The thermodynamic approach to the problem of sorption is the most common and allows you to evaluate sorbability of molecules using the value of the maximum of mass transfer from the solution to the surface of the sorbent. During the sorption material from the water, the free energy of the system ΔG_{ads} decreases, A. Koganovskiy [10] proposed to use this value to predict effectiveness of removal of solutes from water. The equilibrium constant of sorption from diluted solutions K_{ads} associated with ΔG_{ads} by ratio $lgK_{ads} = \frac{\Delta G_{\text{адс}}}{RT}$, which implies that the bigger ΔG_{ads} the better sorbability of substance. The calculated value of ΔG_{ads} for a number of compounds and functional groups during the sorption on KAD-Iodine active carbon, WAU and OC-A presented in Table 1.5.

Table 1.5. **The values of adsorption ΔG_{ads} to compounds and functional groups on activated carbon [17]**

Compound	ΔG_{ads}, kJ/mol	Functional groups	ΔG_{ads}, kJ/mol
n-Nitroaniline	24,8	$-C_6H_5$	21,16
Naphthalene	24,6	$-NO_2$	2,60
Naphthol	23,4	-OH (primary)	2,30
Aniline	22,3	$=CH_2$ (in the alcohols and acids)	2,18
Phenol	21,3	-COOH	1,63
Chlorobenzene	19,4	-Cl	l, 38
Chloroform	18,6	$-NH_2$	1,05
Dichloroethane	18,3	=C=C=	0,88
Methylamine	18,3	$-CH_3$	0,46-0,59
Triethanolamine	17,8	OH (secondary or tertiary)	0,25
Acetic acid	17,8	-OH	0,042-0,084
Nylon acid	17,7	-OH (if NH_x is presented)	-0,25

Continuation of *Table 1.5*

Formic acid	17,7	$=CH_2$ (if $-NH_2$ is presented)	-0,42
Ethylamine	17,7	$-SO_3H$	-1,09
Ethylenhlorhidryn	14,3		
Butyric acid	13,7		
Oxalic acid	13,5		

Some surfactant ΔG_{ads}=21-29 kJ/mole. With ΔG_{ads} lower than 16-17 kJ/mole (or less than 42 kJ/g – to surfactants that are presented in the water as micelles) sorption is relatively low.

The obtained value ΔG_{ads} for functional groups allows to calculate with sufficient accuracy ΔG_{ads} for a broad class of different organic compounds (as the sum of ΔG_{ads} components), thus predicting sorption capacity of these substances. However, data for calculation ΔG_{ads} is reliable only for aromatic compounds.

The idea of the possibility of applying the theory of volume filling of micro pores to describe the sorption of liquid phase was designed by Eltekov and Stadnik [15]. This theory uses the idea of the absence of impact of physical properties of sorbate in the bulk phase on sorption capacity in micro pores of coal and absence of associative, ionic and hydrogen bonds between the molecules of a substance that is absorbed and water, as well as within sorbate. This theory can be used to calculate the sorption of very dilute solutions of substances with limited solubility. The equation of sorption isotherms on microporous AC in this case takes the form:

$$lg\Gamma_{\text{p}} = lg\frac{W_0}{V_m} - 2{,}3\frac{BT^2}{\beta^2}\left(lg\frac{C_s}{C_p}\right)^2, \qquad (1.49)$$

where W_0 – the threshold volume of micro pores of the adsorbent; V_m – molar volume adsorbate is calculated by Fig. 1.10; $B = \left(\frac{4{,}574}{E}\right)^2$ – structural and energy constant; C_S – solubility of compounds in water at a given temperature; C_p – equilibrium concentration in water.

Sorption isotherms, described this equation is linear in coordinates $\left(lg\Gamma_p, \left(lg\frac{C_s}{C_p}\right)^2\right)$, as confirmed by experiments for adsorption of some aromatic compounds.

The advantage of this model is possibility of full analytical calculation of sorption isotherms without performing of experiment, if isotherm of any other (standard) substance is known. Constant *B* that determines the shape of sorption isotherms, can be calculated if we know the average values of the radius of the micropores factor, affinity, form of pores and molecular constants of sorbate and sorbent. Affinity usually is calculated as the ratio of the Krikwood constants $\left(\beta = \frac{C^k}{C_0^k}\right)$ that can be calculated using polarizability and magnetic susceptibility of sorbate and sorbent.

Using equation (1.49) Henry constant *K* can be calculated and change of the free energy of sorption in standard conditions ΔG^0 using equation (1.47):

$$lgK = \left(\frac{\beta^2}{4} \cdot 2{,}303BT^2\right) - lgC_s, \quad (1.50)$$

$$\Delta G^0 = \frac{R\beta^2}{4BT} - 2{,}303RTlg(V_m C_s)^{-1}. \quad (1.51)$$

Using the proposed theoretical model for calculation requires high accuracy and reliability of determination of affinity that requires a cautious approach to the choice of a standard substance.

Summarizing data on sorbability on AC low molecular organic compounds it can be concluded that structurally simple substances in ion form are sorbed less than other. Ability to adsorb organic compounds increased in a row: glycols < alcohols < ketones < esters < aldehydes < undissociated acids < aromatics.

Water is sorbed on areas of AC oxidized surface and prevents sorption of nonpolar aliphatic compounds. Sorbability of organic substances increases with the length of the carbon chain (if it is not limited by pore size sorbent), and for

homologs according to Traube rule, it proportionally increases with the change the length of the carbon chain.

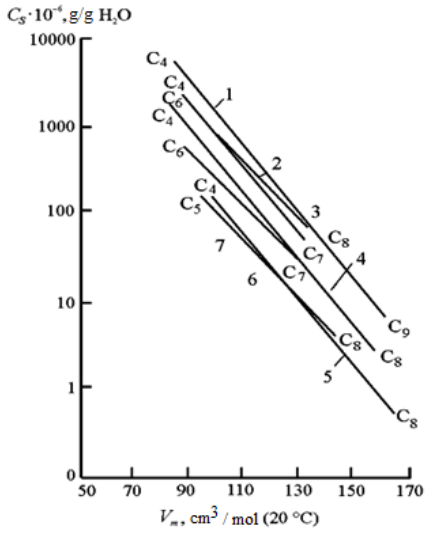


Fig. 1.10. **Solubility in water (C_S) and molar volume (V_m) of hydrocarbon oil:**
1 – acetylene; 2 – aromatic hydrocarbons; 3 – dienes; 4 – olefins; 5 – paraffin;
6, 7 – cycloparaffins.

The ability to sorption increases with molecular weight organic compounds, especially above 30000. A similar dependence with the increasing of micellar mass of colloids. The presence of water, inorganic salts, which increases associates of dye molecules and humates, leads to their better sorption separation.

For sorption of aqueous solutions on AC materials that form solvates, the dependency of volume filling of micro pores from the structural constants B is maximal.

Currently following main brand activated carbon for the adsorption of a liquid phase, SCT-0, AG-3-0, AG-3A, AG-3B, AG-3I, BAU, OC-A OC-B, and especially strong – FAS-C, AG-90, AG-95 is produced. It is used in filters with stationary and moving layers of adsorbent, and by dosing carbon in solution; for bleaching and cleaning solutions in various industries (food, pharmaceutical, chemical); potable

water, wastewater and process of circulating water; in hydrometallurgy of precious, rare and non-ferrous metals (FAS-C, AH-90, AH-95). Parameters of porous structure of certain types of industrial activated carbon are shown in Table 1.6 and 1.7.

Table 1.6. **The specific geometric surface of micro pores**

Active carbon	***S*, m^2/g**
AG	800-1000
BAU-A, OC	400-500
FAS-3	1200-1400

***Table 1.7*. Porous structure of activated carbon for adsorption from the liquid phase**

Active carbons	**Volume of common pores types, cm^3/g**			W_{01}, cm^3/g	W_{02}, cm^3/g	X_1, nm	X_2, nm
	V_{mic}	V_{mez}	V_{mac}				
SCT-0	0,38-0,42	0,15-0,18	0,07-0,20	0,40-0,45	-	0,50-0,54	-
ATSB-0	0,44-0,52	0,20-0,38	0,14-0,30	0,45-0,48	0,03-0,10	0,62-0,67	1,00-1,45
AG-3-0	0,25-0,28	0,10-0,15	0,40-0,52	0,20-0,22	0,08-0,12	0,60-0,65	1,14-1,36
AG-3A	0,25-0,30	0,10-0,17	0,40-0,53	0,18-0,22	0,10-0,14	0,63-0,67	1,17-1,41
AG-3B	0,27-0,30	0,12-0,18	0,41-0,47	0,20-0,23	0,10-0,16	0,62-0,64	1,12-1,48
AG-3Y	0,27-0,35	0,13-0,23	0,50-0,52	0,20-0,23	0,10-0,16	0,62-0,64	1,12-1,48
FAS-3	0,33-0,40	0,30-0,36	0,01-0,02	0,35-0,42	-	0,38-0,42	-
AG-90	0,23-0,28	0,11-0,15	0,29-0,35	0,23-0,26	-	0,65-0,68	-
AG-95	0,44-0,55	0,15-0,18	0,07-0,09	0,47-0,58	-	0,55-0,62	-
OC-A (B)	0,28-0,29	0,13-0,18	0,23-0,41	0,27-0,30	-	0,56-0,60	-
BAU	0,22-0,25	0,08-0,10	1,35-1,45	0,21-0,24		0,56-0,60	-

1.2 Structural chemistry of activated carbon

Activated carbon refers to one of the many kinds of carbon materials, properties and characteristics which vary widely, hence the impossibility of

classification of such products based on information about their chemical composition.

This difference in the characteristics and properties of the activated carbon is primarily due to the peculiarities of the spatial structure of the carbon skeleton, that ratio between porosity and carbon material mass.

In charcoal spatial structure of the carbon skeleton is crucial. This fact is due to the interest in the evolution of ideas about the structure of activated carbon and obtain answers to the questions: What is the activated carbon; How does the nature of the feedstock and the conditions of its processing influence on activity and mechanical properties of coal; which technological methods can obtain activated carbon with desired properties.

To clear classification of characteristics that determine the adsorption properties of activated carbon depending on the spatial structure of the carbon skeleton, primary and secondary structure are distinguished.

Primary structure describes pattern of relative position of carbon atoms in the element crystal (grain) of coal; the secondary includes spatial location of the initial carbon elements, which form main part of its porosity.

In the development of ideas about the structure of activated charcoal a number of theoretical models which are based on attempts to classify activity of coal according to degree of amorphism or crystallinity of its components were considered. Low temperature modification of amorphous carbon offered by Channey in 1919, amorphous carbon – Ruff in 1927, crystalline carbon by Hoffman, Burley, Ulrich in 1930, and finally turbostratic structure Stroks suggested in 1942.

Channey proposed the first working hypothesis that explains the connection of protective characteristics of gas-protection of coal in relation to toxic substances from their original structure, in 1919. He suggested that the activity of coal caused

by the presence in its composition of amorphous modification of carbon. It is formed by the decomposition of plant material at low temperatures. Volatile products released during thermal decomposition are adsorbed on the surface of amorphous carbon and block it. Further increase in temperature promotes the transition of adsorbed products and amorphous modifications into the crystal form. Therefore, Channey's process of activation is explained by the release of the activated surface of amorphous modification of adsorbed substances by sensitive oxidation at low temperatures. For this purpose, it is proposed to use air at activation no higher than 450 °C.

The use of air as the activating agent did not lead to increased activity of gas-protection coal. This, according to Channey, due to high thermal effects of exothermic reaction of oxygen with hot coals, accompanied by burnup first of more activated amorphous modification, also, due to local overheating, transferring amorphous modification in the crystal.

Therefore, Channay recommend getting gas-protection coal in two stages. At first obtain a porous amorphous carbon at a relatively low temperature of thermal decomposition of plant material under conditions that reduce the possibility of deposition of activated forms of carbon on the surface of amorphous carbon. On the second is to remove absorbed carbohydrates with primary coal and increase its porosity by prolonged heating at high temperature using mild oxidizing agents such carbon (IV) oxide and water vapor.

In 1927 Ruff in the study by X-ray diffraction (XRD) of the nature of the activity of coal confirmed that despite the fact that highly activated coal contains characteristic graphite interference fringes, but in fact it is an amorphous material.

Research of Ruff was continued by Hoffman, who on the basis of XRD of graphite, natural fossil and activated carbon derived from different raw materials, confirmed the presence in activated carbon elements of the structure of graphite.

Hoffman for the first time was able to identify quantitative and qualitative differences between the structural elements of graphite and activated carbon.

According to Hoffmann, activated carbon has the same primary structure as graphite, but unlike graphite crystallites activated carbon are smaller and provide blurred X-ray diagram; constant *C,* which characterizes the period of identity of hexagonal planes cyclically polymerized carbon in graphite, is fair and for activated carbon, but with different recurrence: for the activated carbon *c*=3, for graphite *c*=2. Distance between carbon atoms in a hexagonal planes of activated carbon is less than in graphite, and varies over a wide range, 0,132-0,138 nm for activated carbon, 0,141-0,142 nm in graphite; interplanar distances are bigger in activated carbon and equal to 0,36-0,38 nm, and in graphite are equal to 0,34 nm; the number of six-membered cycles in hexagonal plane in activated carbon ~15, and graphite - from 30 to 60; number of hexagonal planes of activated carbon ranges from 5-6, and graphite has much more. Convincing evidence of the crystalline nature of activated carbon in the works of Hoffmann were further supplemented by the discovering of another characteristic type of the primary structure of activated carbon.

In 1942 Stroks presented the results of research by XRD of activated carbon derived from certain types of plant material and synthetic carbon materials that confirmed the presence of another modification of activated carbon.

A distinctive feature of the primary structure of the coal is highly disordered hexagonal planes of cyclically polymerized carbon in coal structure, absence in structure of space-occupying lesions in parallel assigned hexagonal planes that can be recorded by XRD. For these structures, which are characterized by increased disorder, Stroks introduced the concept of turbostratic structure.

Modern view on the structure of activated carbon in finished form was formulated by Riley, is that activated carbon is approximately 2/3 has ordered carbon and 1/3 – with disordered. Orderly carbon represented graphite-like parallel

laid molecules of cyclically polymerized carbon, but the randomly oriented to each other. The relatively high degree of ordering of carbon in these formations, the ability to assess their geometrical sizes by XRD allows to classify them as elements of the crystal structure of activated carbon, called «crystallites». Macromolecules has homogeneous internal structure and are interconnected by side radicals of different shapes. In disordered part of the structure of carbonated compounds, together with carbon, oxygen and nitrogen are included, nuclear factors of which are close to the atomic factors of carbon.

Thus, the activated carbon can be attributed to materials, structural elements which are flat layers of aromatic carbon (macromolecules) with side radicals of different chemical nature. The polymeric frame of carbon material formed mainly by carbon and oxygen links between radicals. The atoms that make up the carbon layers and side radicals differ in their valence state.

The ratio between the structural components of a macromolecule coal, carbon concluded in aromatic layers and unregulated carbon located in the lateral radicals, defines the physical and chemical properties of coal, including reactivity and mechanical strength. Linear dimensions and parameters of the primary structure of activated carbon defined molecular structure and elemental composition of the original organic material, the primary mechanical and chemical processing, methods and ways of treating and activation. But the parameters of the primary porous structure are not indicators that determine quality of activated carbon.

Contingency and strength of activated carbon depend not only on the size of the output crystallites, but also on their relative position between each other, the nature of communication between each other crystallites in the particle of coal, the relative position of these particles that form secondary porosity. Thus, quality of activated carbon is determined by the type of feedstock and the conditions of processing. Unfortunately, the study of processes occurring at different stages of

transformation of carbon raw materials in the activated carbon is limited. This is due to the lack of opportunities for timely and objective information about changing of the characteristics of the output of carbon materials during the heat treatment using the methods of chemical analysis of the solid residue and volatile emissions, XRD and investigation of porous structure.

In general, the physical and chemical processes occurring during heat treatment of carbon materials in the production of activated carbon, are very difficult at direction of reactions and internal structuration transformation of material, which changes its original structure with preserving fragments and the formation of new types of spatial structures.

Typically, heat treatment of carbon materials is accompanied by parallel and simultaneous processes of degradation, polycondensation and polymerization. This orientation of these processes and their relative role in changing the nature of matter and determining the structure of activated carbon depends on many factors, the main ones are: macromolecular structure of the starting material, the conditions of heat treatment, the presence and number of extraneous elements. The latter determines the depth and extent of conversion of the starting material and the quality of the activated carbon.

Technologically, the stage of heat treatment the subsequent processes occur. Destruction of initial molecular components of carbon material, accompanied by a loss of 50-60 % by weight, which is released in the form of volatile and liquid products. The internal rearrangement in the material, which leads to the formation of similar spatial and volumetric structural elements; their mutual fixation of one against the other. The shrinkage of the material in the final stages of heat treatment that promotes the formation of a large number of pores in the carbon skeleton and the minimum proportion of large pores.

In general, the decomposition of the source material passes through a series of successive stages. The initial stage corresponds to the formation of primary germ of crystallization in the hexagonal cycles of carbon. These embryos are further polycondensation substance to form macromolecules with advanced peripheral structure. With further increase in temperature is internal crystalline regrouping, accompanied by further streamlining the structure and decrease the proportion of disordered carbon. The resulting primary elements (macromolecules) are combined in packages ordered carbon and connecting via pieces of disordered carbon in common macromolecules form a spatial structure.

In the process of treating the structural rearrangement of the material accompanied by decreasing its weight by extracting volatile products and the formation of the carbon skeleton, which is 96-98 % of the carbon 1-1,5 % hydrogen and inorganic residue. The primary structure of the crystallites is formed at temperatures below 700 °C and continue virtually remain unchanged.

The variety of raw materials used in the production of carbon adsorbents allows only think about common patterns that occur in the process of pyrolysis, which more or less reliability can be experimentally investigated since temperatures above 400-450 °C. About processes and reactions, occurring in the early stages of pyrolysis can also be investigated on the basis of IR spectra. The latter evidence of absorption bands of condensed aromatic structures and the development of systems of connected intermolecular bonds.

To some extent, the qualitative side of processes at thermal transformations of materials used in the production of carbon adsorbents can be judged by the example of the transformation of the original model element of carbon material starting from temperature of 400 °C and above. Fig. 1.11 present gross formula of carbon balance for a given temperature of heat treatment and its hypothetical model. With increasing temperature of heat treatment simultaneously with the process of

destruction (which occurs mainly at temperatures up to 500 °C), regrouping, accompanied by an increase in the degree of ordering of the material occurs.

Assumption about the processes occurring in carbon materials during heat treatment, does not contradict the results of research by XRD of primary structure of carbon residues obtained from typical raw materials used in the production of carbon adsorbents.

Parameters of the primary structure determined by the type of feedstock, and despite some differences in the output crystallites changes during heat treatment are identical in nature (Table 1.8 and 1.9).

The results of the study of secondary porous structure of carbon residues from modeling material – synthetic polymers, spatial skeleton of non-activated carbon mainly formed at temperatures of about 400 °C. During subsequent heat treatment it undergoes minor structural transformation, due to low shrinkage carbon skeleton with a simultaneous increase in apparent density and volume of pores accessible to molecules of benzene. Structural changes in the mass of the carbon skeleton has almost no effect on the transport porosity.

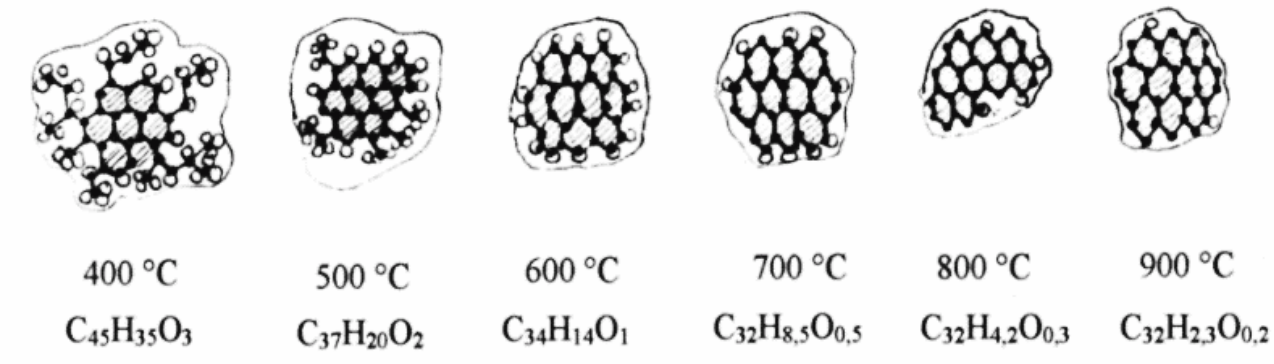


Fig. 1.11. **Structural changes in the model element of carbon material in the temperature range from 400 to 900 °C.**

Table 1.8. **Parameters of the primary structure of non-activated carbon with different origin used in the production of carbon adsorbents [1]**

Initial raw materials	T_{carb}, °C	*C*, wt. %	*H*, %	Dimensions for axes, nm		Distance between, nm	
				La	Lc	-C-C-	Planes
Lignin	700	91,7	1,7	1,66	1,18	0,138	0,369
	900	96,6	0,6	2,04	1,12	0,137	0,369
Peat	700	90,1	1,8	1,70	1,03	0,138	0,360
	900	93,9	0,7	2,00	1,67	0,139	0,346
Anthracite	800	94,3	1,6	1,80	1,27	0,138	0,336
	900	95,3	1,0	1,87	1,28	0,139	0,336
AG-3*	500	89,7	2,1	3,2	0,99	0,138	0,369
	700	94,2	1,6	3,69	1,09	0,138	0,365
	850	96,1	1,2	3,77	1,24	0,138	0,363

* intermediate process of obtaining industrial activated carbon AG-3 (50 % of carbon and 50% of binder, which is a wood or coal tar).

Table 1.9. **Parameters of the primary structure of non-activated carbon derived from phenol-formaldehyde and furyl resins [1]**

Resin	T_{carb}, °C	C, wt. %	H, %	Dimensions, nm		Distance between, nm		Aroma-ticity, %
				L_a	L_c	-C-C-	planes	
Phenol-formaldehyde (Rezol)	800	97,6	1,5	2,1	0,73	0,138	0,356	35
	900	98,2	1,3	2,1	0,75	0,138	0,377	37
	1000	98,6	0,9	2,1	0,76	0,139	0,365	38
Furyl	800	97,5	2,0	2,4	0,70	0,137	0,361	23
	900	98,1	1,4	2,6	0,80	0,138	0,365	40
	1000	98,2	1,4	2,5	0,80	0,138	0,362	42

During the heat treatment of raw carbon material at critical temperature, the excess of which significantly affects the quality characteristics of the finished activated carbon, the accepted temperature is 950 °C. Overheating output activated carbon causes substantial transformation of carbon skeleton, accompanied by a decrease in the volume of micropores, increasing transport porosity and increasing apparent density (Table 1.10).

Table 1.10. **Effect of temperature heat treatment on the parameters of the porous structure of activated carbon with phenol-formaldehyde and furyl resin**

Temperature treating, °C	δ, g/cm³	*d*, g/cm³		V_{Σ}, cm³/cm³		V_{trans}, cm³/cm³
		He	C_6H_6	He	C_6H_6	
400	1,04	1,50	1,10	0,31	0,06	0,06
600	1,09	1,78	1,78	0,39	0,06	0,06
800	1,18	1,95	1,95	0,40	0,08	0,08
1000	1,31	1,86	1,86	0,30	0,11	0,12

Research of porous structure of activated charcoal indicate that the qualitative characteristics of activated carbon are formed at the stage of heat treating of the raw carbon materials (Table 1.11). The decisive criterion in the selection of raw materials in the production of coal by steam activation and potential indicators of future activation ability are apparent density (δ, g/cm^3) and the relative part of the volume of micropores available for molecules of helium and not available for benzene or tetrachloride carbon. The first figure (*d*, g/cm^3) describes the possible degree of removal of carbon from the skeleton of activated charcoal, which ensures the development of adsorbing porosity in the adsorbent without losing its mechanical strength, and the second: the initial volume of micropores for which the process of steam activation ensured availability of molecules typical adsorbate with further increase this amount by increasing the relative size of micropores.

Table 1.11. **Parameters of porous structure of activated carbon from typical raw materials production of carbon adsorbents**

Raw	δ, g/cm³	Σ, cm³/cm³		$V_{\Sigma}^{He} - V_{\Sigma}^{C6H6}$, cm³/cm³
		He	C_6H_6	
Birch	0,61	0,70	0,50	0,20
Peat	0,75	0,63	0,52	0,11

Continuation of *Table 1.11*

Lignin	0,88	0,59	0,40	0,19
The shell of apricot	1,04	0,51	0,28	0,23
Coal	1,25	0,41	0,24	0,17
Saran	1,02	0,48	0,02	0,46

1.3 TECHNOLOGIES OF OBTAINING CARBON ADSORBENTS

By 2000 global industrial production of activated carbon was approximately 500 tons per year, while the US share of about 240 thousand [1]. The major share of it is granulated carbon used in collective and personal protective equipment. At the same time, the US produce up to 60 % powdered activated carbon used in the water treatment, sugar industry and other liquid-phase processes. Table 1.12 shows the main world producers of activated carbon.

Table 1.12. **The main world producers of activated carbon**

Country	**Company**	**Production capacity, ths. tons**	**Initial raw materials**
USA	1. «Calgon Carbon Corporation« Including «Pittsburgh» (USA) «Chemviron» (Belgium) «Degussa» (Germany)	90	bitumen; coal
		60	
		20	
		10	
	2. «Westvaco Corporation»	54	
	3. «Imperial Chemical Industries United States»	45	bituminous coal; coconut shell
	4. «Huski»	14	peat, wood
	5. «Barnebu Cheney»	45	bituminous coal, pulp and paper production waste
	6. «Witco Chemical Corporation»	45	wood, lignin, bituminous and anthracite coal
	Together the United States:	~400	

Continuation of *Table 1.12*

Japan	«Nihon Jescoal» «Futamura» «Meiva» «Curojeha, Takeda» «Oriental Carbon»	64	coal; brown coal; wood; coconut shell; waste from oil and chemical industry
Netherlands	«Norit»	40	peat, wood
Germany	«Berhverhsferband» «Bauer»	32	Coal plant material
England	«Sutcliffe» «Thomas Ness Ltd»	20	coal; coconut shell
France	«Seka» etc.	23	wood; coal

1.3.1 Method of vapor-gas activation

During activation of carbon raw multistage process goes with the removal of residual functional groups of individual crystallites and macromolecules, by the interaction carbon with oxidant. As a result, the structure and activation of porous carbon material are changing. Conditions during this process and the quality of the carbon adsorbent depends on many factors, the main ones are: physico-chemical and structural characteristics of the original raw coal, determined type of feedstock, It's terms of previous processing and carbonization mode; physical and chemical modes of vapor-gas activation process (VGA). Technology concept «mechanism VGA» reflects the totality of all phenomena that occur in the interaction oxidant with non-activated coal (NAC), the progress of which depends on the carbon state in the original coal raw and factors that determine the conditions for adjusting the parameters of porous structure in the activated carbon in the set limits. The basis of VGA is the high-temperature treatment NAC with gaseous oxidants, accompanied by the removal of 30 to 50 % by weight of the carbon source carbon skeleton NAC. Although the production of AC, this indicator is called «burnt», in fact it should be carried out under conditions that exclude uncontrolled removal of carbon, unlike widely used in industrial practice of coal gasification processes.

Non-activated coal NAC is the carbon residue formed during the initial thermal treatment carbon containing materials in an inert atmosphere in which the main parameters of porous structure are formed. The main task of vapor-gas activation process is ensuring accessibility for typical adsorbate already established in NAC volume of adsorbing porosity and increasing its capacitance and kinetic characteristics without noticeable loss of mechanical strength, if it possible.

When activated carbon coal removal must be accompanied by development of porosity and a corresponding decrease in its apparent density. Failure to comply with these conditions leads to surface burnt without porosity of the carbon skeleton.

Soft oxidizers are using as activating agents which can adjust the temperature settings of the process to implement control over the process of steam activation reactivity. The lower limit of temperature range VGA process given the need to ensure the optimal speed activation, and higher limit to eliminate surface burnt coal.

For the main activators that are used in the production AC by method VGA - carbon (IV) oxide and water vapor, when temperature range of controlled influence is in a narrow range from 800 to 950 °C.

Significantly greater uncertainty in understanding the mechanism VGA makes initial NAC. Using of different materials (wood, peat, shell fruits and nuts, fossil coal, synthetic polymers, carbon containing waste, etc.) and methods of their primary processing (milling, shaping, modification, etc.) leads to significant fluctuations in the quality characteristics of the initial NAC, the reactivity of its components and transport porosity, ensuring accessibility of the internal volume of the carbon skeleton NAC for the activating agent and the required thermodynamic conditions for their interaction.

Evaluation criteria of NAC reactivity ratios for the orderly (cyclically polymerized) and disordered (the side radicals) carbon, used in practical technology, sufficiently conditional as in the progressive activation is a constant change in this

ratio. It should be emphasized that these allegations be fully applicable for each component part of the initial NAC. As an example of this position, it can bring the relative rate of removal of carbon from the individual components that make up the industrial activated carbon AG-3 (Table 1.13) [12,13].

Table 1.13. **The rate of carbon removal from the components that make up the AC AG-3, the interaction of carbon (IV) oxide at temperature of 850 °C**

Component	AG-3	Coal weakly sintered	Semi-coke	Forest and chemical resin	Coal tar
The rate of mass loss, %/min	0,56	0,50	1,45	3,56	0,25

Thus, a high degree of uncertainty, which is characteristic of the process of steam activation caused by the variable characteristics of the NAC and its components, which significantly complicates the establishment of precise quantitative relationship to the degree of activation associated with changes in the porous structure and the activation degree obtained activation carbon.

Quantitative measure of interaction with NAC oxidant accompanied by the removal of carbon and the changing nature of its porosity in research and industrial practice is considered burnt, defined as the ratio of carbon burnt to the original mass of coal or the ratio of the difference to reducing the apparent density of the original.

A visual quality changes occurring in the NAC with increasing burnt can be traced based on their research using (RSA), calculating carbon values of density and character of the porous structure. Analysis of structural changes in the process of vapor-gas activation suggests that the interaction with the activating agent NAC, along with the destruction and transformation side radicals affected and nuclear structure of even the destruction of aromatic layers. As an example, in the Table 1.14 presents data on changes in crystallographic parameters carbonated material from various raw materials.

Apparently, the most densely packed layers of fossil coal; interlayer distance of coal char more sugar and are 0,363 nm in coal layers polyvinylidene chloride ordering is not observed either in the original or in activated carbon.

During activation occurs minimal change the basic parameters of the primary elements of bulk carbon skeleton - interlinear and interatomic distances and linear dimensions of the crystallites. Thus, there is a slight increase in the proportion of carbon in an orderly composition coal, the most characteristic of the initial stages of the burnt process between 10-20 %. Last is caused by burnout primarily capable of the most reactionary part of the carbon skeleton - disordered carbon. In later stages of interaction with the activator along with unregulated carbon involved in the process of nuclear and polymer skeleton of coal.

Table 1.14. **Changing the basic of X-ray settings carbon adsorbents AC with different raw materials with increasing burnt [9]**

Initial raw materials (vapor-gas activation)	**Burnt, %**	**Settings, nm**			**Aromaticity, %**
		d*	***c****	***a****	
Sugar semi-coke, T = 850 °C (H_2O_{vapor})	0	0,363	0,98	2,80	69
	3,6	0,363	0,98	2,65	70
	6,8	0,363	0,87	2,75	74
	10,0	0,363	0,80	2,85	76
	19,0	0,363	0,65	2,80	78
Coal, T = 920 °C (CO_2)	0	0,348	1,10	2,60	59
	3,7	0,344	1,10	2,80	62
	8,7	0,344	1,20	2,70	62,5
	0	0,363	0,98	2,80	69
	3,6	0,363	0,98	2,65	70
Polyvinylidenechloride, T = 850 °C (CO_2)	6,8	0,363	0,87	2,75	74
	10,0	0,363	0,80	2,85	76

d, **c***** and ***a**** are X-ray diffraction of crystal lattice parameters studied adsorbents

The correctness of this assumption is confirmed by the changes in values of the density of carbon burnout (d^*) with increasing burnt calculated using the formula:

$$d^* = \frac{\sigma_{in} - \sigma_{fin}}{V^*_{\sum fin} - V^*_{\sum fin}}, \quad (1.52)$$

where * means pycnometric liquid.

Table 1.15 and 1.16, as an example, given the density of carbon that burns coal obtained from phenol-formaldehyde resin (PFR) during its activation. As seen from the Table 1.15, during activation the density of carbon that burns increases, but even burnt values close to the limit, its value significantly lower than the original density of helium (d_{He}) and benzene (d_{C6H6}) for industrial AC (2,10-2,16 g/cm^3), the same data is in radiographic density of carbon. The latter indicates that a significant increase of total porosity in the initial stages of interaction caused by increasing degree of accessibility of the volume of micropores, which in the initial NAC blocked by side radicals of disordered carbon.

This assumption corroborated a study changes in the structure of porous activated carbon with burnt increasing (Table 1.15 and 1.16).

Table 1.15. **Changing the value in process of progressive density of coal activation derived from phenol-formaldehyde**

Burnt, %	**Δδ, g/cm^3**	**ΔV^{C6H6}, cm^3/cm^3**	**ΔV^{He}, cm^3/cm^3**	**d^{C6H6}, g/cm^3**	**d^{He}, g/cm^3**
3,7	0,05	0,118	0,05	0,423	0,91
12	0,16	0,203	0,127	0,79	1,26
27	0,40	0,377	0,281	1,06	1,43

As the data presented, the major changes taking place in the porous structure of coal activation in the process associated with the development of the micropores volume in the early stages (before burnt 10-15 %) by increasing the degree of availability, and the next - with changing their size because of burnout individual macromolecules nuclear skeleton of polymeric carbon. Upper limit of the burnt

limit values is the start of individual crystallites burn coal, that exceeding the upper limit not only reduces its capacitive properties, but also accompanied by a sharp drop in its mechanical strength. Further activation is accompanied by decrease overall adsorption porosity and destruction the spatial bonds in the coal skeleton to ensure its durability.

Table 1.16. **Changing the porous structure of model coal derived from phenol-formaldehyde with increasing burnt degree**

Burnt, %	δ, g/cm^3	d^{C6H6}, g/cm^3	V_Σ, cm^3/cm^3	Pore volume, cm^3/cm^3			W_0, cm^3/cm^3	E_0, kJ/mole
				V_{ma}	V_{me}	V_{mic}		
0	1,16	1,36	0,15	0,14	0,01	—	—	—
5	1,10	1,41	0,22	0,16	0,02	0,04	0,1	—
10	1,05	1,60	0,35	0,17	0,01	0,17	0,13	25,8
15	1,00	1,66	0,40	0,17	0,01	0,22	0,25	22,9
24	0,89	1,73	0,49	0,19	0,02	0,28	0,30	20,5
30	0,80	1,93	0,59	0,19	0,02	0,38	0,38	19,6

The variation of porosity, detected by the example of the AC of the model feedstock, fully manifested the most difficult on the original recipe of industrial active carbon AG-3 (Fig. 1.12), when each component will provide a different nature of certain kinds of pores (Table 1.17).

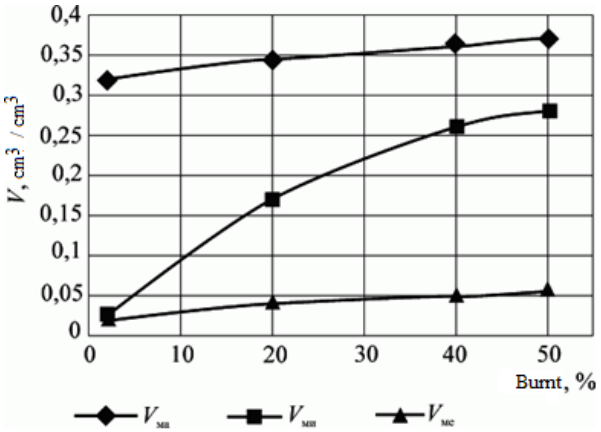


Fig. 1.12. **Restructuring of secondary porous structure of the industrial adsorbent AG-3 with burnt increasing (for weight loss).**

Therefore, the industrial technologies of AC production burns value usually set within closer position to the extremum of the micropores volume curve.

Thus, the carbon processing containing materials at the AC production, the following patterns: materials affects the quality of the coal, degree of its development adsorption and transportation porosity, and their mechanical strength; in vapor-gas activation process development of adsorption porosity volume goes mainly due to the development in the current NAC system micro pores. Further increase of this amount is due to the relative size of micro pores before their transfer to super micro pores, because of burnout individual macromolecules from primary crystallites carbon skeleton; development of meso- and macro pores volume (cm^3/cm^3) at burnt that adopted in the production of activated carbon. It almost doesn't occur; at burnt levels that are close to or above the limit, there is burnout some individual crystallites which leads to drop the volume of micro pores, and leads to increase the volume of macro pores with sharp coal reduction of strength. Therefore, regulation characteristics AC mainly realized by the selection of initial recipes, each component of which contributes to the development of the adsorbent's pore volume in a limited range of energy options microporous structure.

***Table 1.17*. Changing the settings of porous structure components, that are the part of adsorbent AG-3 [12]**

Product marker	δ, g/cm^3		$V_{\sum}$, cm^3/cm^3		V_{ma}, cm^3/cm^3		V_{me}, cm^3/cm^3		V_{mic}, cm^3/cm^3	
	beg.	end	beg.	end	beg.	end	beg.	end	beg.	end
AG-3	1,05	0,56	0,43	0,71	0,35	0,41	0,01	0,06	0,00	0,24
T or CC	1,51	0,76	0,15	0,59	0,15	0,26	0,04	0,04	0,00	0,29
PK	0,84	0,42	0,50	0,79	0,39	0,49	0,08	0,13	0,02	0,17
LHS	0,88	0,46	0,51	0,76	0,38	0,42	0,00	0,20	0,00	0,14
KUS	1,44	0,98	0,21	0,52	0,20	0,47	—	—	—	—

1.3.2 Production of granular activated carbon by steam activation

Industrial production of carbon adsorbents is mainly focused on the production of granulated coal, of which 80-85 % is produced on base of fossil raw materials by steam activation. The advantages of granulated AC include its stable form that ensures optimum aerodynamics and mechanical strength compared with crushed coal and the possibility of its use in a cyclic process with moving layer.

Formed coal has the form of cylindrical particles with a smooth surface diameter from 0,9 to 8 mm and is obtained by forming compositions from coal dust and organic binder by extrusion through calibrated holes.

In the production of granulated coal as a feedstock used fossil coals T and SS brands, carboniferous semi coke and charcoal and as binder – chemical forest and carboniferous resins, acidic wastes of petroleum refining, technical requirements are given in Table 1.18.

Common to all types of granular AC, that produced by the domestic industry is almost constant mass ratio of coal dust and binder, which is 70:30, the specific formula defined by purpose of coal.

Table 1.18. **Requirements for fossil raw materials in the production of granular carbon adsorbents [13]**

Indicator, % wt., no more	**Coal T and CC**	**Semi-coke**		**Raw coal TL**
		PK-1	**PK-2**	
Ash content	6,0	7,2	10	1,0
Volatile compounds	22,0	4-10	0,12	3,0
Sulfur content	0,5	0,5	0,5	—
Moisture content	10,0	9,0	9,0	10

Table 1.19. **Characteristics of chemical forest resin for the production of granulated AC [12]**

Indicator	Conditioned*	Prepared**
Color	Brown-black	Brown-black
Water content, %	3,0	3,0
The share of boiling away oils		
to 220 °C, %	12	12
from 220 ºC to the end of distillation, %	12	12
Peck, %	55-68	55-68
Coke n/m, %	10	10-15

* the resulting of raw or settling resins of pyrolysis of wood deciduous kinds.
** received by dissolving of wood-resin pitch in the wood-tar oils with the addition of green oil in the ratio: 50-55 % of pitch, 20-25 % of oil and 20-25 % by weight of green oil.

Coal of gas type (AG-2) and regenerative type (AR-3) is produced from fossil coals T or SS brands, chemical forest resin; coal carrier of catalytic or chemical sorption additives (DG-3 and DG-5) – from mixture of T (or SS) and semi coke (50:50) with chemical forest resin (70%) and carboniferous (30 %) resin; illuminating carbon for adsorption from solutions (ACS) – based on the composition of fossil coals T or SS brands and charcoal TL brand or chemical forest resin as a binder.

Table 1.20. **Characteristics of carbonated granules in the manufacturing of adsorbents AG-3 and AG-5, which directed to activation [41]**

№	Indicator	AG-3	AG-5
1	Bulk density, g/dm^3	590-592	584-630
2	Porosity by water, cm^3/g	0,45-0,48	0,41-0,47
3	Durability, % by MIS 3 by MIC 8	 98,3-99,8 85,9-86,9	 95-96 78-86
4	The content of volatile components, %	5,1-5,2	4,1-6,3
5	Fractional composition, % 2,75-2,0 mm 2,0-1,5 mm 1,5-1,0 mm	 84,6-87,1 7,0-8,8 -	 - 23-33 62,2-70,4

Characteristics of the starting materials used in the production of granulated AC, presented in Table 1.20.

The schematic diagram (Fig. 1.13) of granular activated carbon production (AG-3) includes follow steps (yield, % wt.):

1. Preparation of raw materials. Supply of stone coal (C) and semi coke (SC) to a warehouse, grinding on roller mill to a particle size around 5 mm.

2. Grinding in ball mills and transport into the hopper. This stage allows to get a uniform dispersion of dust particle size which determines the nature and development degree of transport porosity of coal, its reactivity and mechanical strength. From the batcher coal dust is pumped through dust line to mixing and granulation compartment.

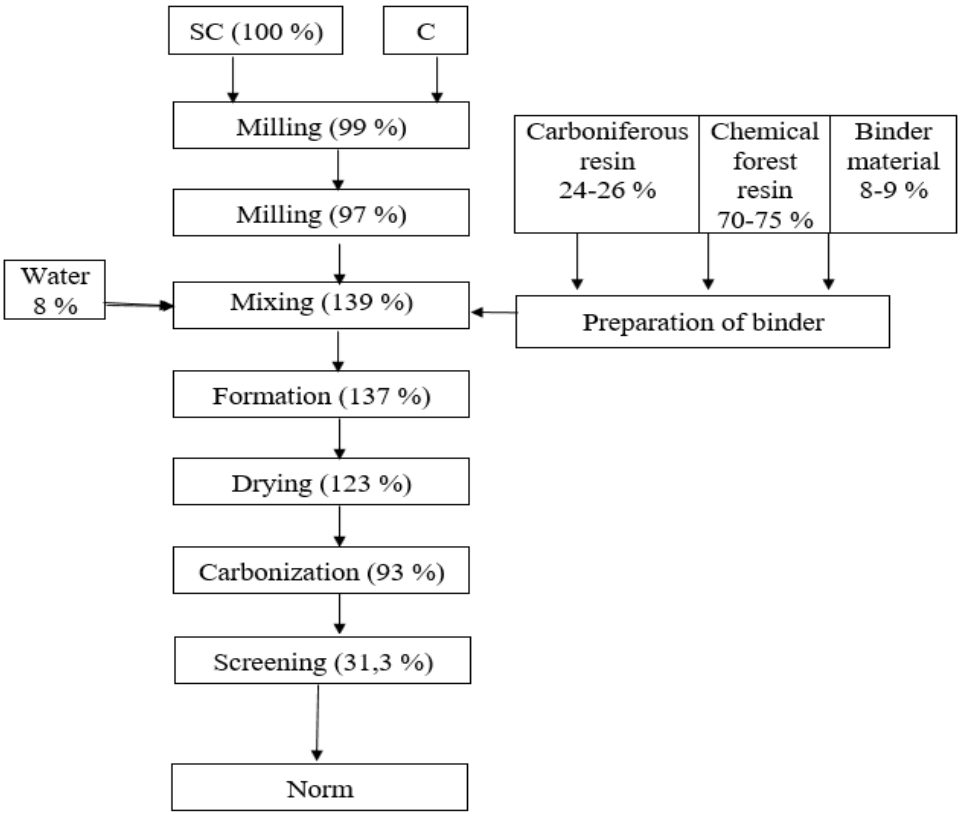
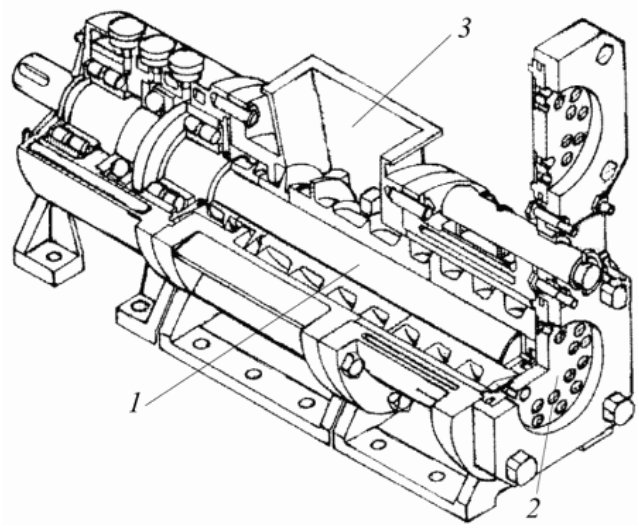


Fig. 1.13. **Schematic diagram of the production of granulated carbon AG-3 adsorbents.**

Preparation of binder: resins and green oil fed to the department, where mixed in a predetermined ratio and pumped into the department container.

3. Mixing and Granulation. Ratio of coal dust and binder (70:30) and the conditions of this process provide a homogeneous plastic paste. The binder, heated to 40-80 °C, from the craft tanks fed into a dosing device, from which merges into the receiver of mixer-granulator, mix with coal dust and is forced through spinneret. Formation of coal-tar composition performed on an auger-press shown in Fig. 1.14. Moving of pasty composition with a temperature of 30-80 °C in the auger-press is held via Archimedes screw with variable step, that reduces in the end and ends by the fifth. Raw pellets are fed to the conveyor, then comes to the intermediate tank, which fed the dryer drum.

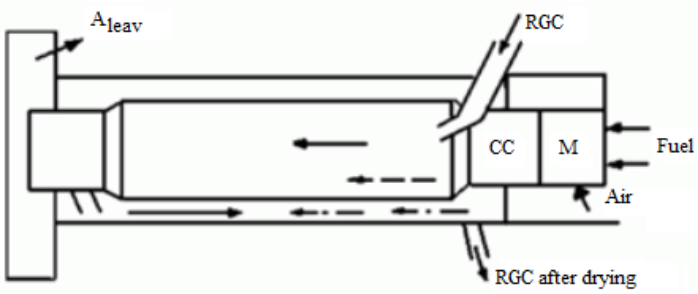


1 – archimedes screw; 2 – spinnerets; 3 – receiver of mixer-granulator

Fig. 1.14. **Auger granulator to form a coal-tar paste.**

5. Preliminary heat treatment (drying) of wet granules to remove moisture from the product, providing initial granule strength and quality improvement of AC. Drying is performed in a rotating drum furnace length of 12 with six sectoral cap, double move of material and separate supply of coolant and oxidant (Fig. 1.15).

Between the shell (diameter 1,6 m) and inner tube (diameter 1,2 m) mounted screw cap from separate plates, ensuring the promotion of coal up at an angle of 3°, and the passage of air. The process of drying and thermal oxidation conducted under vacuum of 5-10 mm of water. The temperature of the gases in the furnace of 800-1000 °C in the mixing chamber – 450-550 °C, in the retort at a distance of 1/3 of the chute – 200-250 °C, exhaust gases – 100-120 °C. These modes provide granules yield at a temperature less than 70°C with thermal oxidation temperature at 80-100 °C and a residual moisture less than 1 %. The residence time of the product in the oven is 30-35 min, productivity – 2,0-2,5 t/h on the finished product. Dried granules in stream direct to the carbonization furnace.



RGC – raw granulated carbon; CC – combustion chamber; M – Mixer; Fuel – the outgoing fuel.

Fig. 1.15. **Drum ovens for drying granulated product.**

6. Carbonation, cooling of granules and scattering of carbonated product. Granules after drying contain about 22 % volatile matter and cannot be loaded into the activation furnace, as this will lead to slag formation in feed and gas channels of furnace. During carbonization occurs removing volatile to a residual content of ~7 % and the formation of the porous structure and strength of the granules. Carbonization process is carried out in rotary drum furnaces with internal heating (Fig. 1.16). The dry granules continuously loaded into the carbonization furnace,

catches by shelves of nozzle and via tilt of carbonization furnace moved to the discharge chamber. Motion of heat carrier and product performed counter current. As heat carrier, serve products of combustion of natural gas. Flue gas temperature at the entrance to the drum is 1340 °C, the output is 300 °C, the temperature of the initial product is 700 °C. Carbonization gases are burned in heat recovery boilers. After end of coal carbonization through the discharge chamber, coal enters to the cooling drum, where it is cooled to 70 °C, and fed to the vibrating screening, which separates coal from coal dust and small particles. Suitable fraction with the characteristics listed in the Table 1.21, distributed on batchers over the activation furnace of shaft type.

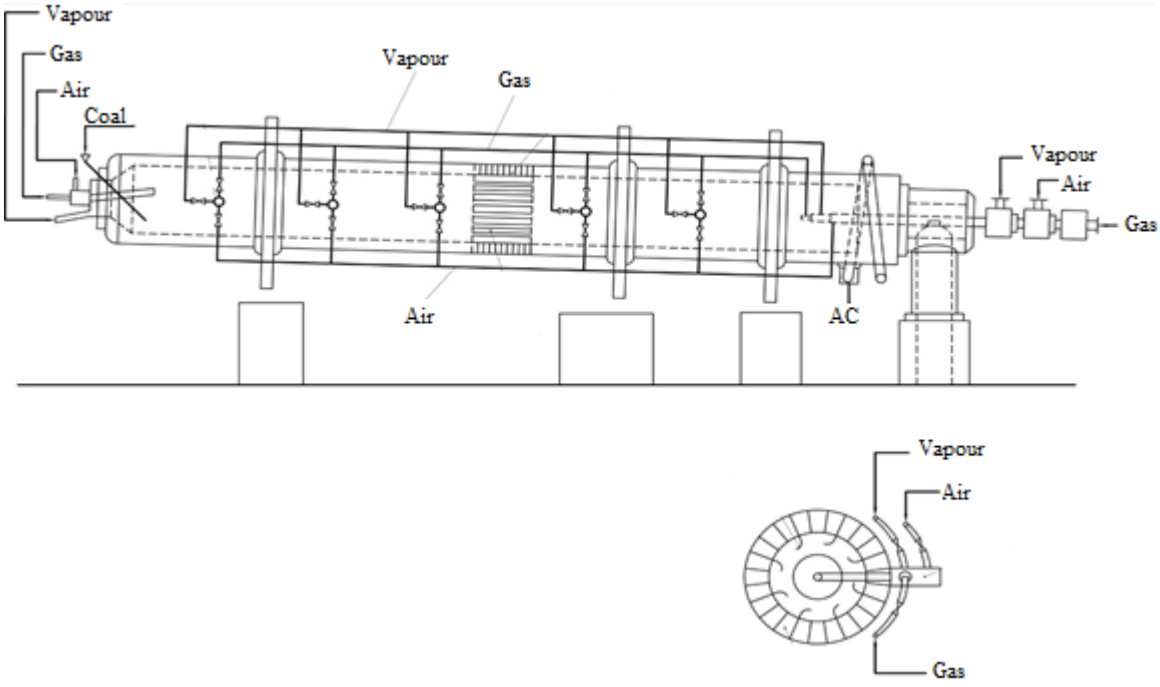
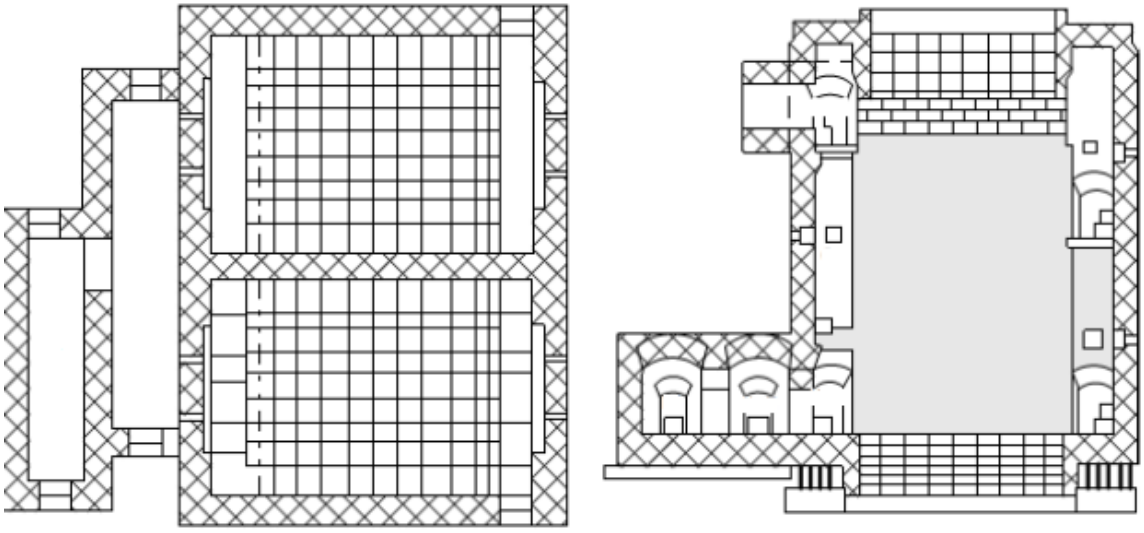


Fig. 1.16. **Rotary drum furnace for carbonization of coal granules.**

7. Activation. Activating pellet conducted at temperatures of 900-950 °C in the furnace shaft type with internal heating. As the activating agent uses water vapor and afterburning product of activated gases. During this process increases the accessibility of volume of adsorbing porosity formed in the no activated coal and increasing of the relative size of micropores. Structural changes and increased

activity is a result of the removal of carbon fragments from coal skeleton of varying degrees of order during its interaction with a vaporous activator. Activation oven (Fig. 1.17) consists of two halves that work in the direction of coal independently and in parallel, and relatively to motion of activating agent and heat carrier - consistently. Each half consists of semi furnace, the upper connecting augers and heat exchanger. Each half consists of semi furnace, the upper connecting bur and heat exchanger. The combustion chamber, the lower connecting bur, chimney camera, smoke bur and pipe are common to the whole furnace. Semi furnace is a camera with special form, lined with fireclay bricks. Structurally nozzle of semi furnace according to its technological purpose is divided into three zones. The first zone-heating and carbonization zone with height of 2,8 m, which brickwork forms a horizontal channel system, which serves for gas circulation and vertical are for moving of coal. In this zone there is no direct contact furnace heat carrier and product and heat transferred to coal through the wall of brick. The second zone - a zone of activation with height 3,6 m, brickwork of product cells and flues whose channels lined with fireclay brick, and its shape provides direct contact of activating agent with coal, its free diffusion into the layer of coal and return of reaction products in the flue channels. For stabilization of activating condition and enhancing uniformity characteristics of the resulting coal, form of channels in product cells promotes mixing of coal as a result of zigzag movement. The third zone – the zone of cooling with height 0,8 m, paved brick shapes, with a free passage for movement AC. Solid masonry equipped by channels for the passage of cooling air supplied to the fan.



a) b)

Fig. 1.17. **Section furnace of shaft type: a) horizontal; b) vertical.**

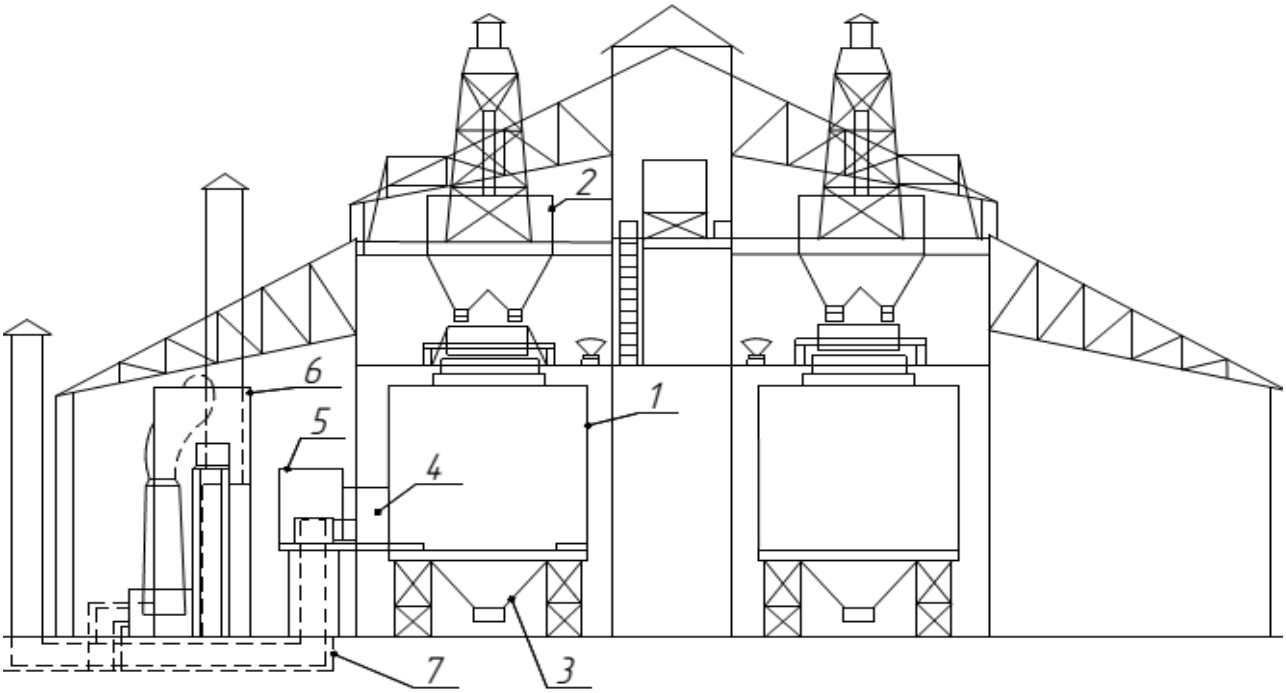
In I and II zones of semi furnace, molded brick lined in width of semi furnace completely, and in length is with free space between the chamber walls and brickwork, forming upland side. In loungers close to the combustion chamber are two floors, which form the bottom close bur (BCB), the average bur (AB), the upper near bur (UNB), and far – one floor, which forms the bottom far bur (BFB) and the upper far bur (UFB).

In loungers is air supply for gases combustion during activation in order to maintain the required temperature and the difference of partial pressures of product and gas channels, thus ensuring proper diffusion process in blend.

Activation process in furnaces with internal heating arranged so that heat from an external source is used only at the stage of heating of furnace and its launching after overhaul.

For this purpose, uses combustion chamber, where burned liquid or gaseous fuel. Functioning and given thermal treatment in a furnace after the heating of furnace masonry and recuperators supported by post-combustion gases generated by the interaction of an activating agent with coal and their utilization in the

recuperator. Last realized by changing the direction of flow of the coolant in semi furnace, that their work in heating and cooling mode by switching the direction of gas flow.



1 – furnace of shaft type; 2 – bunker; 3 – unloading hopper; 4 – lower connecting bur; 5 – combustion chamber; 6 – recuperator; 7 – smoke pipe.

Fig. 1.18. **Section of furnace department.**

Recuperator in furnace is designed for heat recovery from flue gas by heating brickwork and use this heat to superheat water steam. Heat exchanger is a rectangular shaft with height 8,95 m, cross section 2,0×4,0 m, lined with fireclay bricks. Inside it is just like an oven – divided by main walls into two equal parts. In each of the recuperators placed nozzle, which forming stepped vertical channels to enhance heat transfer. Filing pair performed through the dosing valve and then – through steam latch into the bottom of the recuperator. Amount of steam adjust by manometer; steam, which rising up and overheats due to heated nozzle recuperator

to a temperature of 800-1000 °C and via the LFB enters the furnace. Overheated steam passes through the horizontal duct of carbonization zone without colliding with the semi coke, and enters the UCB, where changes the direction. Then vapor goes through upper duct of activation zone where partially dissociates on the hot coals. Vapor and decomposition products entering to the B which again changes direction, passes through the duct activation zone and enters the BFB again changes the direction and goes through the duct area of activation zone to BCB, thence through the lower connecting bur enters the other half of the furnace, which is currently in heating mode.

During the passage of steam through the gas channel of activation zone, it interacts with carbon of no activated coal, which is in the product channels of furnace that can be described by the following reactions:

$$\begin{cases} H_2O + C = CO + H_2 + 125{,}4 \text{ kJ/mol}; \\ 2H_2O + C = CO_2 + 2H_2 + 75{,}2 \text{ kJ/mol}; \\ C + 2H_2 = CH_4 + 79{,}42 \text{ kJ/mol}; \\ 2C + 2H_2 = C_2H_4 + 58{,}52 \text{ kJ/mol}. \end{cases} \quad (3.1)$$

As mentioned above the main reaction of steam vapor is endothermic, this period is called the conditional «cooling». The temperature during the «cooling» is supported the same as during the «heat» - due to partial burning of gas activation beds, which receives air from the bypass line to the reactions:

$$\begin{cases} 2CO + O_2 = 2CO_2 + 284{,}2 \text{ kJ/kg}; \\ 2H_2 + O_2 = 2H_2O + 238{,}2 \text{ kJ/kg}; \\ CH_4 + 2O_2 = CO_2 + 2H_2O + 798{,}38 \text{ kJ/kg}; \\ C_2H_4 + 3O_2 = 2CO_2 + 2H_2O + 133{,}76 \text{ kJ/kg}. \end{cases} \quad (3.2)$$

By burning gas activation furnace temperature is maintained at 850-980 °C.

Steam mixture enters the bottom of the second semi-furnace passes it in reverse order. During the movement of gas-vapor mixture in semi-furnace, operating in heating mode, the interaction unresolved steam coal for reactions (3.1), and sunbeds afterburning products – reactions equations (3.2).

Temperature in the oven regulated air supply in boers for combustion gases activation. The air fed fan in the collector, which in two lines supplied to each half of the furnace. Air consumption per semi furnace governed installed on each line gate. Each duct has outlets for air supply in upland oven. The introduction of air into each hog by two sleeves ending in a furnace distribution grid, which is divided into a number of small streams. In the event of a power outage provides air supply injector.

Couple on the stove is fed through the pipeline, which has two branches each semi furnace and equipped with valves for switching steam. Steam consumption is monitored pressure gauge and flow meter.

Parameters of the oven:

1. The temperature activation (as inside oven) 850-980 °C.
2. The temperature at the top of recuperator 1000-1200 °C.
3. The temperature of the bottom of the heat exchanger 250-600 °C.
4. Steam consumption per kilogram of coal, unloaded, 5,6 kg/kg.
5. The pressure in the lounger’s furnace 2-5 mm of water.
6. Air pressure at the inlet to the furnace 60 mm of water.
7. The oxygen content in the gas activation is not more than 0,4 %.

1.3.3 Production of crushed activated carbon by steam activation

Active carbon is produced mainly from coal processing raw hard wood, as well as coal char (KAD). The industry received coals BAU, APM, OC, MD and TCF.

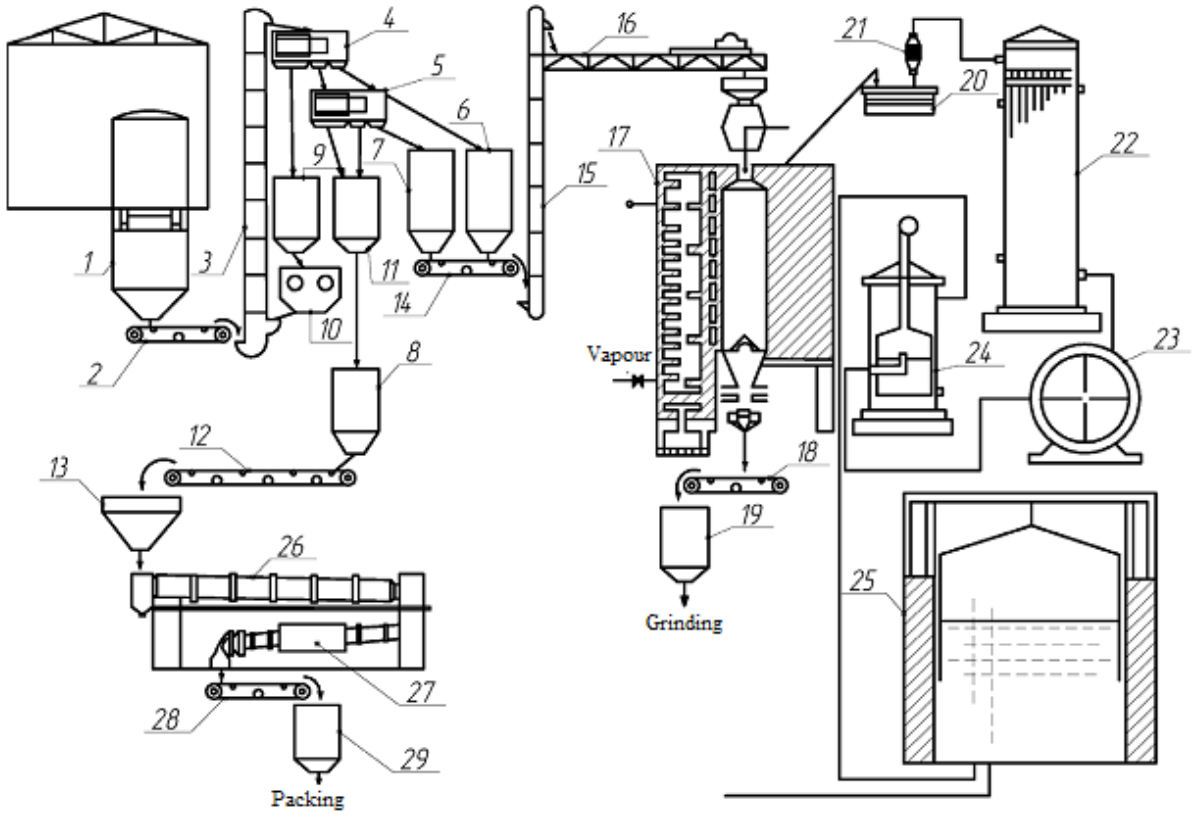
The raw material for the crushed coal BAU serves as coal Raw brand TL - Charcoal. It must meet the following requirements: less than 1 % of ash content; at least 3 % of content of volatile; less than 10 % of humidity.

Typical technological scheme of crushing AC shown in Fig. 1.19 and includes the following steps.

Coal raw silo 1 conveyor belt 2 and elevator 3 is fed to the vibrating crash 4, which is exposed preliminary sorting, magnetic removal of impurities of iron, and then screening for Screen 5 into three fractions: 1 mm; 1,10 mm and 10-25 mm. Coal with a size pieces of 25-100 mm is fed into the silo with a screw gate 6, size 10-25 mm in silo 7, and 1-10 mm in silo 8. A large fraction (100 mm) is fed to the crusher 10 and returns on scattering. Carbon dust (with a particle size of less than 1 mm) is sent to the tank waste 11. small fraction of the silo 8 conveyor belt 12 is fed into the hopper 13 of the rotary kiln activation.

Activation. Wood coal conveyor belt 16 is loaded into three breakout batchers on furnaces. Loading devices coal raw fed to the activation chamber furnaces activation 17. Appearance chamber furnace activate shown in Fig. 1.20. For the production of BAU the median fraction. A large fraction is used for the production of lighting coal, (compared with coal BAU) has a high sorption capacity and total porosity. Activation is performed by steam at a temperature of 850-900 °C in chamber furnaces with external heating. Chamber furnace with external heating is a brickwork with six grocery cameras immured in it.

On the front of the oven are tube superheater, the opposite side is the primary heat exchanger. The bottom of the product chamber is distributing cone when supplied steam. Each oven cavity located between the two firing channels. At the top, before loading device two chambers are interconnected. Dimensions product chamber: length is 1,3 m, width is 0,15 m, height is 5 m.

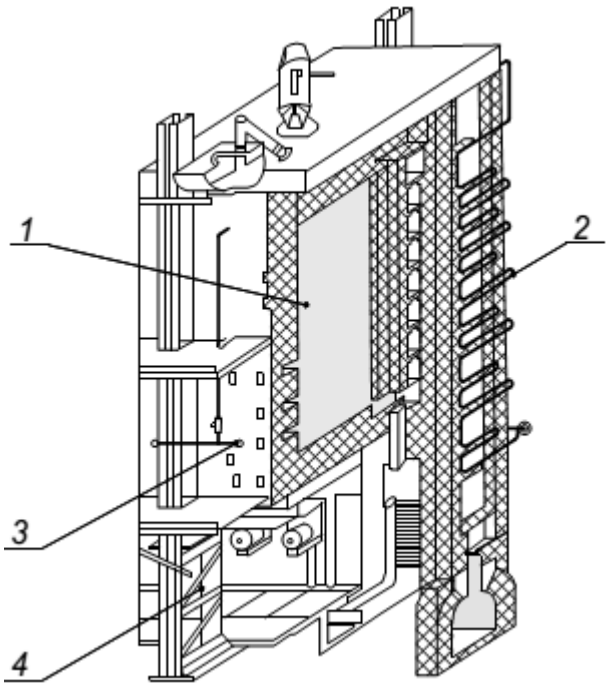


1, 9, 13, 19, 29 – bunkers; 2, 14, 16, 18 – a conveyor belt 3 – elevator; 4, 5 – vibrating screens; 6,7,8 – silos; 10 – crusher; 11 – bunker for wastes; 12 – belt; 15 – elevator; 17 – activation; 20 – hydraulic valve; 21 – scrubber; 22 – upright refrigerator; 23 – Blower; 24 – foam scrubber; 25 – gasholder; 26 – rotary kiln activation; 27 – drum refrigerator; 28 – conveyor.

Fig. 1.19. **Technological scheme of crushed activated carbon.**

Coal being loaded, with distribution cone is distributed on two cameras. Heating chambers held combustion of gaseous fuel that enters the distribution channel. The air supplied to the burners through the air channel heat exchanger where it is heated by the heat of the flue gases. Air from the channels of the primary heat exchanger enters the channels of the secondary heat exchanger located in a narrow gap between the primary heat recovery and proper stove. It

happens the final heat air to a temperature of 450 °C before feeding to the burner located at the bottom of the firing channels.



1 – system product chambers and firing channels; 2 – tube superheater;
3 – distribution cone steam; 4 – fasting dispensing.

Fig. 1.20. **Chamber furnace for activation.**

Warming gases pass furnace space upwards, changing its direction six times, then leave the furnace room, leaving a smoke channel heat exchanger. With flue channel heat exchanger gases through forests and chimney emitted into the atmosphere. Water vapor from vapor transport network enters the superheater located in flue channel heat exchanger and superheated to a temperature of 250-300°C state is fed into the chamber under a cone at the bottom of the camera. Some vapor enters the cooling coal and bulk couples – activation. Water vapor, passing through a layer of coal charge, reacts with hot coals and gases activating consisting of CO_2, CO, H_2 and CH_4 are displayed using the exhauster at the top of the chamber through hydraulics and a refrigerator in the hardware

department. During his stay in producing chambers coal successively passes through zones: drying, which is freed from moisture by the heat of exhaust gases activation; carbonization, which at 450-700 °C from coal raw in the form of volatile distilled tar and gaseous products; activation, which in interaction with charcoal, heated to 750-900 °C superheated steam, is the development of porosity and formation gas activated; cooling the heated coal superheated steam to a temperature of 300-400 °C, followed by cooling to 90-110 °C in handling cones and tank.

Terms activated, temperature activated 850-900 °C; temperature firing channels 1100-1200 °C; total flow of superheated steam to activate 280-290 kg/h of cooling 10-15 kg/h; burnt carbon 60 %; the pressure in the product chamber 5-15 mm of water; craving a flue channel heat exchanger 7-10 mm water column; pressure heating gas (gas activation) supplied to the burners, 6-10 mm of water; shipment of coal from the cameras 100-140 dm^3/h every half hour, loading coal raw immediately after unloading.

The cooled cake mix is discharged opening gate on the conveyor belt 18 and the intermediate hopper 19, and then sent to the department of crushing.

Gas produced in furnaces activated by the interaction of water vapor with carbon passes through the system, the hydraulic valve 20 – scrubber 21 – upright refrigerator 22 and enters the hardware department using blowers 23 through the foam scrubber 24. After water seal gas is fed into the gasholder 25 where gases are activated sent to burning oven compartment.

Charcoal with a particle size of 1-10 mm through the gateway feeder from a silo 8 is fed into a rotary kiln activation 26, which is activated by steam at 850-900 °C. Active carbon temperature 750-800 °C camera discharge enters the drum refrigerator 27, further conveyor 28 goes into the hopper 29 from which the finished product is packaged in bags.

After the furnace coal conveyor belt is fed into the storage hopper and through Gates – a drum mill, which is crushed into pieces of 20 mm. With the mill coal on fed channel to the dispersion, which is divided into fractions 0-1 mm 1,0-3,5 mm and 3,5 mm. Fraction of more than 3,5 mm arrives for additional grinding. Working group of WAU – 1,0-3,5 mm. Coal coke fed into the ball mill and crushed to powdered coal is used for active coal of MD. Finished fraction 1,0-3,5 mm comes to packaging.

Technology for lighting coals OC-A and OC-B is almost identical to the production of coal WAU, except for their production of a larger fraction of medium (20-50 mm) and large (50-100 mm), nut, and additional stages of grinding in ball mill and leach for OC-B.

Grinding medium and large nuts fraction less than 5-10 mm is carried on the roller mill from which by channel enters the drum ball mill. Grinding coal carried wooden or Bakelite balls. With the ball mill coal dust sucked fan and is consistently separator and battery cyclone and badly crushed particles by channel returned to the mill. Mixed dust captured by bag filter and with the dust from the cyclone screw feeder fed into the hopper, which is placed in bags and shipped to customers under the brand OC-A.

Brightening coal of OC-B obtained by leaching, washing and squeezing coal OC-A. Coal dust with compressed air (1,5-2,7 bar) pressed out from the batcher into the reactor, equipped with two turbine agitators. The reactor previously filled with water and served spicy steam to heat water to 60-80 °C. Coal dust is mixed with water and coal slurry formed, mixed turbine stirrers, and then pumped into the reactor leaching, which is equipped with a jacket, which served spicy steam to heat the reactor. Loaded into the reactor coal slurry poured hydrochloric acid per soluble in aced ash contained therein. The process of leaching is carried out within

3,0-3,5 hours at a temperature of 60-80 °C and vigorous stirring of the solution in the reactor. After leaching coal slurry repeatedly pressed and washed on filter-press.

The coal paste with a moisture content of not more than 58 % is fed into the hopper, interlocked with automatic scales and filling machine in which sealed a multilayered plastic or laminated polyethylene paper bags and branded OC-B is sent to the consumer.

The filtrate, washings and water chambers regeneration come to filtering unfiltered remaining pulp. Water from filter-press neutralized with a solution of baking soda and discharged into the sewer.

Water used for cooling activation in hydraulics, scrubber and resin separator and contains a number of phenols and tar is collected in the sump, which is purified coagulation of iron (III) chloride, and after squeezing reused in the chilled gas. Water losses due to evaporation is compensated by technical plumbing.

1.3.4 The technology of carbon molecular sieves

Progress in chemical technology allowed to realize based on synthetic zeolites – molecular sieves (MS) molecular separation processes by critical dimensions, cleaning and drying gas environments, obtaining compounds of high purity, short cycle adsorption without heating etc. Unfortunately, the obvious advantages synthetic zeolites substantially offset their shortcomings, which include: poisoning water vapor, which excludes their usage in wet environments and high catalytic activity towards organic compounds. Unfortunately, the obvious advantages synthetic zeolites substantially offset their disadvantages, which include: the ability to poison water vapour, which excludes their use in wet environments and high catalytic activity towards organic compounds.

In order to address the deficiencies of mineral MS have developed technology for carbon molecular sieves (CMS) based on different (mostly two) types of raw

materials and, consequently, methods of their received. In the first case is used as a raw material industrial activated carbon (AC), which is subjected to mechanical grinding to suppress transport porosity of subsequent secondary forming and heat treatment and the establishment of the outer surface of the shell polymer granules with a given permeability. The second uses a uniform composition, molecular structure and spatial raw materials (synthetic polymers), heat treatment and subsequent activation by mild oxidizers ensured formation developed uniform microporous structure fixed to the availability of critical molecules with different size.

With rare exception, the CMS used in the production of synthetic polymers which provide (compared to fossil plant and materials) a high degree of homogeneity of the raw material.

Synthetic polymers used for this purpose must meet the following requirements: have a high uniformity of molecular fragments of synthetic material; characterized by a high degree of thermosetting.

The resulting carbon residue after heat treatment processed at temperatures of 700-750 °C steam or carbon oxide (IV) to burning, the value of which regulates the accessibility of the internal volume of the skeleton and determine, respectively, the type of CMS. Burning limit values typically do not exceed 10 %, followed by their changes in the degree of accessibility volume of adsorbing porosity presented in Table 1.22 based industrial phenol – formaldehyde resin (PFR).

The fundamental technological scheme of crushed CMS shown in Fig. 1.21.

Raw resole phenol-formaldehyde resin is placed to mixer, which is equipped with a heating casing and blade-type agitator. Upon reaching a mixing temperature 60-80 °C, the resin with constant stirring slowly fed dibutyl phthalate (DBP) as a plasticizer. Mixing of resin with a plasticizer carried out to obtain a homogeneous

composition. The resulting resin composition and DBP evenly placed on the decks of a given layer thickness.

Letters are transferred to the electrical equipment; which composition solidifies at 180 °C for 24 hours in obtaining CMS-6 (0,6 nm). Warming up to the desired temperature thermo– hardening (depending on the type of resin, plasticizer and CMS) is performed with the rate of temperature rise of 15 to 80 °C/h.

The obtained after thermal hardening of flat polymer blocks are subjected to grinding roll crusher, crushed labor fractions of 1,5 to 3,0 mm. Fines and dust collected in the process of scattering as recycle, returns to the stage of mixing.

The selected fraction of the polymer is subjected to heat treatment in a muffle furnace drum with external heating slow heating to 750-800 °C, heating rate not exceeding 80°C/h.

Activation is performed in an atmosphere of steam at a temperature of 700-750 °C for 24-60 hours. The duration of activation determined by the type obtained CMS. After activating the CMS in inert atmosphere cooled to normal temperature and subjected to screening to narrow faction: I – 0,5-1,0 mm; II – 1,0-1,5 mm; III – 1,5-2,0 mm; IV>2,0 mm. After checking the molecular sieve properties of a model for a mixture of methanol, benzene and isooctane obtained CMS classified by type, defined linear size and is sent to the consumer.

Extraction of modifier carried water with a temperature of 70-80 °C to a residual phosphorus content below 0,1 % by weight. Previous granule drying occurs at a temperature of 105-110 °C for 30-35 minutes.

During carbonization temperature in the combustion zone of gas maintained in the range of 550-700 °C, the temperature at the exit of the product from the drum – 500-650 °C, the time of the pellets in the furnace is 2-2,5 hours, and the yield is 46-52%.

Activation is performed in the shaft furnace to the point of burning ~30 % accompanied by a reduction apparent density of 0,99-1,07 g/cm^3 to 0,76-0,78 g/cm^3, which results in carbon adsorbents with advanced volume adsorbing porosity in the range of 0,33 to 0,40 cm^3/cm^3. Then, the packaging and the formation of parties finished product take place.

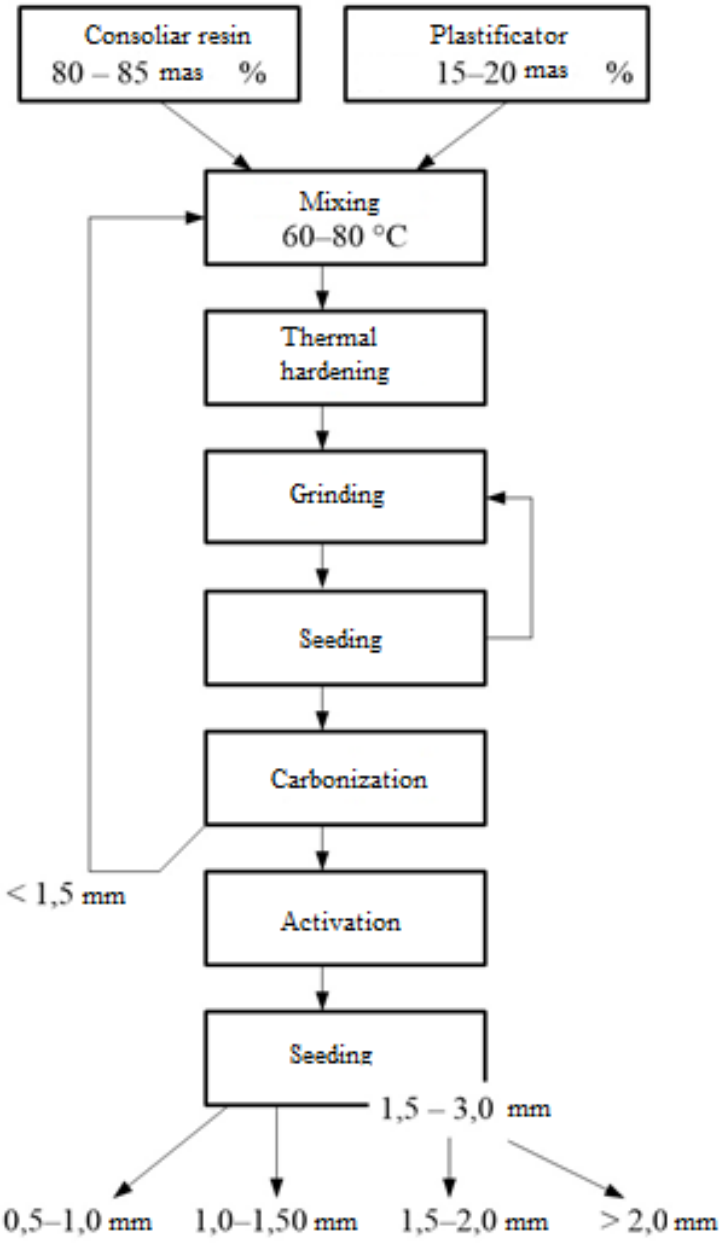


Fig. 1.21. **Principal scheme of the CMS.**

As an example, in the Table, 1.22 given parameters of porous structure of the Japanese industrial materials (MSC) and domestic (CMS) production, and Table. 1.23 – their molecular sieve properties for a model mixture ($CH_3OH+C_6H_6+iso–C_8H_{18}$), which is measured at the time of protective action to breakthrough concentration in the adsorbent layer from the original 0,001 ($q^{0,001}$).

Table 1.21. **Changing the limit adsorption space volume (*W_0*, %) and time of protective action *(q*, minutes) of CMS with CFF for molecules with different critical size (nm) in the progressive activation**

Burnt *W_0*, %	He, (0,22) *	H_2O, (0,38)	CH_3OH (0,44)	C_6H_6, (0,58)	C_6H_{12}, (0,62)	Iso-octane (0,67)	CCl_4, (0,68)	*q*, min	
								Ben-zene	Iso-octane
0,0	0,49	0,39	0,19	0,09	0,02	0,02	0,02	–	–
1,1	0,57	0,41	0,20	0,10	0,02	0,02	0,02	14	0
2,2	0,52	0,44	0,21	0,13	0,04	0,03	0,03	21	0
3,3	0,54	0,46	0,25	0,19	0,05	0,04	0,04	48	1
6,5	0,56	0,49	0,26	0,23	0,15	0,13	0,14	58	5

* in parentheses indicate the size of the adsorbed molecules

Table 1.22. **Options porous structure of foreign samples CMS (Japan) and domestic production**

Samples BMC	*δ*, g/cm³	*d*, g/cm³	V_{mic}	V_{mes}	V_{mac}	E_0, kJ/mol
			cm³/g			
MSC-A	1,10	1,80	0,21	0,00	0,13	–
MSC-5A	0,90	1,80	0,38	0,00	0,18	–
MSC-B6A	0,88	1,80	0,38	0,00	0,21	–
MSC-C7A	0,86	1,80	0,38	0,00	0,23	–
Crushed CMS	0,80	1,12	0,14	0,01	0,21	25,08
Granular CMS	1,00	1,61	0,19	0,01	0,18	25,91
Spherical CMS	0,95	1,72	0,26	0,02	0,19	25,49

Table 1.23. **Molecular sieves properties during separation of the components of the model mix samples of carbon molecular sieve (CMS)**

Molecular sieves	Defence time ($\theta^{0,001}$), min		
	CH_3OH	C_6H_6	C_8H_{18}
MSC-A	20	Instantaneously	Instantaneously
MSC-5A	61	76	Instantaneously
MSC-B	35	168	Instantaneously
BMC-4A	4	Instantaneously	Instantaneously
BMC-6A	21	172	Instantaneously
BMC-7A	14	163	54

3.5 Production of activated carbon from fossil raw materials

Company «Kalhon Carbon Corporation» (USA) – one of the oldest and leading companies in the world in production of activated carbon. The combined production capacity exceeding 100 tons/year. The main production is located in Pittsburgh (PA), which comes to 50 thousand tons/year of coal from fossil raw materials and from 20 to 30 thousand tons/year reactivated after usage [1].

The corporation also includes the company «Hemviron» (Belgium), which produces up to 20 thousand. Tons/year of carbon adsorbents with bituminous coal and coconut shell, and the company «Degussa» (Germany), which produces up to 10 thousand t/year of coal from peat and wood.

The company does not provide active carbon bulk and manufactures tools and systems based on them, installation and maintenance, replacement and refurbishment and recycling of waste material systems. The cost of reactivation of coal that is used to absorb nontoxic substances without noticeable loss of quality does not exceed 75% of the cost of fresh carbon. [1]

As the initial raw materials used in the production of AC bituminous fossil coal vitrinite content of 8 %, 5% humidity; VOC 27-39%, 0,5% sulfur, 3,0% ash; with a melting point of 137 °C. The composition of the original formulation comprising 94 % bituminous coal and 6% coal tar pitch, which is used as a binder

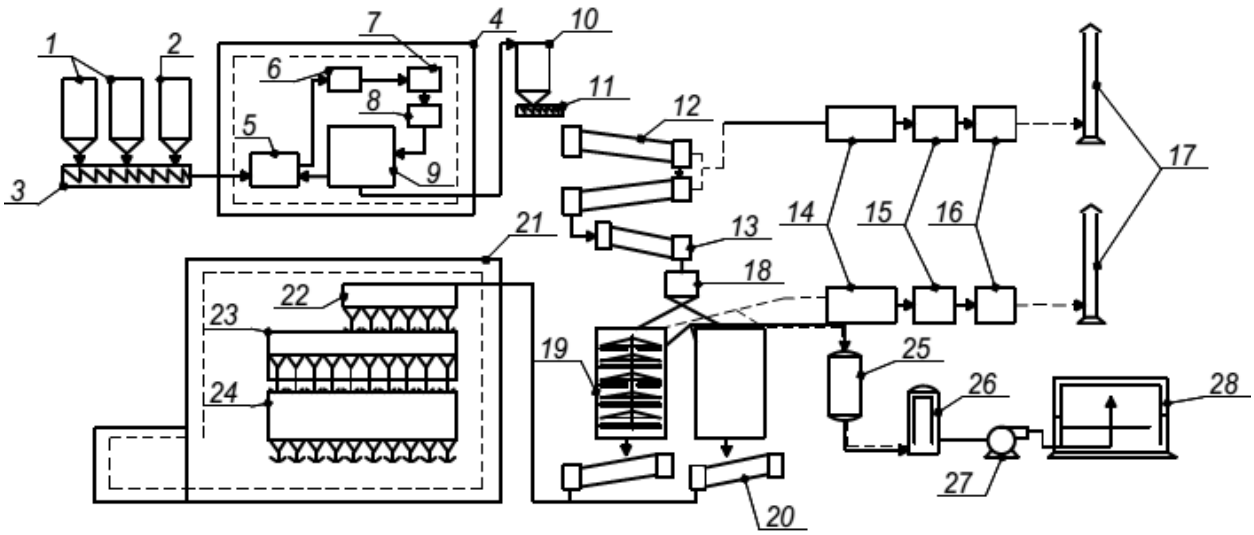
and 10% of retro. Production is based on the use of common technology modules unit capacity to 10 thousand Tons/year of finished product.

Receiving, processing and moving food redistribution carried out by continuous technological scheme, excluding their contact with the environment in complete sealing equipment. Operating unit's flowsheet is in full automatic mode.

Flowsheet is shown in Fig. 1.22 and includes the following steps.

1. Preparation the original recipes and a working faction. Outputs: bituminous coal and coal tar pitch in a weight ratio of 94:6 from bins 1 and 2, the screw feeder 3 serves the inner cavity ring centrifugal mill 5. The resulting composition of the mill goes to heating in termal furnace 6, which is sent to the briquetting for thermal rollers 7. Obtained at 150 °C and a pressure of about 100 MPa briquettes are crushed in roll crusher 8 and dispersed fractions: 0,5-6,0 mm is working, and less than 0,5 mm of retro returned as a mill 5. From department training materials 4 obtained fraction goes into the hopper 10 carbonization furnaces.

2. For two consecutive heat treatment used in the course of product connected rotating muffle furnace length of 50 m, providing a smooth and slow heating the material to 900 °C without direct contact of the coolant and product. The latter contributes to a strong skeleton raw coal highly reactive carbon containing materials. The working group from the hopper 10 by screw feeder 11 fed into the inside of the first drum kiln 12 passing by, goes into the second. The output from the second furnace hot product enters the cooling drum 13 where the temperature drops to normal, and then sealed in the pipeline goes into the hopper 18 furnaces activation.



1, 2 – bunkers; 3 – screw feeders; 4 – department of fragmentation; 5 – centrifugal mill; 6 – thermal oven; 7 – thermal rollers; 8 – roller crusher; 9 – vibrating sieves; 10 – hopper; 12 – drum furnace; 13 – cooling drums; 14 – post- combustion furnace; 15 – boiler; 16 – wet scrubber cleaning; 17 – stack; 19 – Hereshof's furnace; 21 – separation of the scattering; 22 and 23 – sieves; 24 – packaging.

Fig. 1.22. **Technological scheme for activated carbon**.

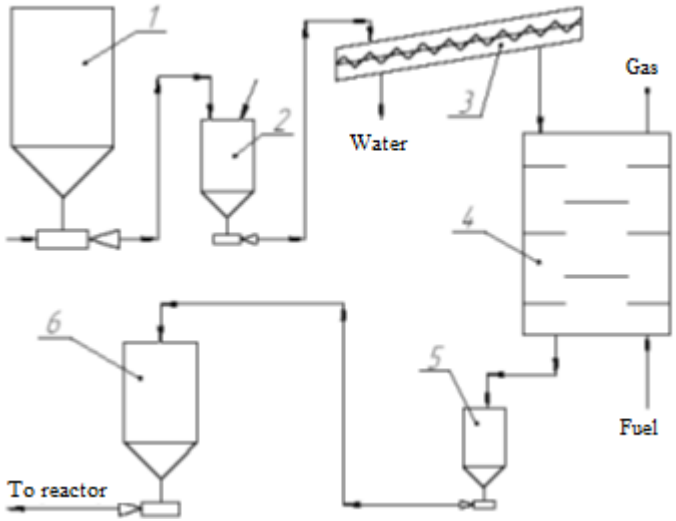
Volatile degradation products from the internal cavity furnace sent to afterburning furnace 14 and then with the flue gases out of carbonization furnaces 12 entering the boiler 15 for heat recovery. After the boiler flue gases, be processed dispersed solution of soda in a scrubber and wet cleaning 16 through chimney 17 are emitted into the atmosphere.

3. To enable use modernized coal mines rotary kiln 19 Hereshof's cylindrical shape (diameter about 6 m and a height of 18 m). In internal cavities shelves are gas burners, thermal management modes which makes a computer that provides highly accurate temperature control. The duration of the product in the oven is from 3 to 24 hours, after which the coal enters the cooling drum 20 after which sent to the department dispersion 21. Performance of Hereshof's furnace is at least 5000 tons/year.

At the stage of dissipation and package involved the largest number of personnel, as her gather all the material flows of all process modules. The stage is fully automated, provides complete sealing sieves 22 and 23, pipeline operations 24 packaging and packaging devices, and additional insulation space 21.

On the 50 tons/year of coal produced about 10 thousand. Tons processed acid to reduce to the minimum coal ash.

Along with the main manufacturing industries AC held on reactivation of the spent carbon. The scheme of technological reactivation shown in Fig. 1.23.



1 – bunker; 2 – feeding box; 3 – draining screw; 4 – reactor;

5 – extinguisher; 6 – multi cyclone.

Fig. 1.23. **Flowsheet reactivation of the spent carbon adsorbent.**

1.3.6 Getting active carbon by chemical activation

When a carbon adsorbent by steam activation as a starting material used non activated carbon (NAC), porous structure is formed in the process of receiving it. The development of porosity in coal raw implemented as a result of its interaction

with gaseous activating agent. This process runs mostly illegally and cannot be accurately regulated in the desired direction [11].

When activated inorganic substances influence unresolved exposed organic matter that provides the ability to manage the activation process since the beginning of formation of carbon skeleton structure until its completion. Unlike steam activation, in which case the activating agent is evenly distributed throughout the mass of the material and its influence on the processes occurring in the material, manifested at all stages.

In the heat treatment of any carbon-containing material at the initial stage of decomposition there arise a large number of crystallization centers. The simultaneous occurrence of a large part of crystallization centers, limited their growth and release of gaseous substances leading to the formation of the porous carbon skeleton.

In the presence of inorganic trigger, the formation of porous carbon structure runs within the space, occupied by the products of decomposition of organic matter and the activating agent, so the formation of structural elements carbon and combinations between them depends on the number, mobility and reactivity of molecules and ions activating agent.

The quality of this method of carbon adsorbent determined by three main factors: the properties of the original material carbon-contain, physical and chemical characteristics activating agent and activation conditions.

Carbon-containing materials are used as initial raw materials must meet the following requirements: characterized by a low degree of ordering of the material; differ sufficiently reactive inorganic activator respect, both during the formation of his song «inorganic carbon – activator» and during subsequent heat treatment.

Modes activation should provide rush the process in terms of contributing to increased yield and carbon residue formation as less volatile, and the formation of a strong skeletal carbon adsorbent.

The role of activating agent in this method of obtaining carbon adsorbents decisive. Inorganic activator in the process of treating the common source material simultaneously performs several functions directly or indirectly determines the quality of the carbon adsorbent.

From the point of view of thermal physical activating agent helps equalize the temperature of the mass of material reduces the effect of exothermic effects in the process of decomposition, and regulate the rate of heating and gassing. Chemical function activating agent lies that affect the performance of processes of degradation, poly condensation and polymerization, it increases the output of coal residue gas emission reduction and release of volatile products in the form of compounds with low molecular weight. Structural role consists in that the activating agent with the introduction of the starting carbon-containing substance gives it plasticity and ability to form forming composition; promotes the formation of primary structural elements strictly ordered structure and small size; sent affects the spatial orientation of primary structural elements to form a homogeneous microporous structure, the size of which can be adjusted number entered inorganic activator.

In view of the above, a substance that is selected as inorganic activator must meet the following requirements. Must have high solubility, which enables a wide variation of concentration of impregnating solution; low melting point and a high boiling point and a small difference in the transition temperature from a solution, bypassing the solid to melt; the ability to form the starting material of the plastic composition is easily formed; be available, nontoxic, safe from a technological and environmental standpoint.

The development of the volume of micropores is able to provide only the inorganic activators which retain mobility since the beginning of formation of the structure until its completion.

The inorganic materials of plant origin (peat, lignin, waste wood, shell nuts and fruits) and brown coal with high vitrine content was using as a starting material in the activation.

Quantitative characteristic activation inorganic substances are impregnated ratio, defined as the ratio of inorganic activator (M_{min}) to dry weight (without ash) carbon-containing material (M_{ccm}):

$$\alpha = M_{min}/M_{ccm}.$$

As activating agents to best match the requirements set forth above, satisfy metal halides groups I and II, and hydroxides and alkali metal compounds sulfur content. The research activity of metal chlorides group I confirmed a clear dependence of the volume of micro pores of solubility, melting point and coefficient of impregnation. However, their activating ability is relatively small, due to a change in the physical state of these salts in the early stages of coal formation of the skeleton and the transition of the solid phase. By activating ability chloride (group I) placed in the following order: CsCl > RbCl > LiCl > KCl > NaCl (Fig. 1.24).

Activity of inorganic activator depends on its solubility, thermal stability and melting point. For typical chloride group II selective development of certain kinds of pores (Fig. 1.25).

Chlorides subgroups Zn (Zn, Cd, Hg) micropores develop a much greater extent than the macro pores, while for chlorides Ca, Mg, Sr and Be characterized by the development of the total volume mainly due to the development of macro pores. This is directly due to increased solubility and reduce the difference between the melting temperature of the salt and the transition from an aqueous solution of salt in the solid state of aggregation.

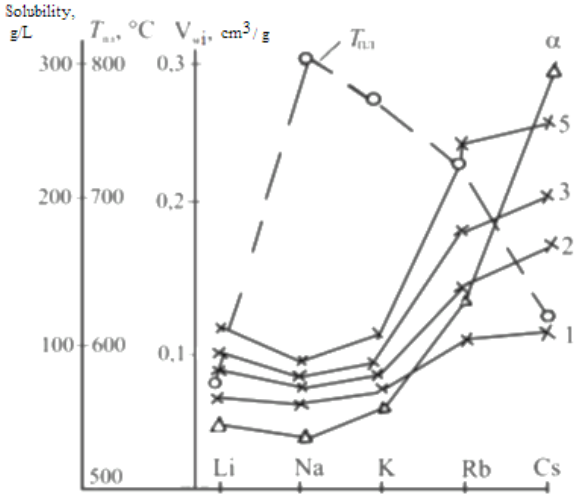


Fig. 1.24. **Dependence of the micro pores volume on the physical and chemical properties of metal chlorides in group I and coefficients of impregnation.**

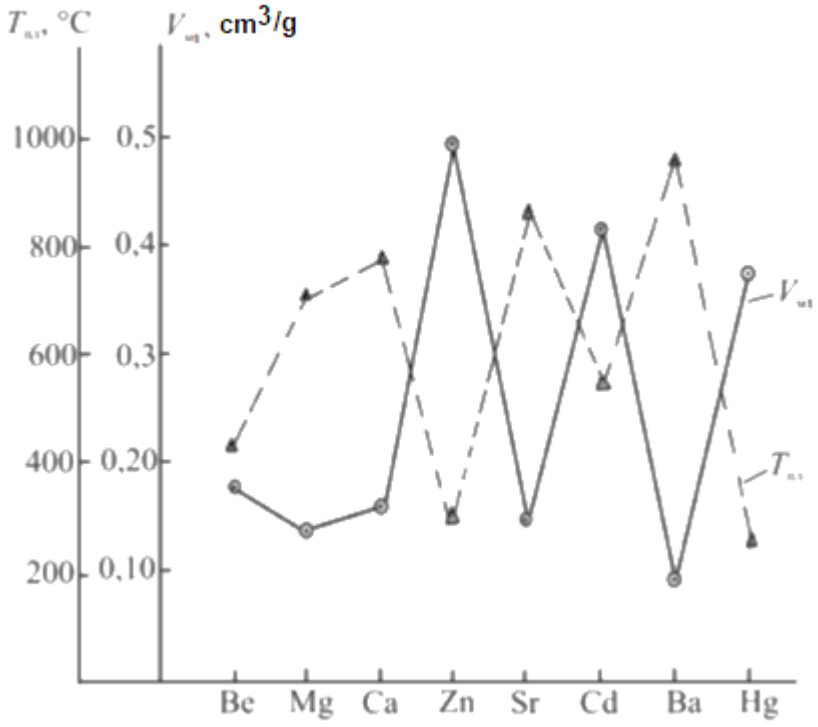


Fig. 1.25. **Dependence of the volume of micro pores on the physical and chemical properties of metal chlorides in Group II (T_m).**

In this subgroup Zn chlorides develop 3-5 times greater volume of micro pores than chlorides subgroup Ca, and 6-8 times greater than the volume of micro pores to NAV. As the degree of specific volumes of micro pores are as chlorides number: $ZnCl_2$ > $CdCl_2$ >> $HgCl_2$ > $BeCl_2$ > $SrCl_2$ > $MgCl_2$ > $CaCl_2$. In the production of carbon adsorbents with plant material and the use of inorganic activators preferred zinc chloride.

The high solubility and low melting point alkali metal hydroxide determine their high activating ability. However, when used as inorganic activators to consider possible transformations they can undergo during thermal decomposition of carbon–containing materials.

In the modified alkali heat treatment carboxylic raw carbon (IV) oxide released in the early stages of expansion, even before the complete evaporation of water, reacts with hydroxide to form carbonates, and alkali activating action will be determined by the properties of carbon dioxide salts. The high melting point of carbonates drastically reduce their ability to develop microporous structure. Temperatures higher than decomposition temperature of formation of carbonates carbon skeleton, and the amount of carbon (IV) oxide released from raw materials and its activity in these conditions is insufficient for significant volume of micro pores.

Activating ability by introducing alkali raise their composition free of sulfur. The interaction of elemental sulfur with aqueous solutions of sulfur contain alkali metal hydroxides. Sulphur, which is in solution joins Me_2SO_3, forming thiosulfate, and Me_2S, polysulfides form. The formation of polysulfides in aqueous alkali depends on the concentration of base, reaction time, temperature and relative content of sulfur and hydroxide. Thus, the effect of activating solutions of sulfur in the pocket more determined action of sulfur, sulfur compounds and their alkali metal thiosulfate.

Thiosulfate of alkali metals are readily soluble in water and decomposed by heat treatment to form sulfites, polysulfides and free sulfur. Sulfite in treating conditions in the presence of coal, in turn, converted into sulfides, which are readily soluble in water and aqueous solutions of hydrolyzed to form MeHS. When heated sulfide is largely decomposition to form hydrogen sulfide. In the air sulfur metal salts decompose with the release of hydrogen sulfide and polysulfides. Thus, even in aqueous solution is a formation of the following compounds: MeHS, Me_2SN, S, $Me_2S_2O_3$ and several other derivatives of sulfur compounds. Polysulfide of alkali metals are readily soluble in water at low temperatures melt or decompose when heated with the release of hydrogen sulfide and other sulfur form low– melting products.

Study activating action of alkali metal hydroxide and their compounds shown that increasing the concentration of the solution activating agent increases the volume of micro pores per unit weight of coal. By activating properties of alkali and sulphur compounds alkali (Fig. 1.26) are arranged in a row: CsOH+S > RbO+S > KOH+S > KOH > NaOH+S > NaOH.

With increasing concentration of the solution activating agent is a growth pore volume and quality change of volume growth first by WS (mainly due to the development of micro pores), and further increase the concentration of the solution leads to a slowdown WS and increase the volume of macro pores.

Based on the study of basic inorganic activators, used in the production of carbon adsorbents from raw materials of vegetable origin, we can conclude that activation properties of these salts primarily determined by their solubility in water and low melting points, providing the presence of an activating agent in a moving state at all stages of formation of the porous structure of carbon skeleton.

In purely physical-chemical characteristics such as solubility, melting point, the development of specific kinds of pores depends on their chemical activity

relative carbon skeleton in the final stages of its formation. Chemically inert chlorides in the final heat treatment temperatures, sulfur compounds and alkali reactive. For substances entering into chemical interaction with the carbon skeleton of coal, the conditions and the conditions of heat treatment process significantly affect the structure of coal produced.

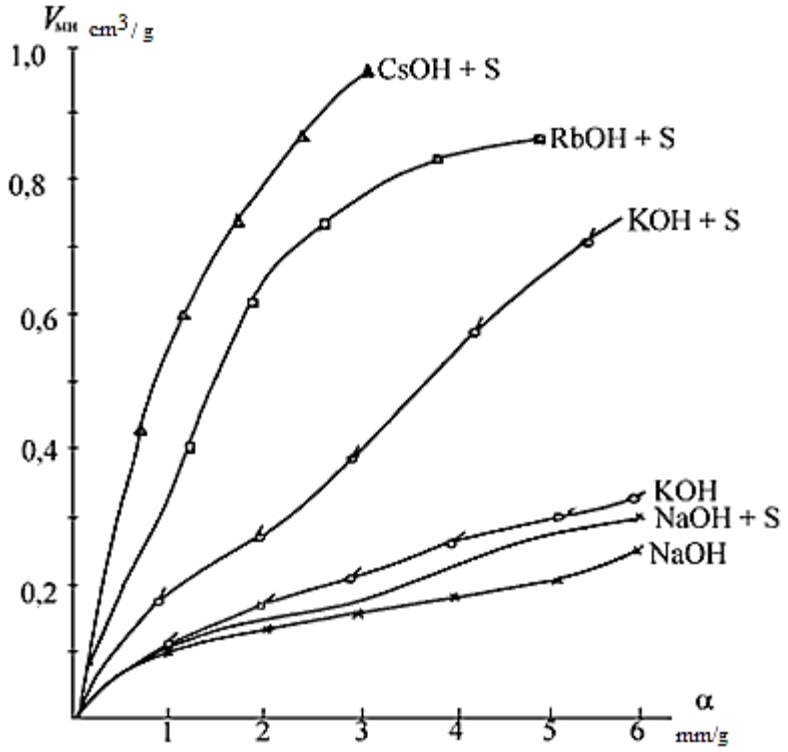


Fig. 1.26. **Activating properties hydroxides and alkali metal sulfur compounds.**

Increase heat treatment temperature from 450 to 750 °C virtually no effect on the apparent density and pore volume of coal obtained from $ZnCl_2$ activation, while the sulfur compounds to potassium rise in temperature leads to a sharp drop in apparent density while maintaining a constant volume of micro pores per unit volume of coal. Further increase in heat treatment temperature of 750 to 950 °C in the case of sulfur compounds is accompanied by a sharp decrease in apparent density and volume of micro pores.

For carbon adsorbents (the apparent density which are within 0,76-0,65 g/cm^3) obtained using zinc chloride and sulfur compounds of potassium, differences in values of typical varieties pores practically not observed. Changing the terms of activation, which reduces the apparent density of the resulting carbon below 0,60 g/cm^3, accompanied by increased volumes of macro pores, a decrease in the volume of adsorbing porosity and a sharp drop in strength.

Optimal conditions for activation are to receive carbon adsorbents with plant material with high strength and adsorption characteristics are achieved at values of coefficients for treatment of zinc chloride within 0,6-0,8 g/h sulfur compounds and potassium – 0,30-0,35 g/h of heat treatment at temperatures in the range of 450-800 °C.

1.3.7 Production technology of peat adsorbent by sulfur-potassium activation

Activated charcoal type SPT (sulfur-potassium peat) produced by chemical activation of carbonaceous material (CAM) based on peat. As the activating agent used in sulfur solution of potassium hydroxide. Production AC is produced by extrusion and granulation of paste, which prepared from the pre-shredded peat and potassium sulfide solution, followed by heat treatment of granules, washing from inorganic activator and mineral impurities, drying and additional steam activation.

Production of SPT active carbon consists of one process stream, located in two cases. In the first case (I) the crushing of peat is carried, dissipation of milled peat, preparing of pastes and its pressing, drying the wet granules, carbonization and activation; in II – leaching, treatment by acid, pre-drying, calcination or additional activation, scattering, packaging and installation for neutralization of sewage.

Granulated active coals SPT is a cylindrical pellet with different diameters from 1 to 5 mm and the length is 1-3 mm.

The lump or milled peat, that meets the following requirements: ash content – not more than 6 %, the degree of expansion is at least 28 % humidity is less than 50 % are used for the type SPT of coal producing.

In the technological process, the peat is loaded into one of the roll crushers via conveyor and then chopped into pieces with size of 40-60 mm, roll crusher conveyor's belt is fed into the crusher hammer– mills. In the hammer crushers, peat is shredded by planting shaft saws, which have rotating speedis 2900 rev/min. After this step, peat is fed to the vibrating sieve by plate feeder. The vibrating sieve has a mesh woven with cell size from 0,9 to 3,5 mm, and then sent to the mixer.

The solution is prepared with the following calculation: potassium is 250-450 g/dm^3, content of sulfur is 125-225 g/dm^3. The density of working solutions of potassium sulfide is between 1,30-1,50 g/cm^3.

The mixing of milled peat with a solution of potassium sulfide held in a special unit – the mixer. The main aim is obtaining a homogeneous doughy paste, suitable for extrusion and granulation. Mixer consists of a rotary basket, which is mounted on the frame. Basket is equipped with a steam jacket for the paste heating. It helps to improve the chemical interaction solution of potassium sulfide with peat.

The recipe of paste for different grades of coal is located in different ranges. For the coal without additive of coal dust, the amount of activating agents which are entered into a paste (for 100 parts of dry peat) is 19-22 parts by weight of potassium and 9,5-11 parts by weight of sulfur.

For achieving coal with good porosity and high dynamic activity for benzene vapors (grade A). Dose of potassium and sulfur must be increased, and injected amount of coal dust- decreased. For more fine-coal high bulk with higher density and mechanical strength (grade B). The dose of potassium and sulfur should be lower, and coal dust-higher. More accurate values recipes are selected depending on the type and quality of peat.

In the process of producing the paste type SPT, into the mixer periodically added calcium (II) chloride at a rate of 1.2 parts by weight of calcium per 100 parts by weight of dry peat. The main reason is reducing the content of silicon (IV) oxide in the liquor in the recycle liquor.

The pressing of pasta is made in horizontal or vertical hydraulic presses. Pasta with receiving trough auger fed by channel cylinder through-socket (rollers) in pastouch press, which sealed rotating rolls. Filled pasta manually fed by the plunger head and empty – Handguns (rollers), which is filled with paste. Pressed paste through the holes in the hard filer thread is under pressure 100-200 atmospheres.

Fillers made from solid alloy tool steel or porcelain. To produce different grades of activated carbon are used filers with a hole diameter: 1,5-1,7 mm for grades SPT-6 and SPT-7 and 2,0-2,5 mm for SPT-2 and SCT-4.

After pressing the paste filaments obtained are fed to a horizontal conveyor belt, then on the inclined conveyor belt. For transportation to the drying drum crashed thread. To reduce the load on the oven of carbonization raw granules dried. An inclined belt conveyor and horizontal conveyor gear pellets fed through a loading funnel in a rotary drum dryer with a diameter of 1,6 m and a length of 10. Drum rotation speed of 3,15 rev./min. Dryer provided shovel-sectoral cap and set at an angle of 2° to the horizontal with a slope toward the discharge. Drying granules held combustion of natural gas diluted with air. Coolant temperature less than 700°C is fed into a loading head and moves forward flow of granules.

The temperature of the gases at the outlet of the dryer does not exceed 150 °C. Time of pellets through the dryer is 30-35 minutes. Wood at the outlet of the dryer must have a residual moisture content not exceeding 20 %.

Wood drying drum with pneumatic fed into a cyclone, located under the oven of carbonization.

Since the cyclone through sectoral pellet feeder to enter the oven of carbonization. It is lined rotating drum enclosed in head still lined with loading devices. The length of the drum is 16 m, internal diameter is 1,19 m, the speed is /min.

The furnace is set at an angle of 2° to the horizontal with a slope toward the discharge head. Heating pellets made gas activation and flue gases emanating from burning natural gas burner. Movement granules and gases on the principle countercurrent direct contact with them. Temperature measurement is performed at three points using a thermocouple connected to a galvanometer. One point is installed on a rotating part of the furnace, and the last two in the still. The temperature at the first point (zone combustion gas) is 550-700 °C, the second point (the output product from the drum) is 500-650 °C and a third point (the output of gas loading head) is no more than 250 °C. Lowering the temperature below the lower limits of the mounting leads to deterioration of porosity of activated carbon, and raising the temperature above the upper limit – weakening coal, but the safety of the process is not affected. Time of pellets in the furnace within 2-2,5 hours.

In the process of passing the granules over the entire length of the furnace occurs thermal decomposition of organic matter in the presence of potassium (I) sulfide. This removes residual moisture and volatiles out as light and heavy straps. On average, 1 kg of dry granules released: H_2O 0,24 kg, 0,035 kg of tar and 0,24 kg carbonization gases containing: 47-54 % CO_2; 6 % CO; 11-18 % CH_4+S_nN_m; 15-22 % H_2; 5-11 % H_2S; 1 % of N_2.

Thus, the carbonization process is carbon saturation of the product and begins the formation of the porous structure of coal. Residual volatiles in the granules after carbonization is 8-15 %, 23-30 % of potassium, sulfur is 6-11 %.

Wood struck after carbonization furnace, coming through the handling head in gutter, where a sectoral feeder gutter sent to the furnace activation.

Activation carbonated beads made in a horizontal rotary muffle furnace, which is a rotating drum unloading the boot and heads. Inside the drum has a refractory lining heater with twelve channels. Muffle heated combustion of natural gas. Gases removed from muffle activation through the loading head and sent into the oven of carbonization.

Hot flue gases move in firing channels, giving its heat through the walls of muffle product. Temperature control is carried out by means of thermocouples registering galvanometer. At the exit gas temperature should be 790-860 °C, in the area of activation is no more than 600 °C. Temperature control is performed by increasing or decreasing the air supply and gas combustion.

Moving product off muffle and gas that heats it in gas channels being counter. Time of pellet stove through activation of 4 hours. Wood after activation depending on the recipe pastes containing 24-32 % of potassium, 6-11 % of sulfur and 10 % of mineral elements.

The cooled pellets through a loading hopper fed directly into the hopper pneumatic separation and washing.

Column leaching is a vertical cylindrical container, equipped with top-cam motor driven central shaft passing through the central axis of the column. On the shaft impaled «plates», which provided an opening for the passage of the liquid phase and cut to adhesion of granules. Leached granules discharged from the bottom of the column and hydraulic water fed to the column laundering.

After leaching and laundering of water contained in coal, potassium ~7%, ~1,5% of sulfur, ash ~11-14%.

On the water column hydraulic washing of pellets fed to the column acid treatment. The column is enameled inside surface which prevents corrosion of structural elements. In the bottom of the column fed is 5 % of solution of hydrochloric acid. Since acid treatment column beads hydraulic water fed to the

column washing. The washed pellet from the last column are fed to the conveyor and elevator further to dry.

Dryer is a metal drum set at an angle of 2° to the horizontal with a slope toward the unloading of the boot and unloading heads.

Coal drying is carried flue gases obtained by burning natural gas in a remote furnace served in boot dryers head and move forward flow. Flue gas temperature at the outlet of the furnace is less than 700 °C, at the entrance to a loading head is no more than 600 °C, the passage of material through the dryer 0.5 hours. With the drying drum through the handling of estrus product enters the furnace, where there is finally drying to a moisture content of 1-5 %.

When grading using nets with holes the size of the upper sieve that is 1,7-2,0 mm lower is 0,7-0,9 mm.

Waste cyclone dust from the drying drum calcination furnace and grading in the finished product up 10-17 % of the finished product released. This waste sent for reuse in the process of making pasta.

Wastewater from the converter after releasing of hydrogen sulfide are acidic (pH<4) and sulfides containing less than 20 mg/dm^3. The effluent from the column with an acid laundering weak acid reaction and is approximately 21 m^3 per ton of finished product. Waste water from the acid neutralizer and columns sent to treatment plants.

Emissions from dryers and dried furnace in the amount of 130 thousand m^3 per 1 ton of product and air with sprinklers containing hydrogen sulfide below the MCL in the amount of 40 thousand. m^3 per 1 ton of product entering the furnace afterburner. Which together with the gases from furnaces activation and carbonization subjected to thermal decomposition. Sulfur contain gases are oxidized to sulfur oxides. With the post-combustion furnace gases in quantities of 160 thousand m^3 per 1 ton of product sent to the catalytic tower where cleaned of sulfur

oxides and released into the atmosphere. After drying drum and additional activation furnace dust particles from the air passing cleaning system cyclones is discharged into the atmosphere.

Average rates of consumption for production of 1 ton of adsorbent gas type of peat when used as inorganic activator potassium (I) sulfide (as well as zinc (II) chloride) are presented in the Table 1.24.

Table 1.24. **The rules cost of production of 1 ton of coal gas type of peat using inorganic activators**

Activator	The amount of peat, tone	Cost				
		Electrical energy, kW•h	Steam, tone	HCl, ton	H_2O, m^3	Activator, tone
K_XS_Y	3,5	1400	18	0,3	230	0,369-0,372
$ZnCl_2$	3,5	1700	9,4	1,29	286	0,4-0,7

1.3.8 The technology of carbon adsorbents with lignite, modified potassium hydroxide

Brown coal belongs to coal of vitrinite group. Vitrinite content of 85-92 % and the degree of coalification is intermediate between peat and coal. Unlike peat, lignite as missing or found in a small number of plants remains unresolved and chemical compounds that make up their composition. Unlike coal, lignite is present in humic acids.

In analyzing the elemental composition of peat, lignite and coal found that with the deepening of metamorphism markedly reduced content of hydrogen and oxygen, coal is hydrophobic, contains less moisture and becomes less reactive, less prone to oxidation when stored in air (aeration). One of the most important properties of brown coal is its high hydrophilic and ability to retain a large mass of water. Since this involves a lot of physical and chemical properties and

technological characteristics of lignite – porosity, swelling, shrinkage, flexibility, strengthening compressive and others. Table 1.25 The content presented functional groups in humic acid fractions of brown coal.

Table 1.25. **The content of functional groups in humic acid fractions of lignite**

Functional groups	**The content of functional groups, mg-eq/g**	
	Diluted	**Undiluted**
Methoxy	1,45	0,61
Aldehyde	0,25	0,91
Ketone	2,58	1,43
Quinoidal	0,78	1,40
Carboxyl	4,40	2,90
Phenolic	2,88	4,25

The presence of brown coal humic acid makes it able to react with strong alkalis such as potassium (I) hydroxide. The result is a radical change in the interaction of nature original brown coal occurrence in coal alkaline composition plasticity and capability to form, the changing nature of decomposition carbon contained lignite components during heat treatment and forming the skeleton of coal residue.

The depth and extent of the transformation of primary material and characterization of porous structure formed in the coal residue depend on many factors, the main ones being preconditioning lignite; the amount injected potassium (I) hydroxide, subject to the alkali coal composition and its heat treatment and laundering of alkaline activator.

Some studies confirmed that lignite is a promising raw material to produce high quality carbon adsorbents, whose adsorption characteristics and strength markedly superior industrial AC from peat and coals.

Table 1.26. **The main stage of obtaining carbon adsorbents from brown coal**

<table>
<tr><th rowspan="2">Stage of producing</th><th rowspan="2">Laboratory equipment</th><th colspan="6">Adjustable parameters for obtaining adsorbents</th></tr>
<tr><th colspan="3">By chemical method</th><th colspan="3">By mixed method</th></tr>
<tr><td>Crushing and grinding</td><td>Crusher, ball mill or vibration</td><td colspan="6">Dispersion 5-80 microns</td></tr>
<tr><td>Preparation modifying solutions</td><td>Agitators Mixer-granulator screw type</td><td colspan="6">Value water and modifier (estimated)</td></tr>
<tr><td rowspan="4">Paste preparation and granulation</td><td rowspan="4">Rotary oven</td><td colspan="6">Paste’s recipe</td></tr>
<tr><td>Brown coal</td><td>K</td><td>H_2</td><td>Brown coal</td><td>K</td><td>H_2</td></tr>
<tr><td>100</td><td>8</td><td>92</td><td>100</td><td>22</td><td>160</td></tr>
<tr><td colspan="6">T_{gran}=60-80 °C</td></tr>
<tr><td>Dryer</td><td></td><td colspan="6">T=80-120 °C</td></tr>
<tr><td>Carbonization</td><td>Rotary oven</td><td colspan="6">T_c=800 °C, lifting speed temperature of 10 deg/min</td></tr>
<tr><td rowspan="2">Activation</td><td rowspan="2">Rotary oven</td><td colspan="3">–</td><td colspan="3">T=850 °C</td></tr>
<tr><td colspan="6">W=30 %</td></tr>
<tr><td rowspan="2">Decarbonization</td><td rowspan="2">Ion Exchange</td><td colspan="6">Washing method</td></tr>
<tr><td colspan="3">alkaline</td><td colspan="3">acidic</td></tr>
<tr><td>Additional activation</td><td>Filter</td><td colspan="3">T=850 °C, W=5-10 %</td><td colspan="3">if necessary</td></tr>
</table>

The benefits of brown coal as feedstock in the production of carbon adsorbents also include the possibility of its use in two production technologies similar to sulfur, potassium activation and mixed activation with the introduction of lignite small amounts of activator (potassium (I) hydroxide) to giving it plasticity and capability to form, followed by steam activation.

In the production of AC from brown coal chemical modification methods and mixed activation can identify the main stages listed in the Table 1.26.

Characteristics obtained by these technologies of coal, compared with industrial carbon from peat and coals are presented in Table 1.27.

Table 1.27. **Comparative characteristics of carbon adsorbents with lignite and their industrial counterparts**

Active carbon	d, g/cm^3	Strength by MIA 8, %	Volume of pores, cm^3/cm^3			S_{me}, m^2/g	Structural constants	
			V_{ma}	V_{me}	V_{mic}		W_0, cm^3/cm^3	E_0, kJ/mole
BK	0,80	86,7	0,14	0,10	0,40	50	0,40	24,8
BCS	0,70	82,6	0,16	0,12	0,40	200	0,40	24,6
SKT-C	0,80	78,0	0,20	0,07	0,36	50	0,36	24,2
AG-5	0,73	75,0	0,40	0,08	0,23	150	0,21	20,4

The amount of introduced potassium hydroxide should be less than 5%

The interaction of brown coal with potassium (I) formed alkali hydroxide coal composition. Behavior alkali coal composition at all stages of processing different from the decomposition of raw materials in the production of potassium– sulfur adsorbents activation. This is due to physical and chemical characteristics of brown coal as raw material and different character decomposition compositions. The impact modifier (potassium (I) hydroxide) begins to show since its introduction in the original brown coal, which is a complex spatial structure with a large number of areas of aromatic character, highly reactive. The presence of humid acids and a large number of functional groups increases the reactivity of the material, resulting in brown coal processing responsive to the alkaline reagents. This initial dispersion are processes of structural elements of breeding material brown coal by a process similar to the process of saponification. There is significant heating of the paste. There is a deep chemical modification of raw materials, leading to the formation of gel-like plastic system with high spatial mobility. Uniform distribution of water throughout the mass activator material and a high probability of formation of compounds that are similar in type to South Africa, contributes to a plastic composition with sufficient initial strength, conditioned by the forces of adhesion.

Increasing the number of modifiers improves the plastic properties of the system, as with humites process structure involved and meadow are reacted of humid acids.

Significant impact on quality pastes are prescribed factors [1] amount of modifier and humidity paste. Empirically, it was found that the dependence criteria for the formation of mass modifier particles and moisture increases with the proportion of moisture in the paste to the maximum. Close to the optimal values of the amount of water used to produce plastic composition can be determined using the empirical equation:

$$\omega = m_{BC} + 0{,}65 \cdot A, \qquad (3.3)$$

where ω – the amount of water in the alkali– coal paste; m_{BC} – mass of brown coal; A – amount of modifier per unit mass of coal.

In a preliminary drying wet granule remove the water. Together occurring capillary compression processes and reduce the liquid layer, which leads to shrinkage of the system, resulting in formation of solid pellets. The process of compressing plastic material is accompanied by the formation of primary transport porosity. The material in the presence of colloidal particles humites after drying still retains a sufficient degree of spatial mobility that is shown in the following stages of heat treatment.

Technological scheme of carbon adsorbents with lignite, modified potassium (I) hydroxide, in respect of hardware and technology of production something identical carbon from peat by sulfur-activated potassium. Since it is presented above in some detail, this section provides a brief description of the main stages of production.

Grinding of lignite. Preliminary crushing is conducted on roll crusher size pieces of 25 mm. Further grinding is performed in the hammer mill, followed by brown coal dust enters the mixer to cook pasta.

Mixing and granulation. In mixing in a mix ratio of lignite and activator solution. The mixing of pasta is 40 minutes. The finished pasta screw discharged in paste receiver, which is directed to granulation.

To the extent necessary, to clean alkaline return of silicon compounds added to the mixer calcium (II) chloride.

Granulation pasta is made on pelleting presses fillers through holes with a diameter of 1,5 mm. Pressed pellets fed to the heat treatment in stages: drying, carbonization and activation.

Drying the granules made in the rotary drum dryer ram flue gases to the residual moisture of less than 5 %. Time of granules in the dryer is 1 hour. Flue gases are fed into a loading head with temperatures up to 500 °C.

The dried granules in the dryer pneumatic sent into the hopper of combined oven carbonization– activation. The furnace is a countercurrent rotating drum muffle furnace division of zones of carbonization and activation, some remote heated furnace. Heating furnace flue gases. Time of pellets in the furnace is 6 hours. Carbonization zone occupies the first third of the oven. It supports temperatures 550-600 °C. In the area of activation temperature is maintained at 850-900 °C. The temperature of the granules after cooling does not exceed 70 °C.

The process of washing held at a temperature of 60-70 °C. To maintain a given mode intermediate capacity provided shirts.

Drying of washed coal pellets made direct contact with heated flue gases. The gas temperature at the inlet is 750 °C, and 180 °C at the output. The residence time of pellets in the furnace is at least 30 minutes.

Additional activation is performed in rotary ovens with drum steam. Steam and coal stoves to move forward flow and heating flue gases towards them-counter. Time of pellets in the furnace is 1,5 hours heated gas temperature at the inlet is 900 °C and 250 °C at the outlet.

After dispersion prepared coal is packed in rigid airtight containers.

1.3.9 The technology of carbon adsorbents from waste wood, modified phosphoric acid

The advantages of this method of obtaining carbon sorbents are: high adsorption and mechanical properties of the resulting coal; dehydration and high phosphoric acid properties, high thermal stability and low volatility, making it one of the best modifiers of wood; availability of wood waste that is constantly renewable raw materials in the process of photosynthesis.

The disadvantages of wood raw material, limiting its intended use in the production of AC without modification, are its high initial porosity caused by cellular structure, the presence of undesirable components (hemicellulose), which does not form a porous carbon, and unnecessarily large loss of volatile components during heat treatment.

Modification of wood helps eliminate the primary structure of wood (reduction in macro pore) reduces formation of tar and other resinous substances.

As the modifier used sulfuric acid, phosphoric acid, zinc chloride, sulfur, potassium and other salts. Most quality modifier is phosphoric acid.

For the modification of wood raw material (sawdust, wood chips, milling chips, etc.) used 85 % phosphoric acid. Choice of phosphoric acid caused by the following circumstances: modifying high capacity at low temperatures and low evaporation at elevated; high solubility and stability in dehydration conditions; the ability to regenerate normal water in a highly multi– stage extraction condition in a form suitable for reuse without prior concentration.

Preparation of raw materials (wood waste) consists of sifting through the lattice of 40x40 mm and a crushing hammer crusher. Further drying of raw

materials to moisture ≤5 % by weight. carried out in a drum dryer at temperatures of 100-110 °C.

Processing is carried phosphoric acid at a temperature of 120-130 °C at a weight ratio of modifier to raw materials 1,5:1,0 or 2:1. Granulation passes through fillers with 1,5-2,0 mm in diameter, followed by heat treatment at 160-170 °C.

Extraction modifier carried water with a temperature of 70-80 °C to a residual phosphorus content below 0,1 % by weight. Previous granule drying occurs at a temperature of 105-110 °C for 30-35 minutes.

During carbonization temperature in the combustion zone of gas maintained in the range of 550-700 °C, the temperature at the exit of the product from the drum – 500-650 °C, the time of the pellets in the furnace is 2-2,5 hours, and the yield is 46-52 %.

Activation is performed in the shaft furnace to the extent burnt ~30% accompanied by a reduction apparent density of 0,99-1,07 g/cm^3 to 0,76-0,78 g/cm^3, which results in carbon adsorbents with advanced volume adsorbing porosity in the range of 0,33 to 0,40 cm^3/cm^3. Then, the packaging and the formation of parties finished product.

Characteristics of the finished product shown in Table 1.28. Table 1.29 shows the average consumption rate for production of 1 ton of coal and gas lighting type sawdust obtained activation phosphoric acid.

Table 1.29. **Characteristics of the porous structure of agglutinate adsorbents in wood syrup (AWS), modified phosphoric acid**

Marks	δ, g/cm^3	d, g/cm^3	Volume of pores, cm^3/cm^3		E_0, KJ/mol	Strength for the MVS-8, %
			W_0	V_{tr}		
ADH-1	0,59	0,99	0,33	0,19	23,7	>85
ADH-2	0,57	0,91	0,36	0,18	22,5	>85
ADH-3	0,50	0,78	0,40	0,21	18,5	>85
SCT-2B	0,46	0,74	0,32	0,33	23,7	>76

Table 1.29. **The rules cost of production of 1 ton of coal and gas lighting type sawdust activation of inorganic additives**

Active carbon	Expense					
	Wood, t	**Electrical energy, kW•h**	**Stream, t**	**HCl, t**	**H_2O, m^3**	**Phosphoric acid, t**
Gas granulated	2,9-3,2	1200	9,4	1,2	280	0,4-0,7
Brightening	3,0-3,2	300	10,0	1,2	250	1,4-1,8

QUESTIONS FOR SELF-CONTROL

1. The concept of total pore volume and the adsorption limit amount of space, methods of determination in the laboratory.
2. What is characterized as expressed porosity and activated carbon?
3. What methods can determine the true and apparent density of the porous body?
4. What is called static equilibrium adsorbent activity? What does it depend on?
5. What is the difference between the total pore volume, the maximum amount adsorbed, the adsorption capacity of the porous space and volume space? What units of measurement are these values?
6. What kinds of pores present in the active carbon, their size and proportion of the total volume of pores?
7. In which processes porous structure of activated carbon is crucial? Explain why.
8. List and expand the core methods for measuring the porosity of solids.
9. What determines the nature of the porosity of activated carbon?
10. What are the values of specific surface area having an active coal?

11. What is the fate of the specific surface area of activated carbon is necessary for every kind of far?

12. What kinds of pores provided the bulk surface active coal? Why?

13. What are the dimensions of the micro, meso and macropores?

14. On the surface pores which are almost all adsorption?

15. What methods investigate adsorption processes, particularly at high adsorbents?

16. As is typical sorption isotherm solid adsorbent?

17. What determines the value of adsorption?

18. What types of sorption isotherms you know?

19. What ways can determine the shape of sorption isotherms?

20. What equations describe the adsorption isotherm? How do they differ?

21. What is the active coal?

22. Analyze the internal structure of activated carbon, describe its features.

23. Synthesis of activated carbon, which are known.

24. What is used as a raw material for activated carbon producing?

25. Examine ways of activated carbon modifying.

CHAPTER 2 TECHNOLOGY OF MINERAL PIGMENTS

2.1 MINERAL PIGMENTS AND THEIR BASIC PROPERTIES

2.1.1 Classification and designation of mineral pigments

Pigment called colored dispersed substances insoluble in the dispersion medium, which is capable of forming protective film-forming substances and/or decorative coating. Pigments are divided into organic and inorganic.

Inorganic pigments are used in many fields of technology, and they perform various functions unlike organic pigments, which are intended only to provide materials of a certain color.

Table 2.1. **Classification of pigments**

Achromatic[1] pigments		
White pigments	Titanium whitewash	TiO_2
	Zinc whitewash	ZnO
	Lead whitewash	$2PbCO_3 \cdot Pb(OH)_2$
Black pigments	Soot	C
	Iron Oxide	$FeO \cdot Fe_2O_3$
Grey pigments	Metal dust	Al, Zn
Chromatic[2] pigments		
Yellow, orange, red	Krone	Chromates Pb, Zn
	Iron Oxide	$FeOOH$, $Fe_2O_3 \cdot H_2O$, Fe_2O_3
Green, blue, violet	Chromium	Cr^{3+}
	Cobalt	Spinel, mixed salts, simple salts
	Copper	Compounds oxides Cu
	Manganese	MnO_x

The classification of inorganic pigments includes two main signs: chemical composition and color. The chemical composition they are divided into salt components and metal oxides. The color pigments are divided into two main groups: achromatic and chromatic (Table 2.1) [24].

[1]Achromatic pigments are characterized mainly refractive index.

[2]Chromatic characterized by color tone (color according to physics - the wavelength of light absorbed determines the color - tone), brightness (characterized by reflection coefficient), saturation (purity determined).

Achromatic includes white, black and grey pigments, and chromatic can be all colors. Last divided into two main groups: those that have their own color tone in the long-wave part of the visible spectrum, and for having its own color tone in the short-wave part of the visible spectrum.

In addition to general – purpose decorative mineral pigments, they may have targeted purpose, namely for heat – sensitive pigments, fluorescent, not overgrown, anticorrosion paints etc.

2.1.2 Application of mineral pigments

Paint and varnish coatings are important in engineering and construction [25]. Paint and varnish coatings should be regarded as an integral part of every machine and every building.

From the total painting costs (including the preparation of the surface) in the construction industry at least 70 % falls on the share of costs associated with the coating, and more than 30 % – the share of paints cost. As part of the paint is the most expensive part of the film-forming substance. The share of the pigment accounts is less than 30 % of the paint. Thus, the cost of acquisition pas pigment is less than 10 % of total coloring. Meanwhile pigment properties largely determine the lifetime of the paint. Often replacing less stable for more stable pigment allows to extend service coverage in 2-3 times. Therefore, pigment properties have a decisive impact on the economy of the paint industry, as well as complex and expensive methods of pigments manufacture are economically feasible unless they significantly increase the service life of the coating.

Paint industry produces paints of different colors and shades, but the most common coverage light colors: blue, beige, pink, light green, etc. Such paints are made from a mixture of pigments, with 80 % of the mixture accounted for white pigments, particularly titanium (IV) oxide (titanium oxide).

In the industry, titanium whitewash used for the manufacture of paint products with improved blanket properties which protects the colored surface from the ultraviolet radiation, aging and yellowing film effects. They are also added to plastic products (window construction, furniture parts, home appliances and cars) that in addition to providing high intensity white color increases their resistance to negative influences.

In ceramics, glass, rubber manufactures – titanium (IV) oxide is often used as a catalyst for chemical reactions or inert base material, which allows them to operate with products in high temperatures. The same additive can increase resistance to fading ink, twisted fiber mat in the manufacture of synthetic fabrics, improve the structure of the paper pulp in its bleaching paper – cardboard industry. We also know the positive impact of titanium (IV) oxide, seeks to protect the wood from sunlight radiation, air purification and improving the efficiency of welding flux.

To satisfy consumer demand wide production of titanium (IV) oxide as pigment dye may have several different factions adapted for a particular application, which determines the size and shape of the crystals and the surface treatment type (organic or inorganic).

In addition, reference material purity to 99,99 %, obtained in the process of thermal hydrolysis is used to make most transparent glass, used in electronics, fiber optics, medicine and piezometer. The most common pure titanium (IV) oxide obtained in cosmetics, food and pharmaceuticals. The latest production is added as a pigment that gives medication sheets and covers hiding pills. In cosmetics ingredient TiO_2 is used as a means of protection from ultraviolet radiation, which is considered one of the best to neutralize the UV rays in the manufacture of sunscreens as white pigment or filler in decorative cosmetics (powder, lipstick, eye shadow), antiperspirants, soaps and toothpastes. The use of TiO_2 in the food

industry (food additive E171) due to its ability to provide certain properties of certain products, such as plastic packaging protection from fading and ultraviolet radiation. This is especially true in the manufacture of powdered products, semi – finished quick cooking, dried milk, etc.

The growing trend of using road, roofing, decoration and construction materials, and the desire to get colored products make it necessary to use pigments and pigment pastes for coloring concrete and gypsum in the manufacture of colored plaster and colored concrete products. Colored concrete may be obtained by coating the surface after curing or direct mixing of pigments in solution or concrete. The use of pigment in weight, more preferably because the color is a composite concrete solution and requires no recovery time operations. For coloring building materials used mainly Fe–oxide pigments.

With Fe–oxide pigments manufactured colored paving tiles, cement tiles polymer -sand tiles, colored concrete fences, colored concrete monument, artificial stone concrete, plaster and other possible colored concrete products and gypsum. Fe oxide pigments and other pigments used for coloring concrete and polymer– sand products to be stable in alkaline environments, lightfast and resistant to environmental conditions; should also be insoluble in water and easily dissipated between the fine particles of cement.

2.1.3 Main pigment properties

Inorganic sorbents are typically insoluble in water and other organic liquids, salts or oxides. In the manufacture of pigments does not concern the problem of obtaining chemicals and treats the problem of obtaining substances with a certain set of characteristics specific pigment (color dispersion, linen, wettability, etc.).

Impurities in the final composition of pigments is quite acceptable if they do not degrade the performance properties of the pigments. However, only knowledge

of the chemical composition of the pigment cannot give full information on its properties. Depending on the crystal structure, which is determined by the conditions of crystallization and the existence of crystal are the same chemicals can have different crystal lattice, and therefore vary in color, hardness, refractive index, density and consequently for the pigment properties – intensity, light, hiding and others.

Natural and synthetic inorganic pigments are crystalline substances which feature is the presence of long-range order (spatial frequency) in the arrangement of the structural elements of solid. With the formation of crystals in normal conditions, especially crystal technology products, strict periodicity in the arrangement of structural elements somewhat disturbed that manifested in defects, which also affects the properties of the pigments.

The crystal structure determines not only the pigment properties but their physical and mechanical properties such as hardness, fragility, strength. In turn, these parameters affect the conditions of grinding, dispersion, abrasiveness.

The structure of the surface had some differences from the average composition of particles due to the influence of the atmosphere, or from deliberate modification of pigments. The chemical structure of the surface of the pigment particles determines their chemical behavior of colloidal systems in colorful (dispersion), adsorption ability, color and so on. Therefore, pigment properties depend not only on the chemical composition, but the method of their production, further processing (modification), and storage conditions.

Surface modification is the deposition on the surface of thin – layer adsorption layers or phases other substances that are different from the substance of the pigment to enhance pigmentary characteristics. There are adsorption and chemical modification. When it is modifying adsorption, it can be observe created monolayers of surfactants on the surface of pigments for improving wettability low

film-forming substances. For chemical modification commonly used organosilicon and as a result there is surface hydrophobicity.

Typical mineral pigments difference is that their chemical composition is not uniquely determine quality indicators. The decisive role of their properties played of the crystal structure and composition dispersed pigments. Therefore, for achieving sustainability decorative and protective properties of synthetic mineral pigments, it is necessary to synthesize them under conditions of controlled crystallization.

The main properties of pigments include:

1. Hiding;
2. Intensity;
3. Oil consumption and wettability;
4. Light stability;
5. Dispersion;
6. Form of particles.

Covering ability – the ability of paint at uniform application of color to make the surface invisible. To maximize the ability of the coating, pigment particle size should not be less than half the wavelength of the visible spectrum, that is, depending on the color, the optimal particle size should be 0,2-0,6 mm. The lower limit applies to white and blue, top – to red pigments.

The intensity (or painting ability) is the ability to transfer the color pigments to other pigments mixed with them. The intensity of the pigment increases with the degree of dispersion, but exceptions are the pigments whose size below 0,5 microns, which may reduce their intensity as a result of the fact that the core particles are unreacted material.

Oil capacity is the amount of oil that should be added to 100 g of pigment to form a plastic mass-paste. Oil capacity depends on the wettability of pigments.

Lightfastness is the ability of pigments by light to keep continuity optical characteristics and composition.

Increasing of dispersion degree, and hence the specific surface area is cause of pigment`s oil capacity increasing (moisture). And for some pigments, different photochemical activity (leading to destruction of film former irradiation covering visible and ultraviolet light), reduces the service life of the coating. Therefore, the aim of pigment synthesis is not receiving shares of the minimum, but optimum size. For example, titanium (IV) oxide rutile form an optimum particle size of 0,2 microns; anatase form for this value is little bit higher than 0,3 microns; for pigments, fillers, which cover ability does not matter, just as important is the impact on the rheological properties of paints and oil capacity (moisture), this value increases to 3,1 microns; for mica over grinding which leads to loss of lameness, and with it the luster to 5 microns or more, etc.

Great importance for the strengthening the film is also a form of particles of pigments. Particles needle or fibrous form (e.g. zinc white, micro asbestos) as its reinforced tape, which improve weather resistance of it. More favorable effect scaly form of particles characterized, for example, aluminum powder. Scales floating in a layer of paint, overlapping one, like a roof tile, forming a waterproof and opaque armor.

The form of the pigment particles depends on the conditions of obtaining and processing. Effect pigments form particles on the properties of paint material is often significant, though not quantified. The shape of the particles affects both the fluidity and at the color of paints.

Constancy of crystallization conditions, providing the desired crystalline form and size of the particles is achieved by supporting sustainability concentrations, temperatures, quantities and properties of the original embryos, whether synthesis proceeds in liquid or gas phase. Intensive mass transfer is one of the important

conditions that facilitate the regulation of the formation of new centers of crystallization at an uncircumcised synthesis.

It is important to ensure the perfection of form crystals; in needle form pigment (e.g. zinc white) when receiving defective crystals increased photochemical activity break point of the crystals and thereby reduces atmospheric stability refinishing. In these cases, additional exposure at the optimum temperature to form a crystal mode enhances the quality pigment.

In terms of controlled crystallization process feasibility is understood periodic preparation embryos during the deposition, for example, metathiamine acid hydrolysis process, as well as in the production of yellow ferric oxide pigments. The particle size of embryos should be about an order of magnitude smaller particle size pigment. From positions of controlled crystallization conditions should be evaluated ferric oxide improving conditions of the quality yellow pigments derived air oxidation of metallic iron in the solution of iron sulfate. This is possible by regulating the growth of crystals of goethite (FeOOH). The limiting factor in this process is not a specific surface of metallic iron, which is a real industrial condition many times necessary, and the rate of oxygen uptake solution of iron sulfate.

Analogous theoretical assumptions should guide the choice of the mode of production of red pigments ferric oxide quality. With a large number of industrial methods pigments «unsurpassed softness and brightness», comes only method similar to the method of yellow ferric oxide pigments production and differs only in the method of preparation embryos (embryos instead of yellow goethite introduced into the reactor embryos red iron oxide).

To ensure the constant conditions of ferric oxide crystals red pigments formation of, such as iron sulfate calcination in rotating ovens, very difficult because the quality pigment obtained in this way lower. Perhaps roasting in a fluidized bed, which provides satisfactory conditions of heat and mass transfer and

allow compliance with temperature constancy of ±10 degrees, will improve the quality indicators pigment. This will improve the technical and economic feasibility of the process, since the liquid phase synthesis of the product considerably more expensive than the product roasting iron sulfate.

Incineration of titanium (IV) chloride vapor in a fluidized bed improves the quality of titanium (IV) oxide rutile form. This is because at any reaction of titanium (IV) oxide primarily obtained anatase, which then, in the absence of stabilizers, recrystallized in rutile. Effective mass transfer and strict constancy of temperature during firing in fluidized bed guarantees a high content of optimum size particles.

Bleaching ability (in arbitrary units) of titanium (IV) oxide rutile forms received by chloride process reaches 2000, while for the sulfate method, the maximum value is 1850.

Regulation of the particles of titanium (IV) oxide formation process during calcination of metatitanium acid can be done by typing the recipe of additional components. For example, the presence of titanium concentrates less than 0,15 % P_2O_3 favorably affect the process as trivalent anion stabilizes anatase, delaying the restructuring of its crystal lattice in rutile and thus inhibits the growth of rutile crystals during recrystallization.

Thus, each new high-quality synthetic pigment must be assessed in terms of the requirements of controlled crystallization.

Completeness of pigment wetting during its grinding to most film-forming substances (oil, alkyd) is achieved faster if the surface of the pigment particles is hydrophobic. Widespread use of emulsion paints requires the release of the hydrophilic surface of the pigment particles.

Some pigments such as titanium (IV) oxide (rutile form), iron oxide red pigments derived firing differ abrasiveness. To address this shortcoming at present

time, most pigments are subjected to surface treatment, in which the particles of pigment applied to the shell of silica, aluminum hydroxide and other mineral or organic matter. The recipe of components shell depends on the purpose of the brand pigment.

The existing standards and specifications for pigments are not standardized their photochemical activity. However, for those consumers of titanium oxide and zinc oxide as paint and varnish industry, this figure is particularly important because it indirectly, but adequately describes the atmospheric stability refinishing.

Obtaining optimum crystal shape and size, printing on their surface embraces improve other properties of pigments: covering ability, oil capacity, ability to rinding.

2.2 SOURCE OF RAW MATERIALS

2.2.1 White pigments based on titanium oxide compounds

There are more than 110 minerals in nature, which contain titanium [25]. The industrial significance has ilmenite, arizonite, rutile, perovskite, titanite.

Arizonite. $Fe_2O_3 \cdot TiO_2$ has a color from dark to gray-steel color. Some experts believe that, this is a mixture of ilmenite, hematite and rutile with anatase.

Rutile. TiO_2 has a red-brown color with various shades of yellow to light brown. TiO_2 content ranges from 94 to 98 %.

The largest natural rutile deposits are located in Australia. Rutile concentrate containing about 95 % of TiO_2 and it is the best raw material for production of titanium (IV) chloride. Rutile sand is a valuable raw material even when the content of 0,2 kg/m^3. Rutile is often found together with isomorphic zircon.

Perovskite. $CaTiO_3$ has a light yellow, red, brown, purple, black and others colors. The content of TiO_2 in the ore is 15 %, and in the concentrate – up to 50 %. Besides titanium (IV) oxide perovskites containing rare earth elements, such as

tantalum and niobium. Here is the approximate composition of perovskite concentrate (Table. 2.2). There are also concentrates with lower of TiO_2 content (less than 40%), which include 1-1,5 % FeO, Fe_2O_3 2,5-3 %, 1-1,5 % MgO, 0,5 % of Al_2O_3.

The titanium compounds move in the solution when the decomposition of perovskite concentrate by sulfuric acid takes place. However valuable impurities such as niobium, tantalum and rare earth elements are lost.

Table 2.2. **The composition of perovskite concentrate**

Substance	Contents, %
TiO_2	45
CaO	45
SiO_2	5
Rare earth elements	1,8
Niobium and tantalum oxides	0,8

Integrated chemical processing of perovskite concentrates by sulfuric acid method with removing of all valuable components greatly complicates the scheme of production, significantly increases the capital costs, and importantly increase the sulfuric acid consumption that lead to unpromising using of perovskite as raw material for titanium (IV) oxide production.

The methods of perovskite treatment by hydrochloric acid are quite interesting, but they are at the stage of laboratory tests.

At the presence of an unlimited supply of ilmenite concentrate, perovskite can be used primarily as a raw material for rare earth elements (tantalum and niobium) simultaneously with the removal of titanium (IV) oxide. The metallurgical techniques of perovskite processing may be more effective in technical and economic terms than chemical one.

Titanite. $CaTiSiO_5$ has a gray, brown, yellow, green, pink and red to white. Mineral sphen ($CaO{\cdot}TiO_2{\cdot}SiO_2$) contains 40,8 % of TiO_2. Titanite encountered on

the Kola Peninsula, like the perovskite. Its deposits are usually accompanying Khibiny deposits of apatite. Titanite concentrate contains 30% of TiO_2.

Ilmenite. $FeO \cdot Fe_2O_3 \cdot TiO_2 \cdot MgO \cdot MnO$ is the titanium-iron oxide mineral, it has dark color. Ilmenite has variable composition from $FeTiO_3$ ($FeO \cdot TiO_2$ – crichtonite) to $MgTiO_3$ ($MgO \cdot TiO_2$ – haikelite) and $MnTiO_3$ ($MnO \cdot TiO_2$ – pyrophanite). Invariably ilmenite may contain a small amount of Fe_2O_3. Typically, the composition of ilmenite close to crichtonite ($FeTiO_3$). Ilmenite concentrate is the best raw material for titanium (IV) oxide production by sulfate method.

Ilmenite is characterized by variable oxides ratios of divalent iron to trivalent iron oxides. For relatively unchanged ilmenite concentrates a ratio (Fe^{2+}/Fe^{3+}) can be more than six for less changed – at least three to highly changed – less than one.

The content of divalent iron in ilmenite decreases with the oxidation to ferric iron and weathering of the latter, leading to the increase of titanium (IV) oxide and to change the properties of ilmenite. The high content of titanium oxide in ilmenite decomposition makes it difficult to sulfuric acid.

The content of divalent iron in ilmenite decreases as its oxidation to ferric iron and its weathering, leading to the increased of titanium (IV) oxide content and changing the properties of ilmenite. The high content of titanium oxide in ilmenite makes it decomposition by sulfuric acid more difficult.

It is known that pure titanium (IV) oxide decomposes in boiling concentrated sulfuric acid. The more titanium oxide in ilmenite, so it is less suitable for sulfate production method of titanium oxide in the «soft» conditions, the «harder» mode of decomposition is required for these ilmenite (higher concentration of sulfuric acid and higher temperature).

There are data (given in the Tables 2.3 and 2.4) of the chemical composition of ilmenite concentrates from different deposits and slag that contain titanium from different suppliers. According to these data, the requirements for the ratio Fe^{2+}/Fe^{3+}

correspond less changed or unchanged following Ilmenite concentrate of Ukraine: Bukynskyy, Livoberezhne (Zhytomyr region) and others.

On the other hand, unchanged ilmenite concentrate, which is well decomposed by sulfuric acid from solution and well filtered, not always available for getting titanium (IV) oxide of high quality. The reason for this is the presence of chromophores impurities in ilmenite concentrate (chromium, vanadium, copper, nickel and phosphorus).

With long-term weathering of ores due to the transition of divalent iron to trivalent and its removal, an enrichment of ilmenite by titanium take place (called Leucoxenization). The content of TiO_2 in ilmenite reaches 60-65 % or more.

Ilmenite concentrates of different Ukrainian deposits contain 50-60 % titanium oxide (IV). Some of them have pure leucoxenization and represent the extremely valuable raw material for the pigmentary titanium oxide production by sulfate method. It should be noted that knowledge of the chemical composition of titanium concentrates, without direct explore the possibility of decomposition by sulfuric acid, is insufficient for evaluating the quality of raw materials.

Table 2.3. **The deposits in Ukraine [24]**

Composition	**Contents, %**							
	Mezhdurechensk (Zhytomyr region)	**Ocheretyanske (Zhytomyr region)**	**Paromovskoe (Zhytomyr region)**	**Stremigorodskoye (Zhytomyr region)**			**Tarasivske (Zhytomyr region)**	**Torchynske (Zhytomyr region)**
TiO_2	54-62	52,85	54,6	53,1	45,2	47,5	61,04	48-51
FeO	12-25	26,6	25,7	33,6	40	42,4	0,07	31-41
Fe_2O_3	12-24	12,82	16,6	10,2	3	3,2	26,51	3-15
MoO	0,13-1,0	1,12	1	0,87	2,7	2,38	0,68	0,64-1,27

Continuation of *Table 2.3*

CaO	0,14-0,51	0,46	0,24	0,28	0,23	0,17	0,28	0,1-0,91
Al_2O_3	0,5-1,7	0,85	0,13	0,46	0,33	0,7	2,1	0,16-1,35
SiO_2	0,9-2,0	0,54	0,44	0,43	4,1	3,5	1,52	0,8-1,81
Cr_2O_3	0,02-0,03	0,02	0,033	0,05	0,05	0,055	2,03	0,01-0,02
V_2O_5	0,2-0,3	0,24	0,34	0,26	0,2	0,19	0,12	0,18-0,38
MnO	0,4-0,5	0,5	0,4	0,53	0,1	0,87	0,71	0,32-0,51
P_2O_5	0,05-0,1	0,04	0,085	0,1	0,16	0,1	0,19	0,06-0,11

Table 2.4. **The chemical composition of titanium slags**

Chemical composition, %	**Norway**	**Canada**	**Vilnogirsk deposit of ilmenite (Ukraine)**	**Zaporizhian titanium slag, (Ukraine)**
TiO_2	73	77,6	83-90	62-72
TiO_2 insoluble	–	1,53	–	0,27-0,35
Ti_2O_3	2,0	14,7	2233	–
Fe (total)	11	5	535	10,35-18,8
Al_2O_3	07	3,1	1,64-1,98	0,76-3,6
SiO_2	3,89	2,78	2-2,25	2,84-4,15
P_2O_5	trace	–	0,004-0,006	trace
Cr_2O_3	0,104	0,46	0,33-0,36	0,02-1,03
MnO	0,37	1,26	1,14-1,19	0,9-1,0
V_2O_5	0,21	0,59	0,2	0,08-0,27
CaO	2,31	0,5	–	2,8-5,6
MgO	2,03	5,2	0,32-0,45	0,26-0,4
Fe (metal)	0,45	531	0,68-1,44	–

Depending on the composition, properties and specific economic conditions, the titanium concentrate could be decomposed by a sulfuric or chloric acid, decomposed by electrofusion or other methods of treatment to increase the content of titanium (IV) oxide and degree of decomposition completeness by sulfuric acid.

Highly percentage slag. The production of slags which contain 80-85 % of TiO_2 organized in our country. With increasing content of TiO_2 in slag, significantly

increases the specific power consumption during melting and decomposition of slags also it becomes hardly decomposed by sulfuric acid. For processing slag by chlorination, it is needed higher contents of TiO_2.

It is established that (Mg, -Fe) $O \cdot 2TiO_2$ compound containing in molten slag, in which dissolved titanium (IV) oxide and lower oxides of titanium. With the cooling of slag and oxidation of the lower oxides under the influence of oxygen, titanium (IV) oxide crystallized from solution. If crystallization occurs at low temperatures, the titanium (IV) oxide produced in the form of anatase, which has no time for recrystallization in rutile and therefore it is readily soluble in sulfuric acid. If crystallization occurs at high temperatures, rutile is mostly produced, which insoluble in sulfuric acid.

Significant simplification of the production scheme with the content of iron–titanium raw material up to 15 % Fe (mass of TiO_2) and reduce the cost of sulfuric acid, make use of highly percentage slags for the production of titanium (IV) oxide – quite promising.

Slag advantageously used for the production of titanium (IV) oxide by sulfuric acid method, even if the cost per ton per cent titanium (IV) oxide in them is 1,7 times higher than the cost per ton per cent ilmenite concentrate containing 45-50% TiO_2.

Impurities in the ilmenite concentrate and titanium slag. For the production of pigment titanium oxide by sulfuric acid method used ilmenite concentrates, which include:

– Ilmenite;
– SiO_2 in the form of sand;
– Leucoxene;
– Pyroxene and other ores.

Besides impurities of various ores, ilmenite concentrate found in almost all rare oxides and trace elements such as hafnium, scandium, niobium, zirconium, vanadium, a significant amount of oxides of phosphorus, chromium, aluminum and others. For the pigment industry the particular importance has impurities that negatively affect for the pigmentary properties and particularly for linen of finished product.

Almost all suppliers of titanium containing raw materials (ilmenite concentrate, titanium slag) indicate the chemical composition of such oxides: TiO_2, FeO, Fe_2O_3, Al_2O_3, CaO, SiO_2, Sr_2O_3, P_2O_5, V_2O_5, MnO, MgO. Let us consider each of them separately:

- TiO_2 – after careful laundering of impurities and handle according to technological regulations – a white pigment, finely dispersed, stable compound.
- FeO and Fe_2O_3 – even in small amounts provide red, cream color for pigment.
- Al_2O_3 – complicates the cleaning of solutions in large quantities, increases their strength, but it is used to improve the pigment properties in the form of aluminum hydroxide.
- CaO – large number in the finished product increases the amount of water–soluble salts by partial dissolution. It is very difficult in the processing of ore by sulfuric acid. It accelerates the reaction of gypsum and deteriorates filtering.
- SiO_2 in the form of sand – it's a ballast. Increase the amount of sludge. If SiO_2 is as a part of mineral, mineral after processing by sulfuric acid and dissolving the sulfuric acid salt by water, SiO_2 remains in the form of impurities, which is difficult to filter.
- Chromium Oxides: CrO – black oxide, Cr_2O_3 – dark green oxide, CrO_2 – black oxide, CrO_3 – dark red oxide. In practice, chrome, available in methatitanic acid, is difficult to remove, and its presence in the amount of $1{,}5 \cdot 10^{-6}$ grams in

terms of Cr_2O_3 per 100 grams TiO_2, makes visible to the eyes brownish–yellow color.

- P_2O_5 – inhibits the transition of anatase form of methatitanic acid in rutile form. Methatitanic acid forms white phosphate iron / titanium by calcining in a furnace. P_2O_5 introduced at the stage of processing salt to inhibit the transition of anatase to rutile to prevent harden the product (for example slag processing solutions).
- V_2O_5. There are several vanadium oxides, black monoxide (VO), trioxide (V_2O_3), dioxide (VO_2) and pentoxide (V_2O_5). The most stable is V_2O_5 – amorphous, red, sometimes orange– yellow compound. Red – at temperatures of 650-690 °C; within a high concentration of sulfuric acid (>75%) $V_2O_5 \cdot H_2SO_4 \cdot H_2O$ compound formed, which transform into colloidal $V_2O_5 \cdot H_2O$ with red– brown color. All other vanadium oxides react with acids and alkalis and form volatile compounds which oxidized by air.
- MnO – manganese impurities are undesirable. There are some manganese oxides: (MnO) – gray – green, (Mn_3O_4) – black – brown, (Mn_2O_3) – brown manganese (IV) oxide – (MnO_2) – black. Salts: $MnSO_4 \cdot 4H_2O$ – pink, $Mn_2(SO_4)_3$ – green, $Mn(SO_4)_2$ – brown. The presence of manganese in the final product in quantities of $3 \cdot 10^{-5}$ g per 100 g of TiO_2 in terms of MnO gives gray color for pigment.
- MgO – magnesium oxide, white powder. Pure magnesium oxide is the standard of linen.
- Sc (scandium) – it is a big part of the sulfuric acid hydrolysis. If it is partially remaining in the product, then with the ignition scandium oxide (white powder) is formed from metatitanium acid.
- Zr (zirconium) and Hf (hafnium) – elements often accompany the titanium. After roasting in ovens, these compounds form oxides such ZrO_2, HfO_2 –

chemically inactive, white. The zirconium compounds behave similarly to titanium compounds.

- Nb (niobium). The most stable white compound – Nb_2O_5. At high temperature yellow, but the color is restored with the cooling.

In the selection of raw material for production of titanium (IV) oxide pigment, be aware that it contains impurities that can negatively affect for the whiteness of the finished product.

In slag, which contains titanium, almost no ferric compounds of iron, phosphorus, but the presence of chromophores such as chromium and vanadium affect the quality of the finished product, as well as ilmenite concentrates. The main advantage of using slag, which contains titanium, is the opportunity to get a finished product with higher quality. The disadvantages include high cost of titanium slag.

2.2.2 Colored pigments containing iron

The raw material for synthetic colored pigments which contain iron are metallic iron and metallurgical wastes (steel shavings, scrap metal, slag and other sludge which contain iron), pure salts of iron (II) and iron (III) and in the form of production waste (sulfuric acid etching solutions – waste rolling mills, iron sulfate (II) – waste of titanium (IV) oxide production).

For the production of natural mineral pigments colored pigments, which contain, iron using natural raw materials, the main of which are: hematite or red iron oxide iron (III) hydrate, hydrohematite, goethite, limonite and others.

Hematite and red iron ore (composed of fine is grained hematite units) crystallizes in the hexagonal crystal system and cryptocrystalline forms of iron oxide. In addition to red hematite and red iron ore to cryptocrystalline forms include red glass head (fine-grained aggregates of hematite) and iron red ocher (loose hematite variety).

Because of the great diversity of hematite physical properties vary widely: hardness between 3,5 and 6,5; shine of the metal to a lack of it; color from iron is black to red.

Oxide of iron (III) hydrate occurs as brown iron ore (Hematite). The ratio between the amounts of Fe_2O_3 and H_2O in hematite widely varies.

Hydrohematite contains 0,8 moles of H_2O per 1 mole of Fe_2O_3. Hydrohematite have a hematite crystal lattice, the water forms with the hematite a solid solution.

Goethite has 1 mole H_2O and 1 mole of Fe_2O_3. It is a form of ironstone with high crystallinity.

Limonite has approximate composition $Fe_2O_3 \cdot 1{,}5H_2O$. It is considered as kind of amorphous oxide of iron (III) hydrate. However, in the X-ray researches it gives interference stripes, but they are weak and vague. These stripes coincide with sharp interference stripes of goethite.

2.3 GENERAL CHARACTERISTICS OF MINERAL PIGMENTS

2.3.1 Characterization and chemical properties of titanium (IV) oxide

The wide field of application TiO_2 requires specific properties of each TiO_2brand. It implements either by surface treatment of finished pigment or under salt treatment before pre-stage of calcination.

Thus, depending on the application in Ukraine, TiO_2 produced the following brands: The P-1, P-O2, P-O3, P-O4, P-O5, P-O7, P-O8, P-O9, where the letter P – rutile modification, O – processed, figures – have a particular meaning. Also, A-1, A-2, A-O1, A-O2, where A – anatase modification.

As can be seen from Table 2.5, the pigment of TiO_2 used in enamels, rubber, concrete, plastic, artificial leather, paints, primers, decorative coatings, paper, printing ink and etc.

Thus, the rutile modification has found wider application because of its atmosphere resistance, more hiding power. Anatase modification is used in paints, enamels, which are mainly designed for use inside the buildings.

Titanium (IV) oxide is one of the major powder materials, widely used for different purposes. It is chemically stable, has a high refractive index, has excellent optical properties, leading to a high degree of coating and linen of composites and coatings materials. This is a valuable raw material in the manufacture of pigments and fillers paint industry of composite polymer materials, dielectric ceramics and ceramic films, catalysts, ceramics and Photocatalytic UV filters with a given gradient refractive index, sensitized solar cells, gas sensors and membranes with controlled porosity.

Currently, the world production of titanium (IV) oxide is estimated at more than 6 million tons per year, with about 60 % is used as a pigment for paints, 30 % as fillers for plastics and papers, and the last 10 % for a variety of needs: a part of

Pigmental titanium oxide is available in two different crystalline modifications: anatase titanium oxide and rutile titanium oxide.

By 1949, people believed that only titanium oxide in the anatase form is a white pigment with high quality. Potassium compounds were added for preventing the possibility of the formation of rutile on ignition metathiamine acid, such as potash.

In 1939, the pigment of rutile form was first made. Unfortunately, it did not meet satisfactory pigment properties due to insufficient dispersion (compared with anatase) and yellowness [23]. One reason for yellowing of rutile titanium oxide is the color of its impurities (lower compounds of titanium).

In 1949 the fine titanium oxide of rutile form was made. He has satisfactory color. His bleaching capacity was 40 % higher than that of titanium oxide with

anatase form. Since that time, the production of rutile titanium oxide is extremely increased.

Table 2.5. **Brands of TiO_2**

Mark	Characteristic	Applications
P-1	Rutile, raw	Enamels for building resin, concrete
P-O2	Rutile– processed by inorganic compounds	Latex paint, plastic artificial leather
P-O3	Rutile-processed by inorganic and organic compounds	Latex paint, plastic, artificial leather, with high decorative properties
P-O4	Rutile-processed by inorganic and organic compounds	Primers with high decorative properties
P-O5	Rutile-processed by inorganic compounds	Paper, plastic, decorative films
P-O7	Rutile-processed by inorganic compounds	Paints and coatings, printing inks
P-O8	Rutile-processed by inorganic compounds	Primers
P-O9	Rutile-processed by inorganic compounds	Enamel, with high decorative properties
A-1	Anatase, raw	Rubber, paper and film materials
A-2	Anatase, raw	Viscose fiber paper
A-O1	Anatase-processed by inorganic compounds	Paints, dispersion paints indoors
A-O2	Anatase-processed by inorganic compounds	Enamel, with high decorative properties indoors

The chemical inertia of the rutile titanium is the most important property. It caused by more compact and asymmetrical arrangement of atoms in the crystal lattice (Fig. 2.1). Scheme of elementary crystals cells of anatase and rutile crystals is shown in Fig. 2.2.

Besides, anatase and rutile modifications, also, there is brookite polymorphs modification. These three polymorphs are crystallized in two crystal systems: brookite in rhombic, anatase and rutile in tetragonal, but the last has another atomic crystal structure (arrangement of atoms and the parameters of the crystal lattice). In the crystal lattice of TiO_2, titanium atoms are surrounded by oxygen atoms octahedrally. Formed octahedrons of $[TiO]_6$, are the main building block of all modifications of TiO_2.

Different relative positions of octahydrates $[TiO]_6$ leads to various types of the crystal structure of TiO_2, which have different resistance. Rutile has denser packing of ions in the crystals. Due to this fact, it excels anatase and brookite in thermal stability, density, hardness, refractive index, dielectric constant and has reduced photoactivity. In connection with, rutile form of TiO_2 pigment was most widely used. Its production is more than 75%.

Entering of anatase titanium oxide to the composition of the paints for exterior coatings is accompanied by the phenomenon of «coated[1]». It appears in a few weeks after painting. The degree of «coated[1]» of anatase titanium oxide depends on the properties of the film-forming substance, which is part of refinishing. The reason of «coated» is a photochemical effect of ultraviolet rays of the solar spectrum, affecting film coating. In these conditions, anatase titanium oxide is the catalyst, that stimulates the formation of particles on the surface of the irradiated peroxide compounds. They destroy organic part of the surface coating. Most particles of titanium oxide are not destroyed, but released from organic film former, and form a white film on the surface coating.

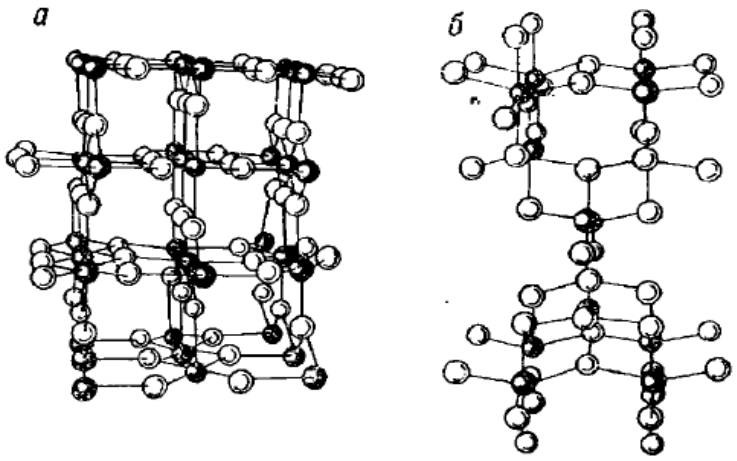
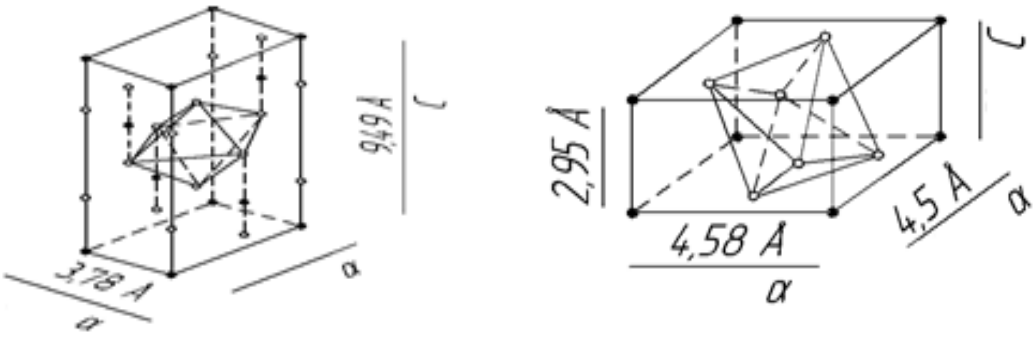


Fig. 2.1. **Crystalline lattices of rutile (a) and anatase (b).**



а б

- titanium
- oxygen

Fig. 2.2. **Crystal unit cell anatase (a) and rutile (b).**

In some cases, slight «coated» it is even useful. Painted building or construction, located in the heart of the industrial area, which has an atmosphere with particles of ash, soot, and other particulate matter, quickly polluted. Slight "coated" provides continuous cleaning of the surface. White patches together with the dust and dirt washed off by rain. After this, the building retains the original bright colors. Significant «coated» leads to cracking of the film coating, loss protective properties and corrosion of the product under the film.

The use of rutile titanium oxide reduces the photochemical effect, also the service life of the finish is greatly increased.

Stabilizers are anions of two- and polyhydric acids, i.e. sulfuric and phosphoric.

The calcination of anatase at the temperature about 915 °C converts it into rutile. In the presence of impurities, which are stabilizing anatase, transformation occurs at temperatures above 950 °C. Stabilizers built into the crystal lattice. It leads to the complicated movement of atoms and groups of atoms, that form a crystal.

Delayed the formation of denser crystal structures. Anions of double – and polybasic acids are stabilizers, including sulfuric and phosphoric.

The temperature of titanium oxide formation from chemically pure metatitanic acid is much lower (about 650 °C). Entering of utilizing embryos to the vibrotic metatitanic acid reduces transition temperature of anatase to rutile to 850°C.

2.3.2 Characteristics, structure and chemical properties of iron–containing pigments

Iron containing pigments have color is caused by the presence in them of one of the iron oxides. These pigments are divided into two groups: natural and artificial. Each of these groups combines pigments of yellow, red, brown and black color.

Iron and oxygen form a series of different oxides, iron (II) oxide – FeO, iron (III) oxide – Fe_2O_3, mixed iron (II, III) oxide – Fe_3O_4, iron (II) hydroxide – $Fe(OH)_2$ and iron (III) hydroxide – $Fe_2O_3 \cdot nH_2O$. Almost, all colored iron compounds, in the presence of cation Fe^{2+} (very weak chromophore) have light greenish– yellow color The presence of cation Fe^{3+} (strong chromophore) – a brownish– red or yellow– brown color. The common presence of ions Fe^{2+} and Fe^{3+} causes a blue or black– blue color.

Iron containing pigments, by chemical compositions, represent the iron (III) oxide, iron (III) hydroxide or iron (II) oxide. These compounds in pure form, in a mixture with each other or mixed with excipients forming a whole range of natural and artificial iron– containing pigments.

Between the chemical composition and color of iron – containing pigments, there is a dependency. Yellow pigments – $Fe_2O_3 \cdot nH_2O$, red – Fe_2O_3, black – Fe_3O_4

and Brown – a mixture of red and black pigments, and sometimes a mixture of all three pigments: red, black and yellow.

The chemical composition of yellow pigments is iron (III) hydroxide, which typically represents one compound of formula $Fe(OH)_3$ or $Fe_2O_3 \cdot 3H_2O$. In fact, there are a number of hydrates of iron (III) oxide, which differs in composition (the content of hydration water), for crystal structure, and the physical state of the particles.

All hydrates of iron (III) oxide have a different color (hue) and various pigment properties. It is possible by changing the conditions of formation iron (III) hydroxide changes color (hue) and yellow pigment properties of iron – containing pigments in a very wide range.

Characteristics, structure, and properties of iron-containing pigments. Currently, iron oxides and hydroxide are among the most common powder materials that are widely used in the manufacture of inorganic pigments and fillers, magnetic media, catalysts, and sorbents.

Substances of this class differ in properties (phase composition, particle size, and shape, the color, the presence of the magnetic properties, etc.) significantly. These properties ultimately determine the area of use. The main types of iron oxides and hydroxides and some of their physical and chemical properties are presented in Table 2.6.

Due to its physical and chemical properties of iron oxides and hydroxides are among the most widespread types of inorganic materials produced by industry

All compounds of iron (III) painted in yellow, red or brown, due to intense absorption in the short– wave spectrum caused by software-transfer (software – charge transfer). It is due to the electronic transformation of the molecular membranes (mainly located on ligands and metal atoms). Expansion of absorption bands throughout the visible region of the spectrum observed for magnetite what is

defined by its black color. In this case, the expansion of the absorption band of light caused by the transition of an electron from a lower cation in cation oxidation higher degree of oxidation. The possibility to receive of non– deficient raw materials with a wide range of colors (different by light resistance and excellent thermal stability).

However, not everyone of iron oxide with good structure can be used like pigment and have the desired color. The pigment particles must have a certain shape and size, the minimum degree of polydisperse, a certain degree of defects in the surface layers of the crystal.

Needle particles α-FeOOH with thickness 0,2-0,4 mm and length 1,5 mm have bright yellow color; by increasing the length of the particle greenish hue appears, while reducing – orange. Oval α-Fe_2O_3 particles with a diameter of 0,2-0,4 mm is brightly red. Reducing the particle size of the pigment makes lighter and increase shifts the shade of cherry tones. However, reducing the diameter size to 0,05 microns or less makes the color pigment in a dull tone, but at lower pigment content in the lacquer coating is transparent. This phenomenon is the base for producing alloying pigments with yellow, orange, red colors and with the same structure, but the smaller size of particles. A large degree of poly dispersed of particles provides an unpleasant shade of brown.

The clear – cut of particles improves the pigment's color. At the same time, it is worse the interaction of pigment particles with the carrier. The particles are easily deposited and cemented at the bottom of the container. So, they are difficult to convert back to a balanced state. It should be noted that the actual pigment particle is a solid unit from primary particles. It has a size about 10-30 microns. Typically, the commercial products consist of fragile agglomerates (secondary aggregates) with size about 100-200 microns, which are destroyed in the process of dispersing at the preparation of paints.

Table 2.6. **Oxides and hydroxides of iron**

Chemical formula	Name	Crystal, lattice parameters	Color	Form of particles	The maximum particle size
FeO	Wustite	Cubic *a* = 4,293 A	Black	Cubic crystals	Several micron
$Fe(OH)_2$		Trigonal *a* = 3,258 A c = 4,605 A	White	Hexagonal plates	Several micron
Fe_2O_3	Magnetite	Cubic *a* = 8,396 A	Black	Cubic or octahedral crystals	Several micron
$Fe(OH)_3$		X-ray	Red-brown	Globules	3-5 nm
α-FeOOH	Goethite	Rhombic *a* = 4,608 A *h* = 9,957 A c =3,021 A	Yellow	Needle crystals [length: width ≥(5-6):1]	Several micron (length)
β-FeOOH	Akageneite	Trigonal *a* = 10,53 A *c* = 3,030 A	Hazel	Needle crystals [length: width ≥(5-6):1]	Several micron (length)
γ-FeOOH	Lepidocrocite	Rhombic *u* = 12,52 A *h* = 3,873 *A* c =3,071 A	Orange	Needle crystals [length: width ≥(5-6):1]	Several micron (length)
δ-FeOOH		Trigonal *a* = 2,94 A c = 4,50 A	Brown	Hexagonal plates	Several micron (length)
α-Fe_2O_3	Hematite	Trigonal *a* = 5,035 A *c* = 13,74 A	Red	Needle crystals [length: width ≥(5-6):1]	Several micron (length)
γ-Fe_2O_3	Maghemite	Cubic *a* = 8,338 A	Brown	Needle crystals [length: width ≥(5-6):1]	Several micron (length)

Also, by usage some ferric oxides should take into account its magnetic properties. Availability, in the iron atom, untouched domestic level ($3d^6$) (which has 4 uncompensated electrons with spin magnetic moment) leads to the appearance of the total magnetic moment equal to 4 Bor's magnetons. The presence of the

magnetic moment of the atom is a necessary condition for the cooperative effects of magnetism. It includes iron magnetism and noniron magnetism, (uncompensated magnetism). Ferromagnetic properties are only of a particular crystal structure and at temperatures not above the critical (for (ferromagnetic – Curie's temperature; for ferromagnetic – Néel's temperature). Thus, between electrons of blank internally adjacent atoms, a strong electrostatic interactions appearance. This cooperation called the exchange. From all iron compound, magnetite (Fe_3O_4) and γ-iron oxide (γ-Fe_2O_3) have strong magnetic properties. It makes them widely used (especially γ-Fe_2O_3) as a powder magnetic material.

It should be noted, that the magnetic properties of materials, particularly coercive force, that prevents involuntary degaussing of magnetic materials, greatly depends on the particle size of powders. Single-domain particles have the maximum coercive force. Large particles are consisting of multiple domains and their magnetization can be changed by a weak magnetic field (by mixing blast walls). In the case of small particles (less than 20 nm for γ-Fe_2O_3) power exchange weakened by heat significantly. The compound is transformed into the superparamagnetic state. For magnetic-using only single-domain particles.

In the case of the single-domain particle, the magnetization reversal is made only by magnetization rotation. The forces of anisotropy (due to the form of particles magnetic -crystal structure of matter and mechanical stresses) prevents this fact. So, for highly coercive powders, is necessary to use a substance that shows high magnetic-crystal anisotropy.

The last one consists of particles with an elongated shape. It is also possible to create particles strongly anisotropic to the mechanical stresses. In γ-Fe_2O_3 powder coercivity force is about 70 % and caused by the anisotropy's shape of particles and about 30 % – magnetic-crystal components; the part of mechanical stress insignificant. The optimal length is γ-Fe_2O_3 particles' length near 300-500 nm

in the form factor of 6-8. The maximum value of the coercive force of powder is 350-400 Oe. To record video generally use a process of cobaltation γ-Fe_2O_3 particles with a layer of cobalt ferrite, thus enhancing the coercive force of 1000 Oe.

Yellow iron oxide. The yellow ferric oxide is a crystalline monohydrate of iron oxide with composition FeOOH or $FeO \cdot H_2O$. It is very clean and has bright ocher-yellow color with shades of lemon yellow to orange.

The crystal structure of yellow iron oxide similar to the goethite. Its share 4, oil consumption ~65,0, the average particle size of 0,3-0,8 microns.

Yellow iron oxide used for the production of paints and enamels of all types: oil-based, glue, facades, and art. In large quantities, the yellow iron oxide used for the manufacture of artificial ocher. A mixture of yellow iron oxide with fillers in a ratio of 1:4-1:5 creates an artificial ocher. It is more superior then natural color and has good pigment properties, especially oil-consumption. In the result, artificial ocher gradually replacing natural.

Red pigments containing iron. Group of red pigments containing iron combines a number of pigments having hues from orange-red to bluish, purple and even red. They consist of pure iron oxide Fe_2O_3 with same crystalline modification named hematite (hexagonal system). The difference in their shades depends on the different physical state of the particles (their dispersion, shape and some other properties). Therefore, these pigments are combined into one group – red iron (III) oxide. Microscopic analyses showed that iron (III) oxide with orange shade consists of particles, which have the form of plates – 0,25 microns, and bluish – with a grain size of 0,75 microns.

The group of artificial red pigments containing iron combines some pigments that are different from the red iron (III) oxide not only color but also the pigment properties (hiding et al.). These pigments, known as the red of Mars, containing in

its composition some impurities and received by a special method; so now they have little practical value.

Red iron (III) oxide is very resistant to sunlight, atmospheric agents, alkalis and weak acids; in strong sulfuric acid, it dissolves only with heating. Red iron (III) oxide has very high hiding – 3-4 g/m^2. So, it surpasses all pigments, beside carbon black; it also has great intensity; specific weight is 5-5,15. Red iron (III) oxide is used for the manufacture of various paints and enamels.

Black iron-containing pigments. Black iron oxide is a chemical composition of mixed oxide lick as Fe_3O_4, usually with a few impurities Fe_2O_3. The content of FeO in the pigment ranges is from 18-26 % and Fe_2O_3 72-74 %. Black iron oxide has a rich bluish-black color, high hiding power, high intensity and great resistance to light and atmospheric conditions. It is dissolved in weak acids, in concentrated nitric acid and ammonia insoluble. Black iron is hardly oxidized oxides at washing and air-drying processes. However, it is easily oxidized at ignition with the air, turning to the red iron (III) oxide. Black iron oxide crystallizes in a cubic system. The share of black iron oxide, 4,73; oil-consumption 28, the average particle size ranges between 0,25-0,50 microns.

Fe_3O_4 used for primer and paint coating metal in those cases, where the film requires high mechanical strength. It is also used instead of carbon black, which tends to float on the surface of the film. In addition, black iron oxide used, as a feedstock to produce a red iron oxide, which it is calcined at high temperatures.

Brown pigment is a mechanical mixture of red and black iron oxide with the addition, if necessary, to increase the color and yellow iron oxide. A combination of these components is very uniform because they all have the same dispersion.

The number of iron (II) oxide pigment in brown shade varies due to depending on the pigment. The most frequently used light brown pigment. It contains 93 % of Fe_2O_3, 6 % of FeO, and 85 % of bright brown Fe_2O_3 and 14 % of

FeO. The share of such mixtures 4,9; oil-consumption 25, the average particle diameter 0,25-0,75 mm.

2.4 TECHNOLOGY FOR PRODUCING OF MINERAL PIGMENTS

There are two methods of producing pigment TiO_2: sulphate and chloride. The quality of the pigments produced by sulfuric technology is no different from the quality of pigments TiO_2, manufactured by chloride technology, but it is much less wastes with the chloride technology than by sulfate one [22,25].

In Ukraine pigment TiO_2 produced by sulphate method. «Crimean Titan» and «Sumykhimprom» are the domestic manufactures.

Foreign producers of TiO_2, which are using sulfuric technology – fully utilize the waste: iron salts – in the production of coagulants, color pigments (red, yellow, black); waste of H_2SO_4 used in the production of CO_2, $CaSO_4$ etc.

The raw material for the obtain TiO_2 by sulfate method are:

1) Ilmenite with the content of TiO_2 not more than 45-56%. With higher content of TiO_2 in ilmenite, the last one badly decomposed by H_2SO_4. The complete lack of natural rutile and the ratio FeO to Fe_2O_3 in ilmenite at least 2 are desirable;

2) Titanium slag, which contain 75-80% of TiO_2. Titanium slag produced in Ukraine in Volnogirsk Mining and Metallurgical Combine (92 % of TiO_2) and Zaporizhzhia Titanium – Magnesium Plant (TiO_2 62-72 %).

When a TiO_2 produced by chloride methods, the raw materials are more diverse: ilmenite, natural rutile, titanium slag (TiO_2 = 85-90 %), other waste, which has a content of TiO_2 more than 90 %.

Table 2.7 shows a comparison between sulfate and chloride ilmenite processing methods.

Table 2.7. **Comparison of methods for processing the ilmenite [22,25]**

Sulfate method	**Chloride method**
Ilmenite concentrate	
Drying, grinding	
Decomposition	drying, grinding coke
Recovery of iron	Melting of the dust in the furnace
Cleaning of the solution	Bottling of iron and slag
Vacuum crystallization	Cooling and hardening
Removal of iron sulphate	Crushing and grinding of slag
Vacuum evaporation	mixing of slag with resin
Hydrolysis	Briquetting of slag
«White» filtration	Chlorination
Processing by salts	Capture of $TiCl_4$
Calcination	1 Rectification of $TiCl_4$
Dry milling	2 Rectification of $TiCl_4$
Wet milling	Burning of $TiCl_4$ in plasma
Hydro-classification	Capture of TiO_2 and Cl_2
Surface treatment	

According to scheme for processing ilmenite by sulphate method carried out as follows: ilmenite concentrate is dried, crushed, decomposed by H_2SO_4, Fe^{3+} is reduced to Fe^{2+}, remove iron sulfate, purified solution is hydrolyses, filtered, treated, grind, and if necessary, carry out surface treatment.

For the chloride process ilmenite concentrate is dried, crushed, mixed with coke, smelt and get iron, separating the titanium slag, crushed slag and mixed with resin, make a briquette, chlorinated a briquette, condensed $TiCl_4$, purified $TiCl_4$, burn, separating the formed TiO_2, if necessary, carry surface processing.

Disadvantages of sulfate method: method have a lot of stages, a large amount of waste. Disadvantages of chloride process: utilization of iron (III) chloride and other impurities, necessity of corrosion resistant materials for manufacturing equipment. However, the chloride process benefits include greater environmental friendliness compare to the sulfate method, continuous of process, full automation.

2.4.1 Production technology of pigmentary titanium (IV) oxide by sulfate method

Pigment industry is mainly interested ilmenite concentrates containing: ilmenite $FeTiO_3$; titaniferous [$TiFe_2O_3 + Fe_3O_4$] with the ratio of FeO/Fe_2O_3 not less than 2; hematite-ilmenite $FeTiO_3 \cdot Fe_2O_3$ with the ratio of FeO/Fe_2O_3 not lower than 2.

Schematic diagram of obtaining pigmentary titanium (IV) oxide by sulfate method. This method is based on processing of titanium concentrates (the ilmenite – $FeTiO_3$, perovskite – $SaTiO_3$, titanite – $SaTi(SiO_4)O$) and titanium slags by sulfuric acid to obtain the solution of titanyl sulfate or titanium oxide-sulfate ($TiOSO_4$), which is then hydrolyzed to form of titanium hydroxide ($TiO(OH)_2 \cdot nH_2O$), followed by calcination of receiving precipitate to obtain a powder of titanium oxide (TiO_2) of anatase or rutile structure.

This method is complicated and consists of many stages, the main ones are:

1) Preparation of raw materials;

2) Processing (opening, expansion) of concentrate sulfuric acid;

2) Treatment the obtained sulfate solutions;

3) Hydrolysis of solutions;

4) Calcining of titanium hydroxide to oxide;

5) The final treatment (cooling, grinding).

The disadvantage of processing the perovskite and titanite by sulfate method is formation of large amounts of gypsum or a mixture of gypsum and silica, respectively. It`s significantly complicates the process, and therefore the most widely used raw material is ilmenite.

Schematic diagram of processing the ilmenite by sulfate method, shown at the Fig. 2.3.

Preparation of raw materials. The method of mechanical unloading, receiving, storing and in – plant transportation of ilmenite concentrate largely depends on its properties.

An important factor is humidity of concentrate. When the content of moisture in concentrate is 1,0%, then in the winter it does not freeze, it has slope angle of 35°, it is non- caking and suitable for storage in silos without aeration. Concentrate which is not grinded by ball mills in concentration plant often differ by irregular shape of the particles, which resulting in increasing of slope angle by 45°. When the content of moisture in concentrate is 1,5 %, then it is freezes, so it mechanized of unloading and transportation is impossible.

If the concentration plant used wet gravity separation or flotation, the enrichment process should end by drying to residual moisture content for less than 1,0 % (with periodic process of decomposition). Drying can be performed by direct contact with the concentrate products of burning fuel, such as rotating drums and fluidized bed furnace.

Continuous decomposition of the concentrate associated with preparing a mixture of concentrate with oleum. In this case, the residual moisture content in the concentrate should not exceed 0,1 %. To achieve such low moisture content, it is requiring installation of the dryer. The oil or gas can serve as fuel. In the latter case it is possible burning gas directly inside the drying drum. Overheating concentrate to 300-400 °C does not affect the course of decomposition. The residence time of

the concentrate in the dryer with the initial moisture content of 5-6 % is only 6 minutes. Thus, drying performance is very high.

Concentrate usually crushed in a ball mill of continuous operation with air separation in a closed loop. Fig. 2.4 shows the schematic diagram of drying and grinding ilmenite. Ilmenite from the batcher 1 is fed into the dryer drum 9 to achieve residual moisture content in the concentrate less than 0,1 %. Next, dried ilmenite concentrate fed to elevator 2 by conveyor 10, which fall on the ball mill and grinding to 3-45 microns. Then concentrate is fed into the air flow separator 5, where coarse fraction of the dust returns to the mill and thin air rushes into the battery cyclones. The excess air gets into the system as a result of suction, suction is released through the bag filter 7 with automatic shaking.

The disadvantages of the scheme include high frequency of circulation needed for minimal content of coarse milling fractions in the product, which inevitably entails a significant content of fine fraction of the material is returned to the grinding cycle. In addition, the content of fractions <40 microns in the initial concentrate is insignificant and partial allocation during its previous separation by a large multiplicity of circulation, does not compensate for the harmful further processing of concentrate, which is over grinded.

Decomposition of titanium concentrate. Typically, finely ground titanium concentrate decomposed with concentrated sulfuric acid (85-95 %) in batch reactors. The reaction mixture is heated by acute steam and simultaneously mixed with compressed air. Since the reaction between ilmenite and sulfuric acid is exothermic, it is begun at a temperature of 120-135 °C, it is rapidly proceeding with heating the reaction mass to 180-220 °C for several minutes. Then occurs frothing, then the mass hardens. The overall yield for the ilmenite is 94-97 %. After cooling for several hours, fusion cake leached by water at 55-65 °C.

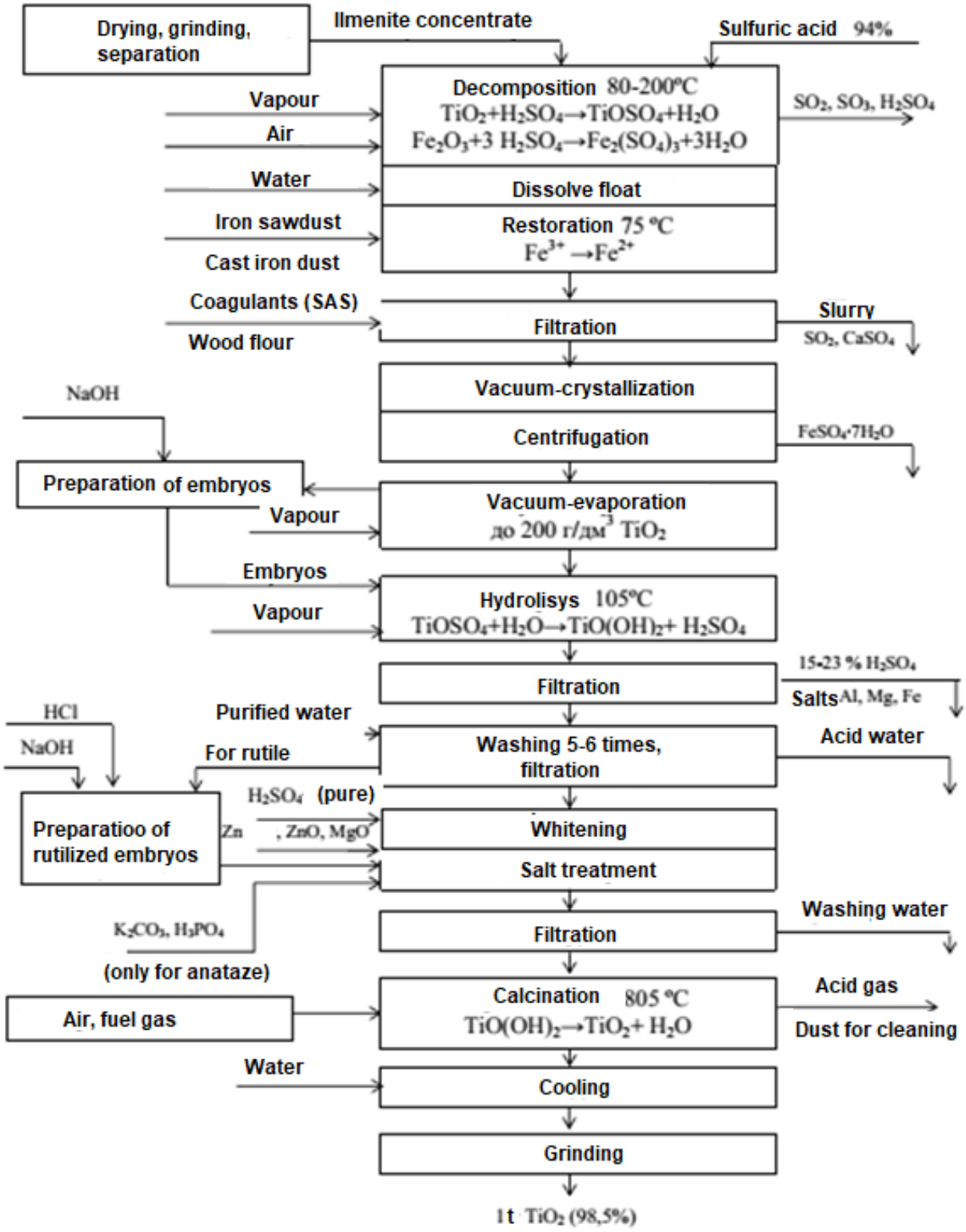
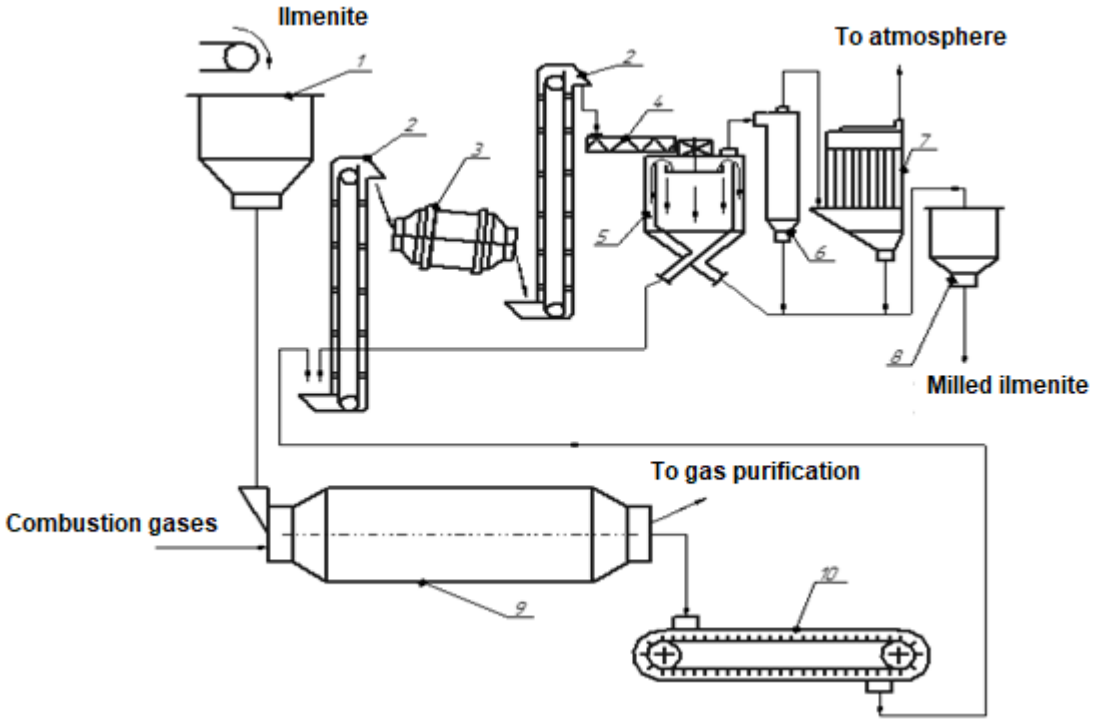


Fig. 2.3. **The basic scheme for obtaining pigmentary titanium (IV) oxide by sulfate method.**



1 – consumable batcher; 2 – elevator; 3 – tubular mill; 4 – feeders; 5 – air separator; 6 – cyclone; 7 – bag filter; 8 – batcher issue; 9 – dryer drum; 10 – scraper transporter.

Fig. 2.4. **Schematic diagram of drying and milling of raw material.**

The resulting acidic solution has a complex colloidal chemical composition, depending on the acid content, temperature and exposure time. The optimal composition of the solution is: 110-120 g/dm^3 TiO_2, 40-100 g/dm^3 iron sulphate, 220-240 g/dm^3 of active H_2SO_4 impurities and other sulfates. Also, part of the insoluble impurities contained in a colloidal suspension.

In the process of decomposition of the ilmenite by sulfuric acid take place the following reaction:

$$TiO_2 + H_2SO_4 \rightarrow TiOSO_4 + H_2O, \quad (2.1)$$

$$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O, \quad (2.2)$$

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_{3+} 3H_2O \quad (2.3)$$

and other metals:

$$MeO + H_2SO_4 \rightarrow MeSO_4 + H_2O. \quad (2.4)$$

The mechanism of titanium slags decomposition by sulfuric acid is more complicated:

$$TiO_2 + H_2SO_4 \rightarrow TiOSO_4 + H_2O, \quad (2.5)$$

$$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O, \quad (2.6)$$

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2, \quad (2.7)$$

$$4Ti_2O_3 + H_2SO_4 \rightarrow 8TiO_2 + H_2S, \quad (2.8)$$

$$Ti_2O_3 + H_2SO_4 \rightarrow 2TiO_2 + SO_2 + H_2O, \quad (2.9)$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O. \quad (2.10)$$

To provide a high enough degree of concentrate decomposition, it is necessary to conduct operations with a large excess of sulfuric acid or quickly remove water from the reaction zone. Method of decomposition based on the rapid removal of water from the reaction zone, which is also known «Solid Phase expansion».

Reactions of ilmenite decomposition by sulfuric acid, is followed by large heat release. Moreover, the higher the TiO_2 content in the concentrate, the less heat is released from the decomposition and the more heat is required for supply from the outside to the mix of the concentrate with acid. Correlation between mass quantities of sulfuric acid and titanium (IV) oxide is 1.22. For obtaining of TiO_2 with satisfactory pigment properties, it is necessary that in the solution, which is goes to hydrolysis, mass ratio of active sulfuric acid and titanium (IV) oxide was 1,9-2,0.

It is impossible to increase excess of sulfuric acid without bad influence for the quality of hydrolytic solution. Some enterprises in order to save sulfuric acid, the ratio in the fusion cake after decomposition is reduced to 1.7, and the required

amount of sulfuric acid is introduced in the leaching afloat by using acidic wash water from these operations. In this case, the cycle returns titanium (IV) oxide contained in the wash water.

The most important distinguishing feature of the of titanium oxysulfate solution- continuous change its composition over time. Since the formation of the solution, begins consolidation of molecules, accompanied by decoupling of SO_4^{2+} groups and replacing them for OH groups. Prolonged standing of solution, leads to molecules aggregates formation with colloidal size, and then solution becomes turbid and form white precipitate of metatitanic acid.

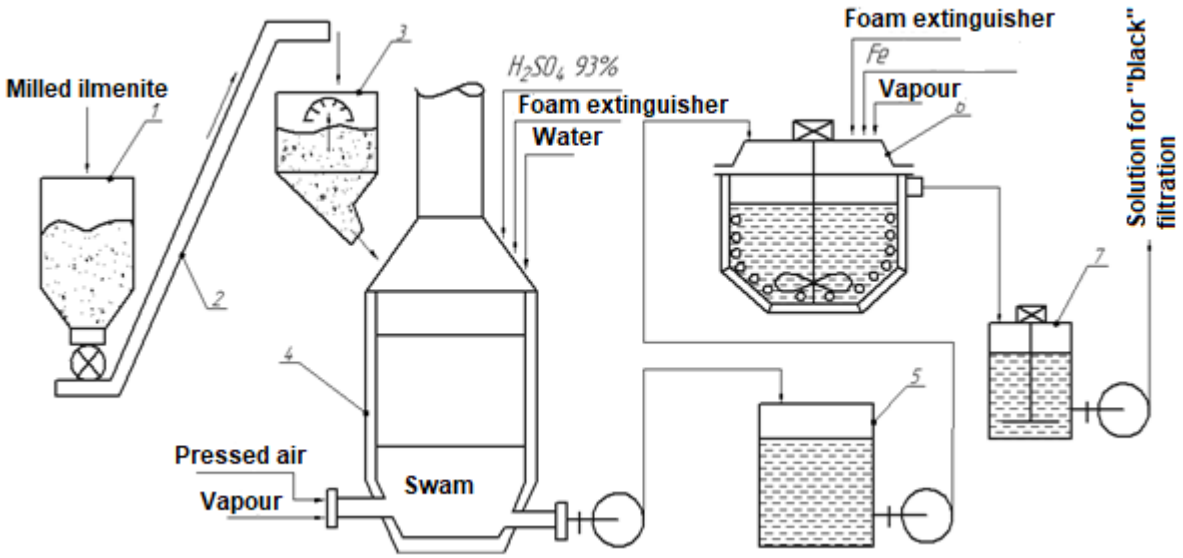
The degree of stability of the solution is determined as follows: 25 cm^3 solution is diluted with water in a volumetric flask for 250 cm^3, filtered and selected 10 cm3 of filtrate in 500 cm^3 flask, in which add the water in portions of 50 cm^3 (2 times) and then 100 cm^3. Sample is shaken after each adding of water, it is needed to mix the solution and, if the sample becomes turbid for 1-2 minutes, it is needed to add the next portion. When opalescence appears or weak turbidity it is needed to add to50 cm^3 of water to a significant turbidity.

The degree of stability is characterized by the total number of cm^3 of water, which added to 10 cm^3 of filtrate (i.e. to 1 cm^3 of stock solution). For the solution with required quality this number is 600-700. If it is below 300, it is believed that the solution has lost stability and is not suitable for hydrolysis. Clean, filtered solution is stable during 2-3 days. However, the storage of unfiltered solution leads to significant reduction in stability, which is reached by the end of the first day. The stability is falling if in solution hit the particles of metatitanic acid, that can serve as nuclei which promote hydrolysis. Harmful effect on the stability has the temperature fluctuations, even a slight dilution of solution by water and especially heating the solution by acute steam.

The high concentration of iron sulfate (130 g/dm^3 in terms of iron) – second feature of the solution. Even at 45 °C crystals of iron sulfate heptahydrate starts to precipitate, accompanied by increasing concentration of titanium oxy-sulfate in solution.

The third important feature is high corrosion activity towards the solution of ferrous metals. The presence of a strong reducing in solution (trivalent titanium) causes the destruction of the oxide film that passivates the steel surface. For example, the common brand stainless steel 1H18N9T fairly stable in 20% sulfuric acid but in industrial solutions of titanium (III) sulfate, which contain the same concentration of acid, it is unstable (except reduction process).

Let's consider the schematic diagram of titanium raw materials destruction (Fig. 2.5). From the bunker 1 prepared milled ilmenite concentrate is loaded by scraper 2 into the bunker 3, which is equipped with weights.



1 – batcher of grinded ilmenite; 2 – inclined transporter; 3 – batcher–balance; 4 – reactor of decomposition; 5 – intermediate reactor; 6 – recovery reactor; 7 – container of recovered solutions.

Fig. 2.5. **Scheme of titanium containing raw material decomposition.**

From the bunker, concentrate fed into the reactor of decomposition 4, in which also added 93 % H_2SO_4, defoamers, water, acute steam and pressed air. The presence of ammonium sulfate increases the output of $TiOSO_4$. The obtained, fusion cake through the intermediate reactor 5 enters to the reactor of iron (II) recovery 6.

As follows from the obtained solution in the process of decomposition (for reactions 2.2 and 2.3), the main impurity is iron (II) sulfate and iron (III) sulfate. The iron (III) sulfate is hydrolyzed and precipitated by pH 2. Therefore, to prevent deposition (Fe (III) together with titanium hydroxide) it is conducted a preliminary recovery from Fe (III) to Fe (II). (The start pH of deposition is 6) adding a solution of iron shavings. The end of the reaction is determined by the appearance of violet color, that is, the formation of ions Ti^{3+} (in an amount of 3-5 g/dm^3).

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2, \quad (2.11)$$

$$Fe_2(SO_4)_3 + 2H^+ \rightarrow 2FeSO_4 + H_2SO_4, \quad (2.12)$$

$$Fe + Fe_2(SO_4)_3 = 3FeSO_4, \quad (2.13)$$

$$2TiOSO_4 + H_2 + H_2SO_4 \rightarrow Ti_2(SO_4)_3 + 2H_2O. \quad (2.14)$$

Compounds Ti^{3+} is strong reduction agents, and they prevent the possibility of re-oxidation of Fe (II) to Fe (III) and, accordingly, precipitation and adsorption to iron hydroxide titanium.

The recovery operation can be performed both periodically and continuously. Continuous recovery designed for continuous leaching can be combined with periodic decomposition. In this case, between the decomposition and recovery devices set intermediate tank with a mixer.

Flakes cast iron the reducing agent is continuously supplied to the first along the recovery process unit, equipped with a mixer. There is continuously fed a solution of intermediate capacity. Consistently includes at least three sets of recovery. Submission of cast iron shaving adjusted automatically depending on the

content of trivalent titanium solution that follows. Dimensions of pieces of cast iron shavings coming to the plant should not exceed 3 mm, otherwise they must be provided for grinding.

Simultaneously with the process of recovery occurs oxidation of solution by oxygen supplied to the device for mixing. Therefore, the quality of shavings is paramount. Trimmings must not contain oils, scale, and impurities of alloy steels. Poor quality of scraps increases the duration of recovery up until the balance between the speed of the metal and the rate of oxidation of trivalent titanium oxygen. The temperature of solution drops, the solution has heated by acute steam, due to the decrease of its stability. Cast iron shavings must conform to the chemical composition listed in Table 2.8.

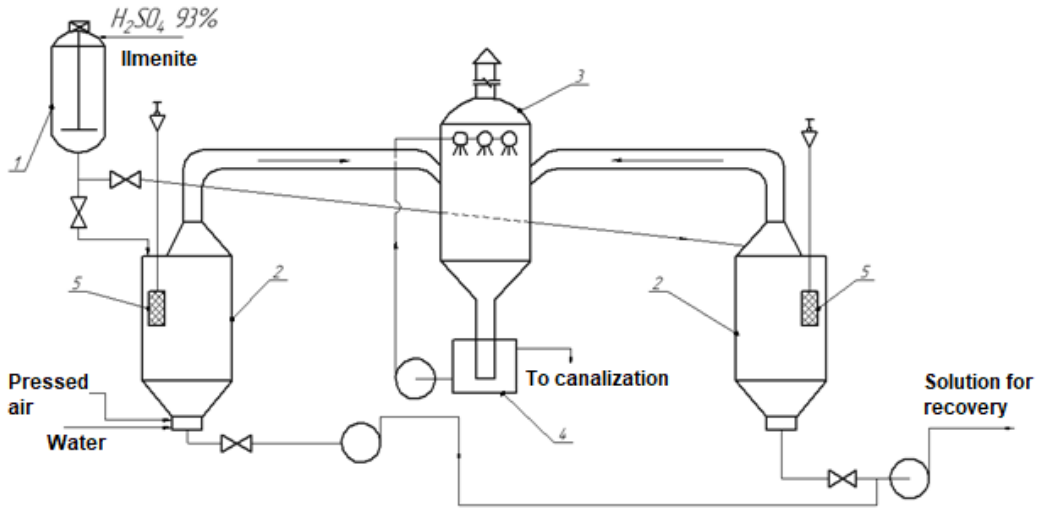
If recovery is conducted in a separate unit, the capacity of decomposition unit reaches 300 m^3. In the shops of less power, which are used reactors with a capacity of 45 m^3 or less the process of recovery carried out in the same apparatus of decomposition (Fig. 2.6).

Table 2.8. **The composition of cast iron shaving**

Substance	**%**
Fe, not less than	85,0
Cr, not less than	0,1
P_2O_5, not less than	0,4
Mn, not less than	1,25
Moisture, not less than	4,0

According to this scheme, 2-3 hours after the leaching unit of decomposition through the top hatch load a packaged pruning black tin to recover trivalent iron contained in the solution in divalent iron. By the end of the leach decomposition in the machine using hoists lowered basket packed with stainless steel trim, and 2-3 hours of recovery ends.

Thanks to the protective action of tin of scraps that dissolved, basket made of stainless steel 1H18N9T that other operations producing titanium (IV) oxide quickly exposed the corrosion.



1 – dosing mixer; 2 – reactor of decomposition; 3 – irrigation of exhaust gases; 4 – water seal; 5 – baskets with edged tin.

Fig. 2.6. **Schematic diagram of a combined decomposition and recovery.**

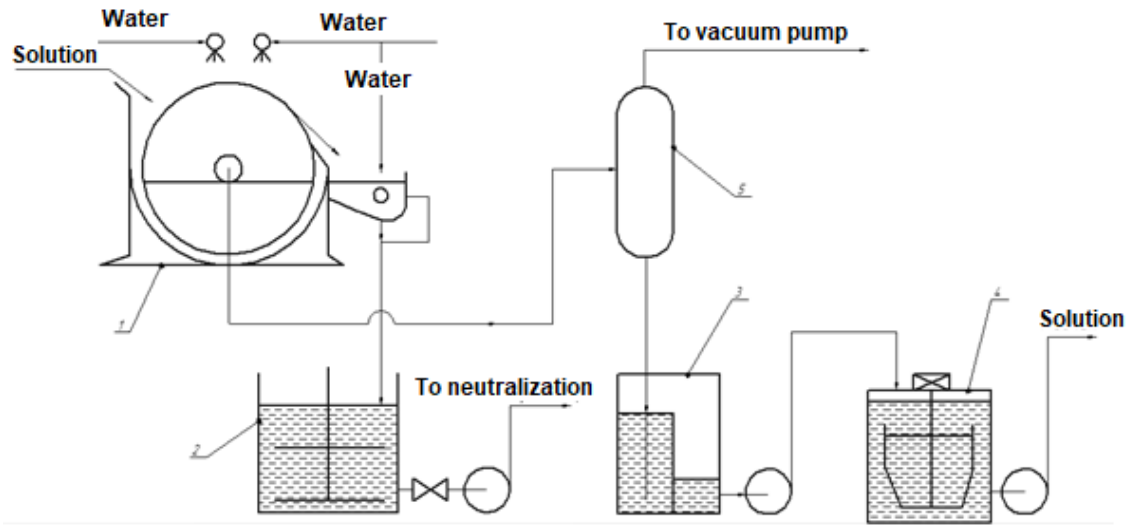
Structure and key indicators of reduced solution is given in Table 2.9 [23,25].

Table 2.9. **Structure and key indicators of reduced solution**

Indicators, composition	**Value**
TiO_2, g/dm^3	130-140
Ti^{3+}, g/dm^3	2-3
Sludge, g/dm^3	20-30
Ratio: Fe:TiO_2 H_2SO_4:TiO_2	0,90-0,95 1,9-2,0
Stability	700
Temperature, °C	65-70

Cleaning of sulfate solution. Then the resulting solution washed on alluvial filters of sludge. They carry out so-called «black» filtering. (Fig. 2.7). Sludge that

remains in solution after decomposition and reconstruction, contains an average of 25% TiO_2, 40% (SiO_2+Al_2O_3), 30% iron oxide.



1– drum vacuum filter; 2 – collector of sludge; 3 – water seal;

4 – collector of filtered solutions; 5 – vacuum separator.

Fig. 2.7. **Schematic diagram of the "black" filtration.**

According particle size sludge is divided into two factions:

1) Crude fraction containing particles of silica sand, ilmenite, which is not decomposed, and other minerals, those have a high deposition rate;

2) A fine fraction, which is a product of decomposition of ilmenite, rich in silicic acid and precipitated very slowly.

Coagulation is used for clarification of solution, but even with the introduction of fine fractions their deposition rate is not high. The deposition rate of slurry in general can vary depending on the properties of concentrate enrichment method used and the nature of the reagents (coagulants and flocculants). Great influence on the speed of clarification has a degree of stability. Coagulation (flocculation) of colloidal particles is usually carried out using flocculants – Surfactants or HMC.

Then clarify solution cooled from 50-60 °C to 10-15 °C, and crystallization of iron sulphate ($FeSO_4 \cdot 7H_2O$) take place.

The dependence of the iron (II) sulfate solubility on the concentration of sulfuric acid at different temperatures, characterized by diagram shown in Fig. 2.8. Crystallization is carried out to a residual ratio in the solution $Fe:TiO_2$ = 0,25:0,30.

The cooling of the solution is achieved by evaporation under vacuum in a vacuum crystallizer of continuous operation, which is supported by the multi steam vacuum ejector unit, which strictly requires constant steam pressure in the network.

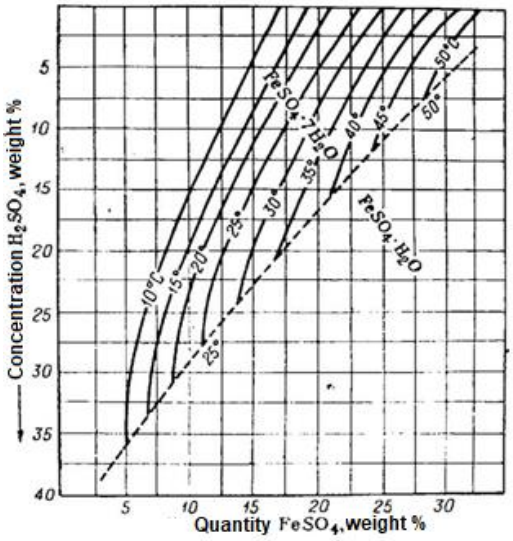
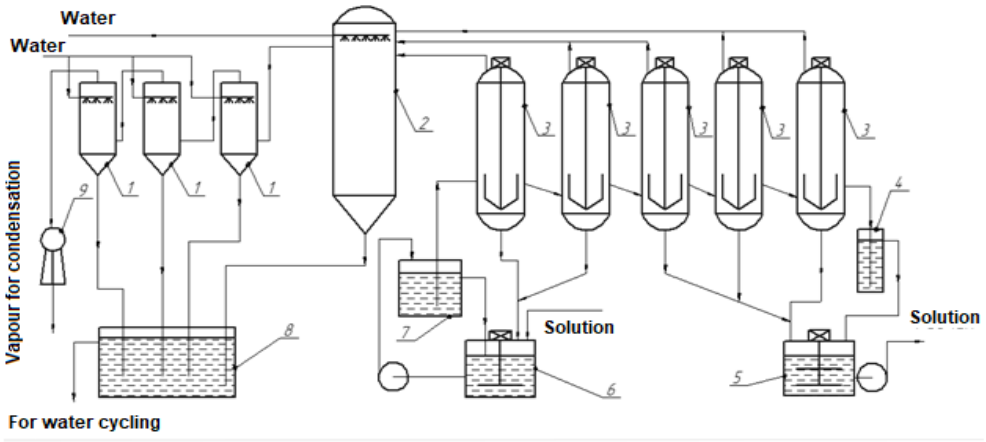


Fig. 2.8. **Diagram of solubility $FeSO_4 – H_2SO_4 – H_2O$ system.**

Clarified solution from thickener or drum vacuum filters enters to the vacuum crystallizer 3 and is consistently goes at least three such units, where solutions boil under vacuum, the water evaporates, the solution becomes supersaturated and form iron sulphate crystals. A solution of iron sulphate crystals flows into a collector 6 (Fig. 2.9).



1 – auxiliary condensers; 2 – the main condenser; 3 – vacuum crystallizer; 4 – water seal pulp; 5 – a collector for pulp; 6 – collector for solution; 7 – water seal solution; 8 – water seal; 9 – steam ejector pump.

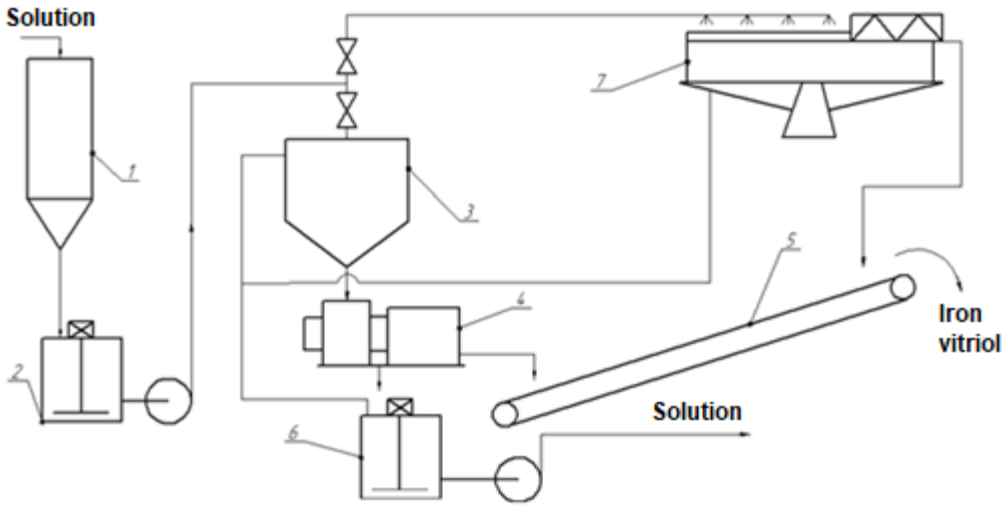
Fig. 2.9. **Schematic diagram of five steps crystallization of continuous operation:**

After that, the suspension of crystals $FeSO_4 \cdot 7H_2O$ goes to the centrifuge and filters (Fig. 2.10), where the crystals are separated from the solution by centrifugation or filtration. For 1 ton of TiO_2 goes 3,2-3,6 tons of $FeSO_4 \cdot 7H_2O$, which then can be used in the production of yellow and/or red pigments which contain iron.

The resulting purified acid solution has the next composition: 140-150 g/dm^3 TiO_2, 280-300 g/dm^3 active H_2SO_4, 25-30 g/dm^3 Fe. For the hydrolysis of obtain pigment – titanium oxide the most suitable solution containing 200 g/dm^3 of TiO_2 and having an acid factor near 2 (ratio between H_2SO_4 and TiO_2). Therefore, the solution is evaporated in vacuum evaporators at 70-75 °C and 200 g/dm^3 of TiO_2 and sent for hydrolysis.

Hydrolysis of titanyl sulfate solutions. To avoid premature hydrolysis, the solution is evaporated at a temperature of 55-57 °C and residual pressure of 60-80 Torr. Fig. 2.11 shows the continuous evaporators. The solution from the tank

5 through the pressure tank 1 enters to the evaporator 2 and discharged to the collector 7. Formed steam passes through the barometric condenser 4, not condensed gases are sucked by steam ejector unit. Hot water goes through hydraulic valve down the drain or used in the water cycle. The approximate composition of the solution is shown in Table 2.10.



1 – water seal; 2 – collector of suspension; 3 – thickener; 4 – centrifuge; 5 – transporters; 6 – collector of transparent solutions; 7 – plan-filter.

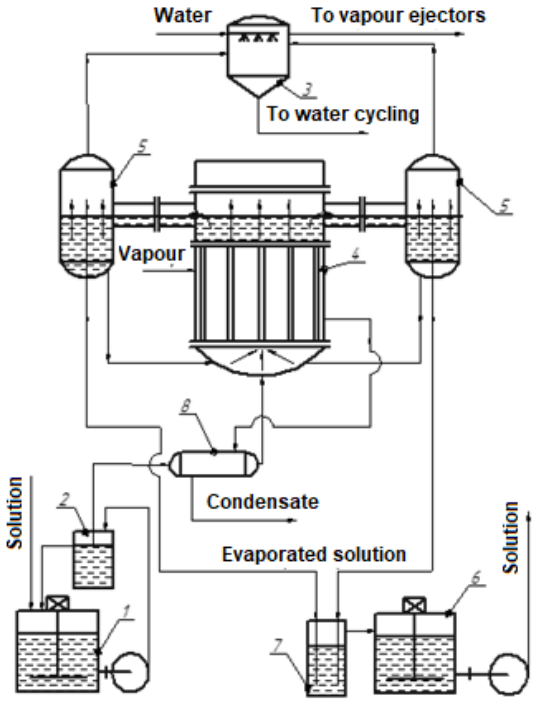
Fig. 2.10. **Schematic diagram of removing iron sulfate from suspension using centrifuges and filter plan.**

Table 2.10. **The composition of the evaporated solution**

Substance	**Content, g/m^3**
TiO_2	220
H_2SO_4	420
Fe	60
TiO^{3+}	2-3

To accelerate the hydrolysis, increasing the yield, and most importantly, to obtain titanium hydroxide particles of a certain size in the before hydrolysis solution injected specially prepared embryos of titanium hydroxide. Usually for obtaining

embryos, it is selected a small part before hydrolysis acid solution (0,3-0,5 % wt. of the total content of TiO_2) and in a separate reactor neutralized with NaOH solution to pH 3 maintaining the sediment for 1-2 hours at 60-80 °C. Hydrolysis is carried out mainly periodically in reactor equipped with a stirrer and coil for heating and cooling. Before hydrolysis acidic solution is heated, add the resulting embryo Sol and carry out the process of boiling the solution (105-110 °C) to 96-97 % conversion of titanium oxy sulfate in titanium oxy hydroxide. Duration of hydrolysis operation, including loading and unloading, is 7 hours.



1 – tank for working solution; 2 – water seal; 3 – condenser; 4 – the main heat exchanger; 5 – evaporator– separator; 6 – tank for the evaporated solution; 7 – water seal; 8 – heat interchanger.

Fig. 2.11. **Schematic diagram of two-flow vacuum evaporation unit.**

The exact mechanism of hydrolysis is unknown, in practice, considered that the following overall reaction takes place:

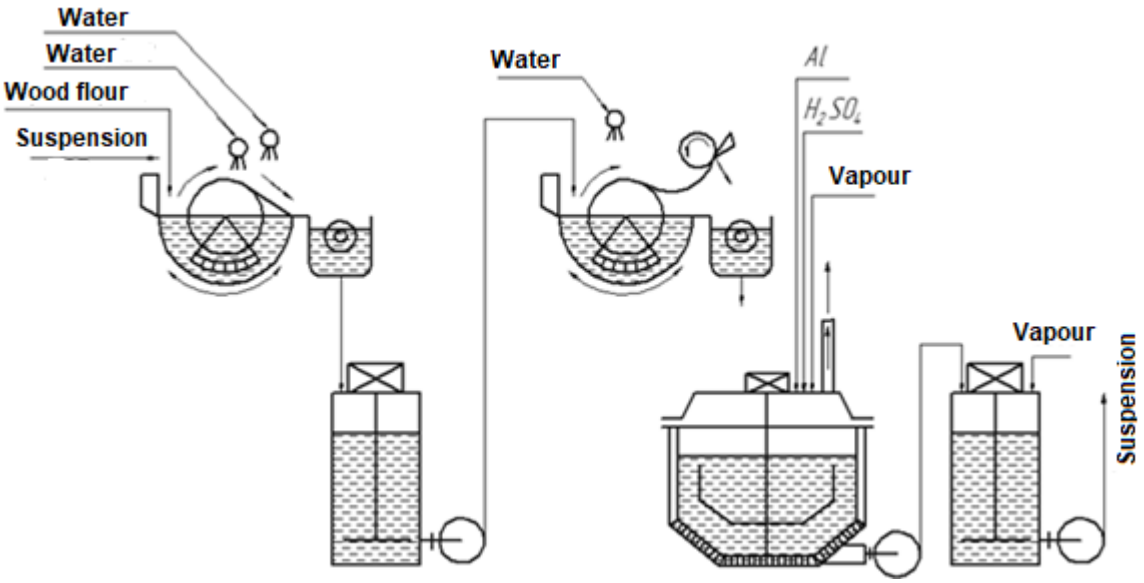
$$TiOSO_4 + 2H_2O \rightarrow TiO(OH)_2 + H_2SO_4. \quad (2.15)$$

The formation of $TiO(OH)_2$ or H_2TiO_3 (metatitanic acid) passes through a series of complex changes, depending on the acidity, TiO_2 concentration, temperature etc. In general form micelles, which are transformed into ash (tin group), then they coagulate and precipitate. And the next so-called aging precipitate the tin group converted to oxo-group that are more stable and less reactive able. The process of hydrolysis is completed when all ortho titanium acid ($TiO_2 \times 2H_2O$) under the influence of temperature, time, embryos precipitate as metatitanic acid ($TiO_2 \cdot H_2O$).

The precipitate that has rough structure of $TiO_2 \cdot 0{,}71H_2O \cdot 0{,}07SO_3$ filtered and subjected to 3-6 times the washing on the vacuum drum filters. To remove the residual adsorbed iron ions, conduct so-called «bleaching», restoring the Fe (III) to Fe (II). For this injected aluminum metal powder and chemically pure sulfuric acid. Fig. 2.12 shows the process of filtering and washing metatitanic acid at the drum vacuum filters. Suspension after bleaching contains 240 g/dm^3 of TiO_2 and 50-80 g/dm^3 of H_2SO_4.

Before calcination, metatitanic acid is processed with salt in a blender. For salt processing, as well as for washing, purified water is used. The recipe of salt additive depends on the desired crystal form of titanium oxide. The content of titanium oxide in suspension in the operation of 270-290 g/dm$^{3.}$ The process is conducted without heating.

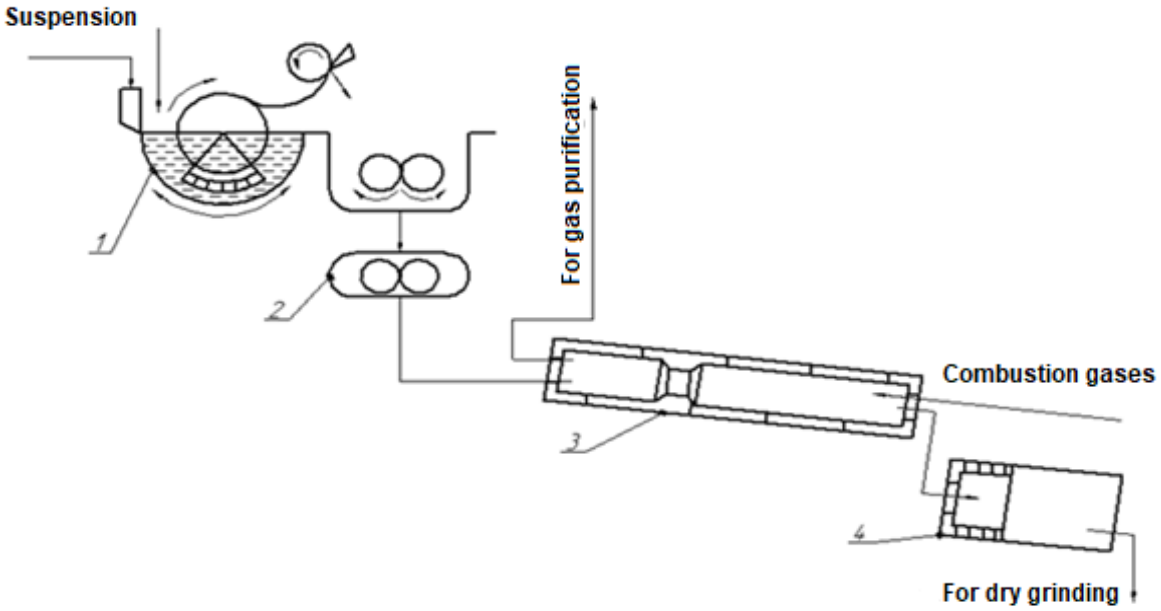
For rutile form of TiO_2 is added to 3 % by weight to ZnO and specially prepared rutile germs. For anatase form input mineral potash $K_2CO_{3,}$ which facilitates the removal of water in the ignition, and 0,5 % phosphoric acid, which stabilizes anatase form.



1 – drum vacuum filter with alluvial layer; 2 – collector; 3 – drum vacuum filters with rollers removing mechanism; 4 – bleaching reactor; 5 – collector.

Fig. 2.12. **Schematic diagram of I and II stages of filtering and bleaching.**

Calcination of titanium hydroxide (Fig. 2.13) is conducted in a tubular rotary furnace 1 using countercurrent flow with direct contact with the material products of combustion. Strict sustainability process and temperature control – an essential condition for obtaining a pigment with specified properties. Maximum temperature of titanium (IV) oxide anatase forms 900-950 °C. However, calcination should be maintained so as to achieve the most comprehensive distillation of sulfuric acid at temperatures up to 800 °C. Therefore, the length of stay of titanium (IV) oxide in the rotary kiln is very big and is about 14 hours.



– drum vacuum filter; 2 – gear pump; 3 – oven for calcination;
4 – cooling drum.

Fig. 2.13. **Scheme of VI stage of filtration and calcination.**

The temperature of the gases at the outlet of the furnace should be in the range of 350-400 °C, the lowest temperature at the outlet can cause condensation of sulfuric acid in the feed chamber. The speed of the gas at the outlet of the furnace reaches 2 m/sec. Despite the high degree of dispersion of pigment titanium oxide, dust removal is small and does not exceed this speed at 5 % loaded titanium (IV) oxide.

Stripping of hygroscopic moisture ends at a distance of a quarter of the length of the furnace from the loading end.

Average temperatures along the length of the furnace is controlled by multipoint recording potentiometer with a few thermocouples installed along the length of the furnace and connected with slip rings, which are located on the body of the furnace.

The furnace is heated by natural or generator gas, free from tar and dust. The gas is burned in a remote furnace.

The final processing. Micro crushing and surface treatment can be carried out dry or wet. The treated TiO_2 pigment obtained by «wet method» subjects drying, steam micronization in a jet mill with subsequent packaging in containers. Using the dry method of surface treatment, the surface of titanium (IV) oxide is coated by aluminum oxide film by introducing it by vapor stream mill. For more common «wet method» after repulpation of milled titanium (IV) oxide in water with a small addition of sodium silicate, subjects for classification in settling centrifuges with subsequent wet grinding coarse fraction on ball mill in a closed cycle with hydro cyclones or settling centrifuge type. For this purpose, the continuous ball mill is applied, which internal surface adapted for ceramic lining.

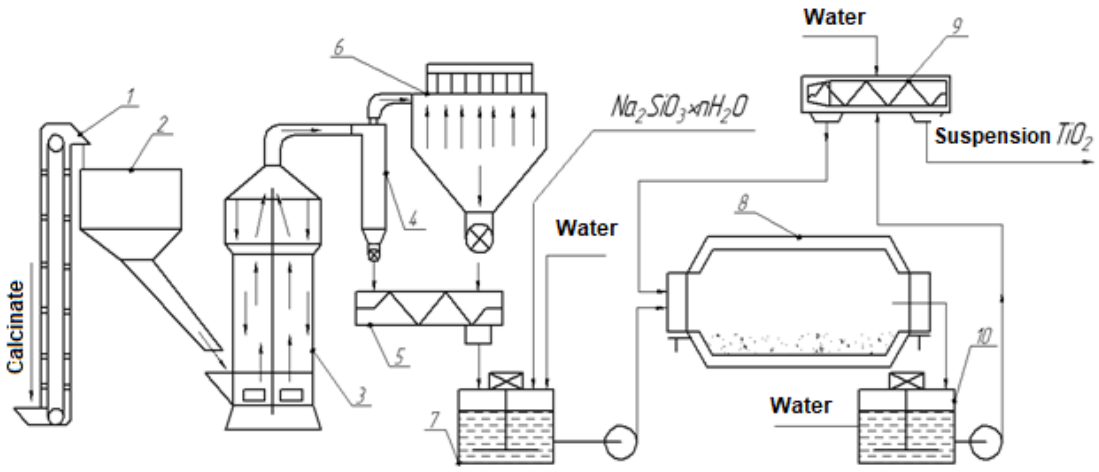
The distinctive feature of settling centrifuge type NOHSH-500-3N used for classification of titanium (IV) oxide is the length of the cylindrical part of the defending zone where the centrifugal force reaches a maximum value, corresponding to the separation factor (for large diameter) in 2000, about 3 times the length of the conical zone settling. This device provides almost complete isolation in the sediment particle diameter of 2 μm and above. After hydro classification the coating of external shell occurs

Many sorts of titanium (IV) oxide anatase and some sorts of rutile forms are not undergoing surface treatment, but for the use of pigment titanium (IV) oxide in rutile form in the paint industry surface treatment is required.

Wet grinding in ball mills, especially in cases where milling is subject to all titanium (IV) oxide, not just crude fraction that is separated in settling centrifuges, adversely affect the quality of pigmentary TiO_2. Despite the fact that grinding bodies and mill lining made of white durable material – hard porcelain or steatite,

impurities extraneous material, characterized by the dispersion of titanium (IV) oxide inevitable.

There may be more economical scheme. So, here's version of wet surface treatment of titanium (IV) oxide (Fig. 2.14). The distinctive feature of this circuit – no wet grinding without duplication of micro crushing.



1 – elevator; 2 – storage batcher; 3 – Raymond mill; 4 – cyclone; 5 – the screw; 6 – bag filter; 7 – repulpator; 8 – wet grinding mill; 9 – settling centrifuge; 10 – collection.

Fig. 2.14. **Schematic diagram of the dry and wet grinding of titanium (IV) oxide.**

Common drying and crushing coarse fractions occur in the annular jet mill new type with a larger cross section area drying and grinding. Under this scheme, it is possible to produce 85-90% of the products with the high quality.

Surface treatment is applied to the surface of titanium (IV) oxide film of aluminum hydroxide, silica acid, zinc oxide and other mineral or organic components that along with a reduction in abrasiveness rutile contribute to atmospheric stability (reduced photochemical activity surface), as well as providing pigment hydrophobicity (for marks used in alkyd enamel) or, hydrophilic (for marks used in water-soluble inks).

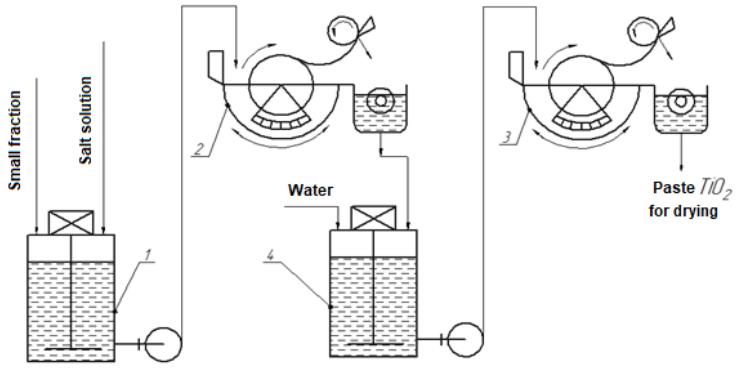
The composition of additives injected with surface treatment, dosage, mode and sequence of their introduction is the subject of numerous studies. Today has explored the impact of compounds of aluminum, silicon and titanium on the physical and technical properties of titanium (IV) oxide.

Most of the recipes for the surface treatment includes laundering titanium (IV) oxide from the electrolyte formed, for example, the interaction of aluminum sulfate with sodium silicate,

$$Al_2(SO_4)_3 + 3Na_2O \cdot n\,SiO_2 + 3H_2O = 2Al(OH)_3 + 3Na_2SO_4 + 3nSiO_2 \quad (2.16)$$

Washing can be made using vacuum drum filters with rollers removing sediment by filtration and repulpation (Fig. 2.14).

Pasta washed titanium (IV) oxide is dried in the dryer with a tape forming device or a spray dryer. In both cases, the fuel (natural or refined gas) should be burned in a remote furnace. Pasta of titanium (IV) oxide as pasta of metatitanic acid has thixotropic properties, under the influence of vibration, mechanical mixing, when moving through the pipes, it becomes fluid. This allows spray drying of pasta while adding to it a small amount of water after filtration, but prevents the use of loop dryers (used for drying lithopone), because as paste, which is in a cells, flows out without full drying.



1 – repulpation reactor; 2, 3 – vacuum filter; 4 – repulpator.

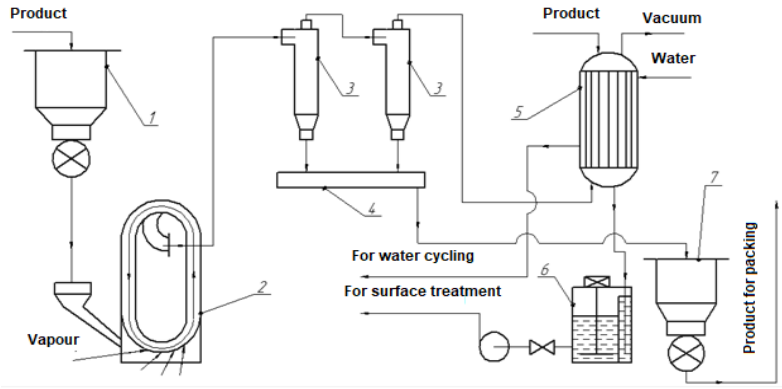
Fig. 2.15. **Schematic diagram of the control surface treatment and filtration.**

The dried titanium (IV) oxide undergoes a micro-crushing in vapor-stream flat chamber or ring mills (the latter is more appropriate).

Fig. 2.15 shows the schematic diagram micro crushing of titanium (IV) oxide.

Titanium (IV) oxide from the bunker 1 enters the vapor stream mill 2, after cyclones 3 is discharged to a screw conveyor 4. Not separated in cyclone dust is sweeped by steam in the condenser 5. The condensate containing slurry of titanium (IV) oxide which flows into the collector and use 7 washing titanium (IV) oxide after surface treatment. Titanium (IV) oxide with a screw conveyor 4 enters the tank 6, and then – on the packaging machine 8. Titan (IV) oxide packed in enterprises of 30 kg multiwall paper bags craft-cellulose (mainly 6 layers).

Packing can be made by automatic scales in open bags, which are then sutured separate by sewing machine on a conveyor belt. It is also possible to package in valve bags using aerated packing machines.



1 – batcher; 2 – jet mill; 3 – cyclones; 4 – screw;

5 – condenser steam; – collector of condensate; 7 – batcher of crushed product.

Fig. 2.16. **Scheme micro crushing.**

The actual stage taking place at the «Crimean Titan», shown in Fig. 2.16.

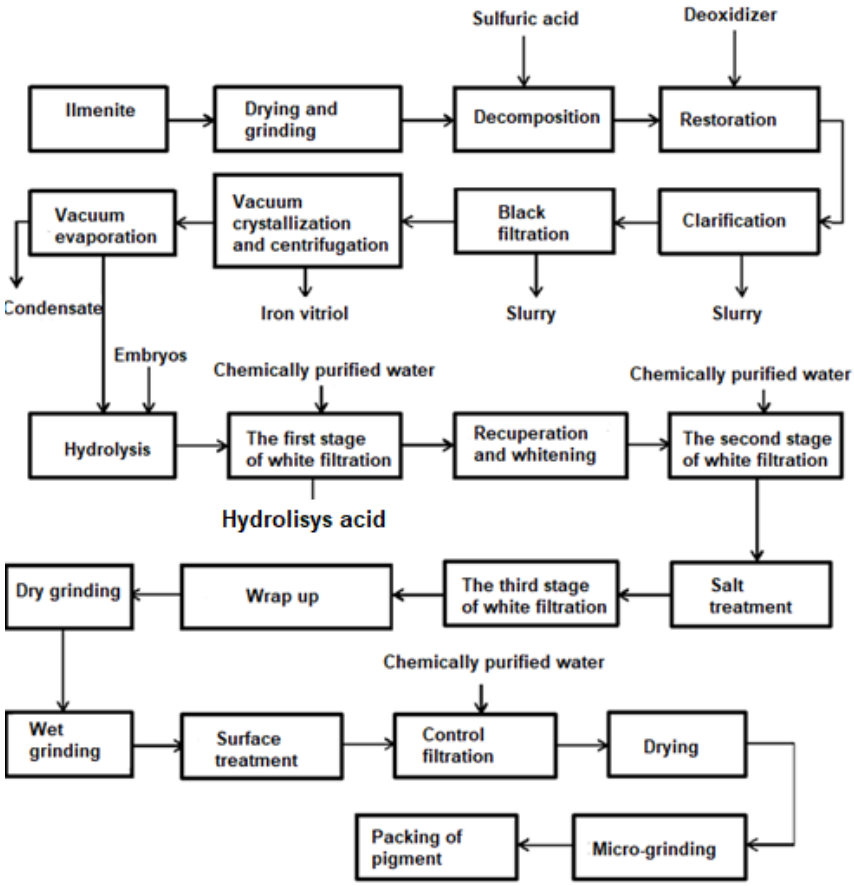


Fig. 2.17. **Stages production of pigmentary titanium (IV) oxide sulfate method.**

2.4.2 Technology for pigmentary titanium (IV) oxide chloride process

An alternative method for manufacturing nanodispersed powder of titanium oxide based on high-temperature reactions titanium (IV) chloride in the gas phase. It uses two methods: vapor-phase hydrolysis and oxidation.

Vapor– phase hydrolysis reaction is based on:

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl. \quad (2.17)$$

The process is carried out in two ways: at low temperatures (300-400 °C) and high (>900 °C). Low-temperature process technology is easier to implement. Formed anatase transforms to rutile quickly, but the resulting TiO_2 products may be contaminated with incomplete hydrolysis, which requires its additional heat

treatment. Quality of the product is higher for method above, but the question of selection of corrosion-resistant materials for used apparatus. Thus, the main disadvantage of vapor phase hydrolysis process is very complex to create a closed loop by chlorine, since chlorine regeneration requires higher costs.

Oxidation of oxygen is more promising process that allows you to create a closed cycle for chlorine:

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2C1_2. \quad (2.18)$$

Oxidation begins at 600 °C, but the reaction rate is low. To achieve technologically appropriate velocity process is carried out at 1100-1300 °C. Progressive way is burning of $TiCI_4$ in the high-frequency plasmatron where oxygen in the air preconized by heating to 2000 °C. Next TiO_2 particles obtained are subjected to rapid cooling, so-called «quenching» to prevent their growth, aggregation and sintering.

The most preferred feedstock for the production of TiO_2 is the chloride process rutile concentrate containing 95-98 % titanium oxide. However, world reserves of rutile small, so often used as a feedstock titanium slag.

Generally, high content of titanium in feedstock is a critical requirement for use in the chloride process. This requirement is related to the regeneration of chlorine opportunity, not as pigmentary titanium oxide, which is also associated with chlorine during chlorination.

The production process of titanium oxide chloride method is divided into the following stages.

1) Chlorination of titanium concentrate (including briquetting or pelletizing operations).

In case of chlorination TiO_2 in the presence of carbon possible reactions:

$$TiO_2 + 2Cl_2 + C = TiCl_4 + CO_2, \quad (2.19)$$

$$TiO_2 + 2Cl_2 + 2C = TiCl_4 + 2CO, \quad (2.20)$$

$$TiO_2 + 2Cl_2 + 2CO = TiCl_4 + 2CO_2. \quad (2.21)$$

Chlorination begins at 400 °C, at 800 °C degree of conversion of TiO_2 to $TiC1_4$ close to 100 %. The dominance of a reaction depends on the temperature and the system determined by the equilibrium carbon–oxygen. Rutile, titanium slag chlorinated in the form of petroleum coke briquettes; the speed chlorination affects the composition and grinding the mixture, the size of the cake porosity. Chlorination of material occurs in shaft periodic or continuous furnaces. After chlorinators steam– gas mixture fed to condensator (pre-treatment).

2) Treatment of titanium (IV) chloride rectification.

Condensation of products of chlorination of titanium raw materials is a very complex process, chlorides are hygroscopic and susceptible to hydrolysis, so all devices must be completely sealed. For condensation difference in boiling point and melting point of chloride used for pretreatment of $TiCl_4$. Were tested on an industrial scale different scheme of condensation (resolution, common); was the most effective combination scheme. After condensation $TiCl_4$ still contains a small amount of impurities ($VOCl_3$, $TiOCl_2$). It is sent for purification in the distillation column.

3) Burning titanium (IV) chloride in the gas phase (including preheating of components).

Titanium chloride oxidation occurs according to reaction that allows to close production cycle for chlorine:

$$TiCl_4 + O_2 = TiO_2 + 2C1_2. \quad (2.22)$$

The degree of conversion $TiCl_4$ in TiO_2 depends on the temperature and the ratio of O_2 and Cl_2 in the gas phase, but due to equilibrium reaction specificity (two

gaseous substances formed solid) is not achieved. The process is almost irreversible. The resulting TiO_2 consists of a mixture of anatase and rutile.

The method is simple, but its technical implementation associated with a number of difficulties: complicated selection of structural materials; necessary to heat the reactants (500-1000 °C) or reactor, because despite the exothermicity of reaction, the generated heat is not enough to create a hydrodynamic regime that excludes overgrowth of communications by firm TiO_2 and it provides a desired dispersion.

Combustion method is applied on an industrial scale, competes and displaces sulphate method for producing titanium oxide pigment.

4) Dry catching of titanium oxide.

5) Calcining titanium oxide (chlorine removal).

6) Additional (wet) surface treatment of titanium oxide on the scheme, which is similar to that used in sulfuric acid method.

7) Capture of chlorine or return it directly to chlorination.

At present, a combined method of producing titanium oxide pigment is very perspective. The combined process is based on a combination of sulfuric acid decomposition of relatively poor concentrate to obtain titanium oxide from titanium chloride. According to this first stage sulphate method is implemented, then the resulting solution of titanium thiosulfate saturated with gaseous hydrogen chloride, resulting in formation of yellow crystals of the complex compound K_2TiCl_6. Then the crystals are washed and heated to 300-500 °C. There is a thermal decomposition of complex salt to form titanium (IV) chloride. Then titanium chloride reaches the condensation and the steps to obtain pigmentary titanium oxide. Also, the obtained titanium chloride is suitable to produce titanium metal.

2.4.3 Production of iron– containing pigments

There are several basic types of plants disperse powdered iron oxide. Abroad, there is a way to get the yellow and black iron– contained pigments of vanillic production. This method is called «Lauks» («Laux») process that uses, for example, the company «Bayer» (the world's leading manufacturer of paints, including pigments) at the factory for the production of pigments. Uirdenhen (Germany).

According to this technology in obtaining aniline dyes feedstock – nitrobenzene – restored cast – iron chips. This chip is oxidized to form Fe_3O_4 (black) or α-FeOOH (yellow). The process is carried out so that the receiving oxides can be used as pigments.

All other types of technological processes of iron-contained powders based mainly on the use as feedstock solution of iron (II) sulfate, which can be obtained from:

1) etching sulfate solution (rolling waste in production) or iron sulfate ($FeSO_4 \cdot 7H_2O$). If iron sulfate derived not from etching solutions and, for example, is leaving the production of titanium (IV) oxide. The raw materials should be cleaned of related substances; however, it may require a rather complex processing method. Without the use of cleaning materials, the obtaining process not recommended;

2) steel shavings, scrap metal. The metal dissolved in sulfuric acid and ferric sulfate resulting solution is used as feedstock;

3) scale. The scale is reduced to sponge iron and dissolved in sulfuric acid to obtain a solution of ferric sulfate, which is used in the synthesis. If slag has some oil, it burned in the recovery and does not interfere with the further process. This technology requires higher costs and production and capital investment enterprise, but it is still economically justified:

4) iron-contained sludge. This is even more costly technology since it requires processing sludge and leaching solution is ferric sulfate, although economically it is usually beneficial. The difficulty is that not everyone is suitable for such sludge processing. All components necessary to recycle sludge, or will own waste. Therefore, the question of disposal of sludge byproducts is crucial in determining its possible use in the manufacture of pigments.

Also, processes based on the use as one of the precursors of salt solution (sulfate) iron (II), can be divided into calcinate, precipitation and mixed type (precipitation followed by heat treatment product synthesis).

Lauks method [26]. Yellow iron oxide (FeO or $FeOOH \cdot H_2O$) or Fe_3O_4 black pigments obtained by oxidation of metallic iron with aromatic nitro compounds in solution or sulfate acid iron chloride. In this case, the pigment is a by-product of obtaining aromatic amines, resulting from recovery nitro metallic iron. For the oxidation of iron using nitrobenzene, nitronaphthalene, the nitro sulfonic acid number of other nitro compounds. As a result, recovery they go to aniline, naphthylamine and amino sulfonic acid. Aniline recovery nitrobenzene obtained metallic iron in an aqueous medium in the presence of a small amount of hydrochloric acid. The process is rapid and runs under the boiling point. Hydrochloric acid is formed by the impact of hydrochloric acid on iron, do not participate directly in the process, but accelerates oxidation of metallic iron.

Reactions occurring in the interaction of nitrobenzene with metallic iron to obtain Fe_3O_4 black can be represented as a schematic overall equation:

$$4C_6H_5NO_2 + 9Fe + 4H_2O \rightarrow 4C_6H_5NH_2 + 3Fe_3O_4. \qquad (2.23)$$

Mixed oxide, Fe_3O_4, formed as a result of this process is a coarse powder. It has not saturated colors and low pigment properties, resulting in long found use as a pigment in factories producing aniline in large quantities as waste. But then it was

suggested to change the restoration of nitrobenzene in aniline, in which you can get oxidized iron not as Fe_3O_4, but as another oxide (Fe_2O_3, $Fe_3O_4 \cdot nH_2O$, FeOOH). For the formation of a certain iron– contained pigment need further use or electrolytes ($FeCl_2$, $FeSO_4$, NH_4Cl, $MgCl_2$ et al.) Or certain metal salts (aluminum, chromium, tin, cerium and other metals). Thus, during the oxidation of metallic iron nitrobenzene form iron oxides, composition and color depend on the type of electrolyte in the presence of oxidation which occurs, for example, in the presence of electrolytes that cannot be hydrolyzed by boiling with metallic iron, produced only black Fe_3O_4, and in the presence of hydrolyzed electrolytes – different compounds from black Fe_3O_4 (the small content) to light yellow ferric oxide hydrate ($Fe_2O_3 \cdot 3H_2O$) with high content of electrolyte [28].

The easiest way is formed a mixed iron oxide black. Getting as other compounds, iron (III) oxide anhydrous, hydrated, especially crystalline iron oxide hydrate occurs only as a result of the impact of the metal oxide hydrate (mostly trivalent) salt and iron (II) oxide formed by the hydrolysis electrolytes second group.

The process of iron oxides of different composition and color in nitrobenzene oxidation of metallic iron can be represented by the diagram shown in Fig. 2.18.

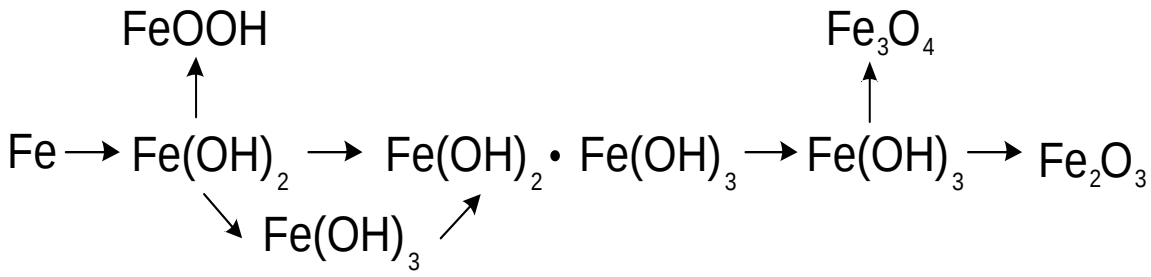


Fig. 2.18. **Scheme of iron oxidation.**

As a metal iron used mainly iron and steel fewer chips. Cast iron chips very easily crushing and grinding, but it contains a significant amount of impurities of carbon, manganese, etc., which, while remaining pigment somewhat contaminate it. These additives also have some influence on the oxidation of metallic iron, so that when applied pigment turns a dull color, so for higher grades of yellow iron oxide used steel chips.

Metal shavings before applying crushed and subjected to purification to remove impurities from it: dust, rust, bolts, nuts, etc. impurities. The best method of cleaning the chip is screening and magnetic separation.

The recovery of nitrobenzene to aniline is produced in reducers, which provided with refrigerators. To restore nitrobenzene and oxidize the metal iron into a yellow iron (III), the hydride oxide in the reducer is charged with water and a solution of aluminum chloride, after which the steam– steam solution is brought to a boil. Chips are loaded from a bunker installed above the gearbox funnel.

After boiling the solution is steaming in the reducer is completed and loaded with parts nitrobenzene and shavings. The boiling temperature at this time is supported by the exothermic reaction. In order to prevent over- rapid passage of the reaction, the chips should be added not immediately, but gradually. The last loading of chips is done after filing all nitrobenzene.

When the reaction begins to slow down (as judged by the decrease in the amount of re condensate), the reducer is again steamed and, heating the solution, bring the reaction to the end. At the end of the restoration, the condensate, which is observed in the overhead glass on the return line, takes the form of a white emulsion. At this time, a sample is taken through a sampler tap, and, being convinced of the absence of nitrobenzene in it, stop feeding steam in the gear unit. The reaction mass is then blown with air until it is cooled (80-90 °C). After which it is allowed to stand for a few hours. During this time, the formed aniline expands to

the surface, the residue of the unreacted iron precipitates to the bottom, and the pigment remains in the suspended state in the mother liquor. The top layer containing 60% aniline is drained by siphon and directed to the settling tank. Aniline remaining in the mother liquor and siege is distilled with a water vapor. Dispensing is carried out as long as the content of aniline in the condensate will not be lower than 0,2-0,3%. After distillation of aniline, the pigment suspension is pumped into a conic tank, in which the metal iron is separated, and then directed for washing, drying and sifting. The pigment can be washed directly on the filter press or on the filter press with regulation; at a large volume of production, washing is carried out in continuously operating machines operating on the principle of counteracting. Simultaneously, on these devices, and the classification of pigment is carried out in order to isolate from it large dark particles formed during the reaction.

As for washing machines, it is possible to use installed successively conventional single-chamber rail classifiers, in which the material is washed and passes from one classifier to another, and in front of it moves the washing water. Rough particles settle down to the bottom of the first classifier, from where they are gradually taken off by a pump and sent to a separate collection. The thickened pulp of the pigment after the classifiers is separated from the liquid on the drum vacuum filters, and then dried in aerosol dryers.

The dried pigment is passed through a disintegrator operating in a closed loop with a separator.

Burning methods for obtaining a red fermentation pigment. In Ukraine, red ferrous pigment (Sumy «Khimprom» and the Crimean «Titan») are obtained by thermal decomposition of iron sulfate $FeSO_4 \cdot 7H_2O$ (waste of titanium (IV) oxide sulfate acid production) in rotary ovens. The process is carried out in two stages:

1) Production of iron sulfate monohydrate (II) by drying iron sulfate:

$$FeSO_4 \cdot 7H_2O \rightarrow FeSO_4 \cdot H_2O + 6\,H_2O, \qquad (2.24)$$

2) Production of pigmental α-oxide of the forum by thermal decomposition of iron (II) sulfate:

$$2FeSO_4 \cdot 7H_2O \rightarrow \alpha\text{-}Fe_2O_3 + SO_2 + SO_3 + H_2O. \quad (2.25)$$

At the same time conducting the process at a temperature of 700-725 °C leads to the receipt of red-orange powder, and red at 730-780 °C. Further growth of temperature up to 850 °C, which is accompanied by an increase in the size of particles, leads to purple-purple color. The resulting α-oxide of the iron is then ground, washed, dried.

The advantage of this process is its cheapness, and the main drawbacks: low quality pigment, due to the non-optimal flow of process in the rotary ovens; the presence of a large amount of non-utilized sewage; Difficult to dispose of sulfur gases, the content of which in the spent gases does not exceed 1,5 %.

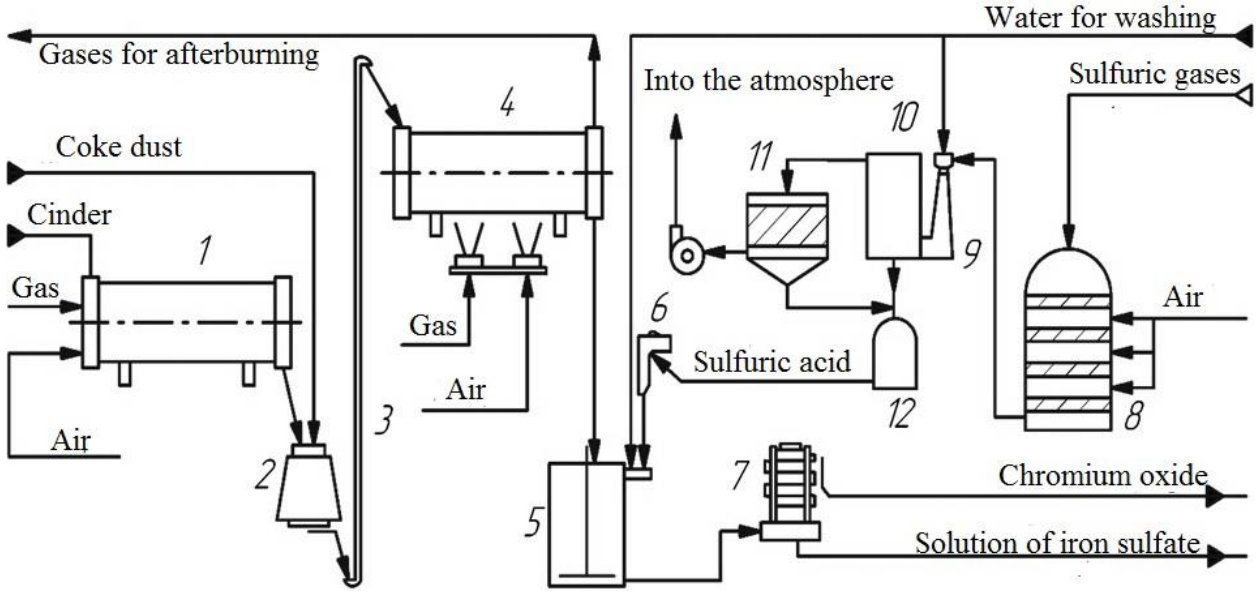
In the improved technological process, replacement of rotary furnaces with furnaces of a fluidized bed was carried out. According to this method, as a raw material, waste is used for metal – production – scale. Oiled and wet scale after separation of mechanical contaminants is dried in a rotary oven 1 and grinding in a crusher 2 together with coke dust (Fig. 2.19).

The dried scale is mixed with graphite and smeared, after which it is fired without access to the air. Scaling is restored to spongy iron:

$$nFe_2O_3 \cdot mFeO + (3n+m)\,C \rightarrow (2n+m)\,Fe + (3n+m)\,CO. \quad (2.26)$$

In this case, the oil is also a reducing agent and partially replaces graphite in this process. Carbon (II) oxide, which is formed, is burned in the burners of the furnace, or in the flare, depending on the design decision. The mixture of the dispenser 3 is fed into a tubular stove 4, where it is reconstituted to a spongy iron. The heating of the furnace 4 is carried out through the wall by gas burners. Present in the scale of impurities of chromium, vanadium, and manganese remain in the form of oxides and subsequently removed; They are returned to the metallurgical

process. Garbage containing carbon dioxide (Oxides) leaving the oven is fed to the oxidation (in the torch or in the furnace burners).



1 – rotary kiln; 2 – crusher; 3 – dispenser; 4 – tube furnace; 5 – reactor; 6 – dispenser; 7 – filter–press; 8 – contact devices; 9 – Venturi scrubber; 10 – spray traps; 11 – filter; 12 – collection of sulfuric acid.

Fig. 2.19. **Technological scheme for iron sulfate solution (1-7) and reverse sulfuric acid (8-12).**

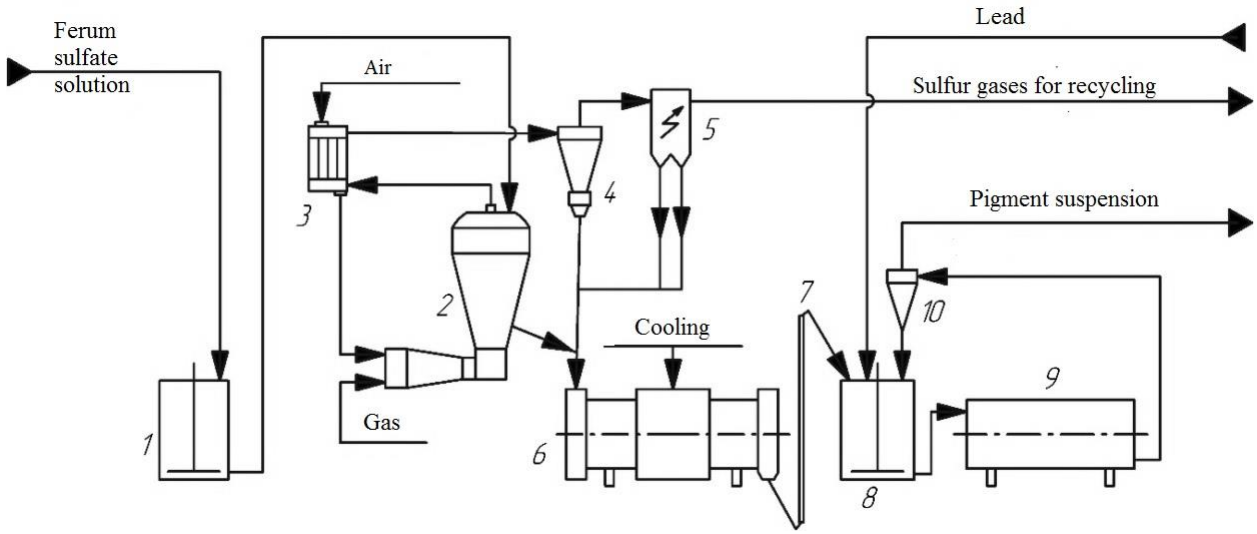
The reconstituted sponge iron is fed to reactor 5, where it is dissolved in the reverse sulfate acid (supplied by the dispenser 6), to obtain a solution of iron (II) sulfate:

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2\uparrow. \qquad (2.27)$$

The acid is pre-diluted with flushing water, which is obtained by washing the pigment. The resulting solution of iron (II) sulfate is purified from suspensions on the filter press 7 and accumulated in apparatus 1 (Fig. 2.20) [24]. Suspensions, which contain mainly chromium oxide, are returned to metallurgical production as an additive to iron chromium.

The filtered solution of iron (II) sulfate is fed into the oven of the boiling layer 2, where the decomposition of salt occurs at a temperature about 800°C:

$$2FeSO_4 \rightarrow \alpha\text{-}Fe_2O_3 + SO_2 + SO_3. \quad (2.28)$$



1 – intermediate apparatus; 2 – furnace of a boiling layer; 3 – heat exchanger; 4 – cyclone; 5 – electro filter; 6 – refrigerator; 7 – dispenser; 8 – repulpator; 9 – ball mill; 10 – hydro-cyclone.

Fig. 2.20. **Technological scheme of thermal decomposition of ferrous sulfate (II) to obtain pigment ferrous oxide.**

The precipitation methods of yellow and red iron-containing pigments. This group of methods based on the deposition of an alkaline agent salts of iron (II), further oxidation of the resulting suspension to obtain compounds of iron (III), which is either a final product (receipt pigments) or intermediate (receipt magnetic powders).

In this regard, often supplemented deposition stage is the next stage of heat treatment. There are two main modifications deposition method to obtain iron-contain in powders:

1. Penniman process, which based on the oxidation of metallic iron with

oxygen in the air suspension, the solution containing iron (II) sulfate and specially prepared priming of crystal particles of iron compounds;

2. Martin`s method, or «ammonia method» based on ammonia salts precipitated iron (II) oxidation with subsequent suspension in obtaining seed as compounds of iron (III) and further increase its number due to gradual neutralization and oxidation reaction mixture.

It should be noted that both options can be used for the production of pigments (like yellow and red) and magnetic powders. The difference is only in the specific conditions of synthesis in some way.

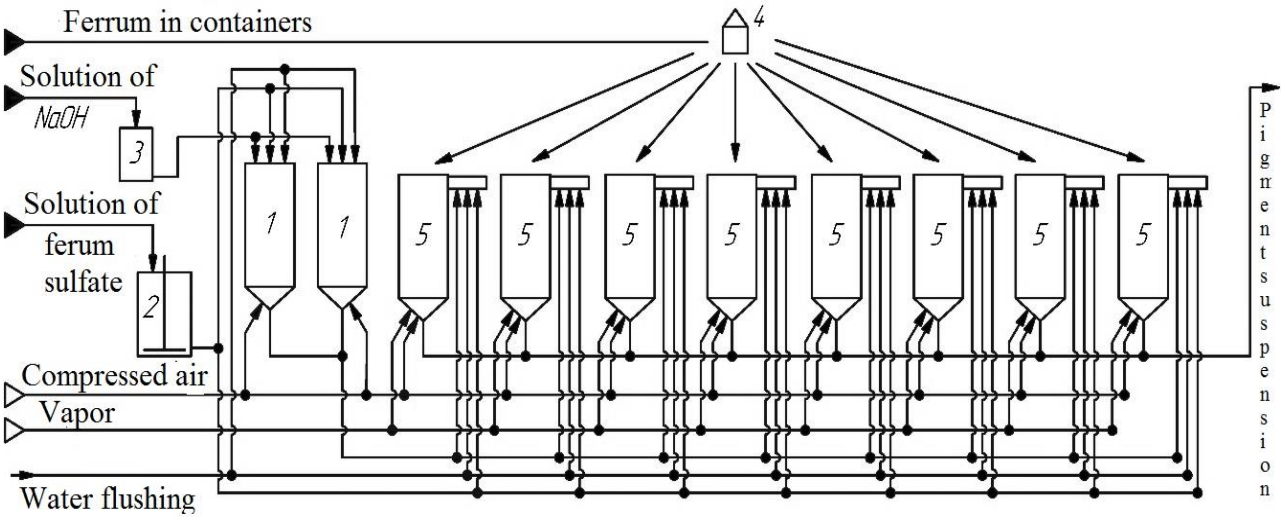
Penniman process [24]. This method is widely used abroad. It is used such firms as «Bayer», Germany «Mahnoks» US «Herdillna» India.

This method is two-stage. In the first stage by precipitation and subsequent oxidation of iron compounds (II) are crystalline particles of compounds of iron (III)), which then serve as the seed for the second stage of the process. To this reactor synthesis seed 1 (Fig. 2.21) loaded solution of iron (II) sulfate from the device 2, water and sodium hydroxide tank 3 partly receiving iron (II) hydroxide is oxidized by air to iron (III) oxy hydroxide. In the second stage the resulting suspension was loaded into reactors seed growth 5 where crane beam fed from the metallic iron (from scrap steel) in the container 4, then the reaction mixture is heated vapor acute to the desired temperature and oxidize air for 36-48 hours. With proper conduct of the growth process of small seed particles to pigment size takes place without the formation of by-products of iron corrosion.

Finished pigment suspension is then pumped into a collection and filtered to the filter press scheme similar to shown in Fig. 2.21. Mother liquor containing 15 g/dm^3 sodium sulfate and 30 g/dm^3 iron sulfate, separated and disposed of. Pigment paste is washed with water directly on the fabric filter. Flushing water can be reset to the city sewer. The washed paste is dried in a dryer. Ready pigment is

packed in paper bags or in containers rotary rubber.

It should be noted that this process can obtain yellow (α-FeOOH) and red (α-Fe_2O_3) pigments by changing the conditions of oxidation (primarily type crystal structure and temperature on seed growth stage). Thus, obtained α-FeOOH particles are not only prepared pigment product, but also can be used as an intermediate in obtaining magnetic powders. Further heat treatment under mild conditions that preserve the initial size and shape anisotropic particles of α-FeOOH, provides a needle powder γ-Fe_2O_3 with high magnetic characteristics.



1 – the synthesis of reactors primers; 2 – device with a solution of ferric sulfate; 3 – tank with sodium hydroxide; 4 – containers with metallic iron; 5 – growth reactors.

Fig. 2.21. **Flowsheet synthesis of iron oxide pigment by the Penniman method.**

Martin`s method or «ammonia method» implemented on production in the former Czechoslovakia and the firm «Montecatini» in Italy. This is the only industrially implemented on a large-scale method for producing yellow pigment solution of iron (II) sulfate in Russia. The method is based on the use of ammonia as precipitant, application is very soft due to the need to neutralize the regime – only under these conditions can get a high-quality product. Soft mode provided strong

neutralizing dilution air gaseous ammonia, so that his place in contact with the reaction mass was not exceeded local pH. It is also possible to use as precipitant ammonia water or carbamide (urea). Using of urea due to the fact that it can be dissolved in the reaction medium, without entering into interaction with it, evenly distributed over the volume slowly hydrolyzing by temperature increasing and the formation of ammonium ions:

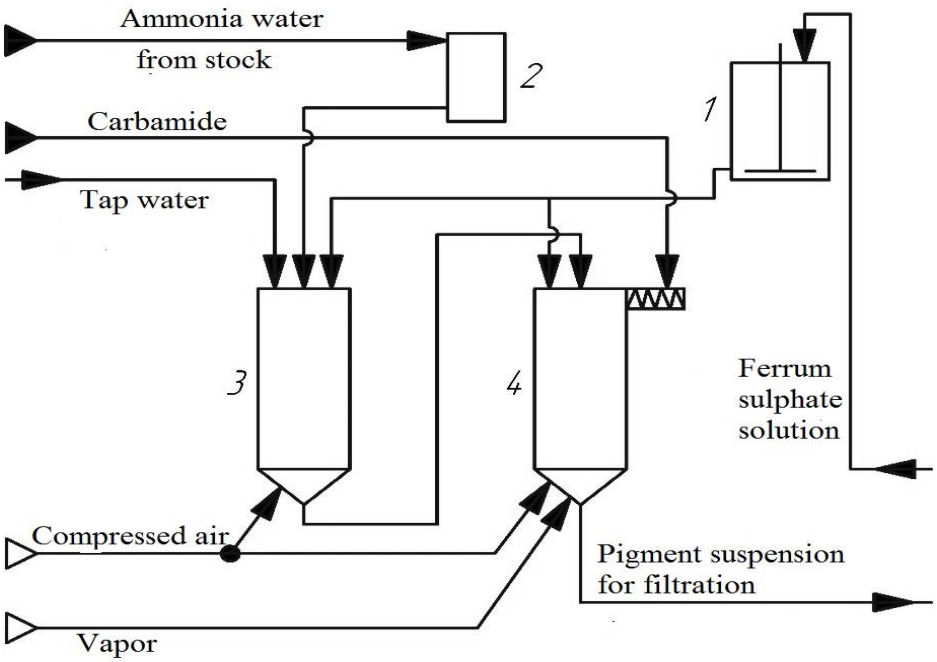
$$(NH_2)_2CO + 2H_2O \rightarrow (NH_4)_2CO_3. \quad (2.29)$$

This is implemented very soft neutralization mode without local intersection by pH.

Other catalysts such as sodium hydroxide or potassium hydroxide, must be diluted with water, but it`s very undesirable dilute them as it leads to an excessive increase in the reaction mixture.

The process of iron containing pigment obtaining (as well as in the way of Penniman) is carried out in two stages. In the first stage by precipitation and subsequent oxidation of iron compounds (II) are crystalline particles of iron (III) compounds, which serve more as a seed for the second stage of the process. To this solution purged of impurities of iron (II) sulfate pigment production is sent to the apparatus 1 (Fig. 2.22). A solution of iron (II) sulfate was loaded into the reactor (3), ammonium tap water and water from whichever 2. Neutralization of iron (II) sulfate solution spend partly. The reaction mass is blown with a strong jet of compressed air to give a suspension of seed particles with the structure of α-FeOOH).

The slurry seed fed to the reactor 4, there is loaded and a solution of iron (II) sulfate from the apparatus 1. The reaction mass is heated by steam to 60-80 °C and it is blown through a mixture of ammonia from air oxidation of compounds of iron (II) compounds ferric (III). By ammonia water using begin its gradual dosage in oxidized suspension.



1 – device with a solution of ferric sulfate; 2 – dispensing; 3 – reactor of pigment synthesis; 4 – reactor of primers synthesis.

Fig. 2.22. **The synthesis scheme of iron containing pigments. "Ammonia method".**

By usage of carbamide it is served to the reactor via screw feeder. As a result, pigment particles grow to a size close to half wave length of visible light. By using of ammonia (ammonia water) reaction described by equations:

$$4FeAn_2 + 8KtOH + O_2 \rightarrow 4FeOOH + 8KtAn + 2H_2O, \quad (2.30)$$

$$4FeAn_2 + 8KtH + O_2 \rightarrow 2Fe_2O_3 + 8KtAn + 4H_2O, \quad (2.31)$$

or

$$3FeAn_2 + 6KtOH + 1/2O_2 \rightarrow Fe_3O_4 + 6KtAn + 3H_2O, \quad (2.32)$$

An – anions Cl^-, $1/2SO_4^{2-}$; Kt – cations NH_4^+, Na^+, K^+,

The next equations (2.33-2.34) described the process if carbamide is using:

$$2FeSO_4 + 2(NH_2)_2CO + 5H_2O + 0{,}5O_2 \rightarrow 2FeOOH + 2(NH_4)_2SO_4 + 2CO_2, \quad (2.33)$$

$$2FeSO_4 + 2(NH_2)_2CO + 4H_2O + 0{,}5O_2 \rightarrow \alpha\text{-}Fe_2O_3 + 2(NH_4)_2SO_4 + 2CO_2. \quad (2.34)$$

The process takes about 36 hours; the end of reaction product is determined by the achievement of the desired color (standard color matching). It should be noted that this point is also consistent achievement oxyhydroxide particles of a certain size.

Then suspension of final product is pumped into averaging, so the capacity of the mixer, which accumulate more product syntheses, averaging properties. With averaging suspension served on filter press to separate from the cells of filtration. Mother liquor containing dissolved ammonium sulfate is collected, from which it using by steamers. Pigment on fabric (filter wash by condensate from evaporation of ammonium sulfate solution, washing water is collected and used as industrial water in the production cycle). The washed pigment paste unload filtered and served in the dryer with a weighted layer of inert material. The dried pigment or separating exhaust gases or cyclone and bag filters, and served on the packaging. Dust-free gases emitted into the atmosphere.

It should be noted that the «ammonia» process (as well as the previously described Penniman method) makes it easy to obtain both yellow (α-FeOOH) and red (α-Fe_2O_3) pigment by changing only the oxidation conditions without any substitution equipment. The resulting pigment has a very high quality and meets world standards.

Yellow pigments can be obtained by other methods. For example, the interaction of iron chloride with chalk with subsequent oxidation of precipitation by air. At the same time, a reaction runs through which can be represented by the following equation:

$$2FeCl_2 + 2CaCO_3 + 3H_2O + 0{,}5O_2 \rightarrow 2Fe(OH)_3 + 2CaCl_2 + 2CO_2. \quad (2.35)$$

The reaction conditions have a great influence on the quality of the pigment

obtained. For a pigment of bright color of the chalk should be introduced into the reaction in excess of the calculated amount, the solutions should be strongly diluted and heated not above 20 °C. Oxidation should be carried out at a temperature not exceeding 10-15 °C. At this temperature, the oxidation runs slowly. Sometimes a small amount (3-6 %) of $NaNO_2$ or $ZnCl_2$ is added to the $FeCl_2$ solution, whose role is to accelerate the oxidation process.

The pigment obtained by this method has a very beautiful velvet yellow color and high resistance to the action of light and alkalis. It is used mainly for facade lime paints; For oil works it is unsuitable due to its high oiliness, poor coverage and insufficient stability in oil paints to the action of atmospheric phenomena.

The obtained ferric (III) oxide hydrate (yellow Mars) is an amorphous substance, which explains its low pigmentary properties, as well as its activity in conjugated substances, especially oil.

To obtain the yellow Mars, using this method, a solution of iron chloride containing $FeCl_2$ of 50-100 g/dm^3 is prepared in a wooden tank (reactor), chalk (100-120 % by weight of $FeCl_2$) is added to it, and then passed through the whole mass at Stirring up a stream of air until the ferment is completely deposited and its oxidation into iron (III), an oxide of hydrate. The sludge formed on the yellow Mars is washed off from water-soluble salts, filtered and dried. The flushing of the pigment can be done by decantation or on filter presses, since the yellow mars is well defended and filtered. The drying of the yellow mars should be carried out in order to avoid a change in tint, that is, at a temperature not higher than 80 °C.

Another method for obtaining a yellow Mars is the oxidation of carbonic iron by air. At the first, this method obtains a carbon iron with the interaction of iron sulfate with soda, then the resulting carbon dioxide is oxidized by air or beryllium salt:

$$2FeSO_4 + 2Na_2CO_3 \rightarrow 2FeCO_3 + 2Na_2SO_4, \quad (2.36)$$

$$2FeCO_3 + nH_2O + 0{,}5O_2 \rightarrow Fe_2O_3 \cdot nH_2O + 2CO_2. \quad (2.37)$$

To get the pigment, it needs to put into the reactor with the mixing 10% solution of iron sulfate and soda. As a result of the reaction between them, a light green precipitate of carbonic acid is deposited, which is then oxidized by air at 20-25 °C or a solution of potassium chlorate at 50-60°C. Oxidation with air lasts about 10-12 hours, and 3-4 hours for potassium chlorate. Initially, the oxidation runs very fast, and then slows down significantly. The oxidation process can be completed in the presence of up to 5-6 % of the ferric salt (II) in the siege, as the pre-oxidation of the iron salts (II) occurs during the drying of the sediment.

An increase in the temperature of oxidation greatly affects the color of the pigment. So, at the temperature 70-80 °C black or black-brown products are formed.

Mars, produced by this method, has a brown tint, brightness and velvety, and does not differ from the mars, obtained by the interaction of iron chloride with chalk, but has a greater coverage, less oiliness, inactive in the bundled materials, and can find some application for the production of oil paints. It also has a forestry and therefore it is used for the production of artistic paints.

Red ferric-containing pigments can also be obtained by calcining precipitated iron (III) hydroxide or precipitated mixed ferrous oxide at 600-700°C. Obtaining of ferrous oxide by calcining precipitated iron (III) hydrated oxide is based on the ability of the latter to easily dissociate at elevated temperature:

$$Fe_2O_3 \cdot nH_2O \rightarrow Fe_2O_3 + nH_2O. \quad (2.38)$$

$Fe_2O_3 \cdot nH_2O$ dissociates almost completely at 300 °C, but formed at this temperature, Fe_2O_3 does not possess the necessary pigmentary properties: pure and

bright color, high coverage, etc. Iron oxide acquires these properties only as a result of calcining the ferrous oxide of hydrate at 600-700 °C due to crystallization under these conditions.

Red ferric oxide is formed, in addition, when fused with a mixed ferrous oxide Fe_3O_4 or $FeO \cdot Fe_2O_3$, that is, from the black iron oxide. Oxidation of Fe_3O_4 in Fe_2O_3 occurs at relatively low temperatures (275-300 °C) and runs through the reaction:

$$2(FeO \cdot Fe_2O_3) + 0{,}5O_2 \rightarrow 3Fe_2O_3. \quad (2.39)$$

However, in this case, just as in the case of fired hydrated oxide fermium, the pigment of the required color is obtained as a result of the calcining of the precipitate only at a temperature above 500 °C, namely at 600-700 °C. Black ferrous oxide (Fe_3O_4) is formed in large quantities as a by-product in the production of aniline, and therefore its use for the production of iron oxide red, which is of practical interest.

Also, red iron-containing pigments can be obtained from pyrites. The sulfur dioxide, which is the waste of sulfate production, consists mainly of ferrous oxide, and therefore their use as a pigment is very promising. Pyrite nuggets have a dim violet color and contain a large amount of impurities in the form of compounds of cuprum, sulfides, basic salts, water soluble salts, free sulfate acid, and black ferric oxide. The total sulfur content in the gutters reaches 3-4 %, compass to 0,6 %, zinc to 1,5 %, and therefore their direct use as a pigment is impossible.

Studies have shown that less polluted fractions with an acceptable bluish-red color can be distinguished from pyrite nuggets. After grinding and appropriate wet treatment for the purpose of removing impurities from them, these fractions contained in the insecticides in the amount of 30-40 % are used as pigments. They contain the largest amount of ferrous oxide and the smallest – impurities; separating them from the insoluble dry or wet can obtain raw materials suitable for

processing on red iron oxide. Typical chemical composition of red iron oxide with pyrites: 90 % of Fe_2O_3; 6 % of SiO_2; 2,5 % of Al_2O_3. The specific gravity of such a pigment is 4,95; the size of the particles 0,2-20 microns; the color is dark violet–red.

Black and brown pigments. Mixed iron oxide, Fe_3O_4 is found naturally in the form of a magnetite mineral and can be obtained by artificial means from the salts of iron (II) and iron (III) by wet methods. It is a spinel of the type $MeO \cdot Me_2O_3$, in which the iron is present in the form of both bivalent and trivalent oxide. According to this, the composition of the mixed oxide of the iron can be represented by the formula $FeO \cdot Fe_2O_3$.

All methods of obtaining $FeO \cdot Fe_2O_3$ by wet methods are based on the ability of iron oxide hydrates to interact with each other to form a mixed oxide iron under such a scheme:

$$2Fe(OH)_3 + Fe(OH)_2 \rightarrow FeO \cdot Fe_2O_3 + 4H_2O. \quad (2.40)$$

The possibility of interaction of hydrates is due to the acidic nature of $Fe(OH)_3$ and the basic nature of $Fe(OH)_2$. The reaction of $FeO \cdot Fe_2O_3$ formation is reduced to obtaining the hydrate additions of $Fe(OH)_3$ and $Fe(OH)_2$, which are then dehydrated:

$$2Fe(OH)_3 + Fe(OH)_2 \rightarrow Fe(OH)_2 \cdot 2Fe(OH)_3 = FeO \cdot Fe_2O_3 \cdot 4H_2O \rightarrow FeO \cdot Fe_2O_3 + 4H_2O. \quad (2.41)$$

The conditions of synthesis have a very great influence on the composition and properties of $FeO \cdot Fe_2O_3$. $FeO \cdot Fe_2O_3$ is often obtained as a non– stable active compound that adsorbs a significant amount of water and is easily oxidized by oxygen to air into the oxide or ferric hydroxide (III). Such $FeO \cdot Fe_2O_3$, in particular, is formed by the interaction $Fe(OH)_2$ with freshly deposited amorphous $Fe(OH)_3$.

The basis of this method is the interaction of the iron (III) salt with caustic

or carbonic alkalis and the oxidation of the formed sediment in $FeO \cdot Fe_2O_3$, which consists in oxidation of $Fe(OH)_2$ with air oxygen to $Fe(OH)_3$, which interacts with not yet oxidized ferric hydroxide (II):

$$2Fe(OH)_2 + H_2O + 0{,}5O_2 \rightarrow 2Fe(OH)_3, \quad (2.42)$$

$$2Fe(OH)_3 + Fe(OH)_2 \rightarrow FeO \cdot Fe_2O_3 + 4H_2O. \quad (2.43)$$

Instead of $Fe(OH)_2$, a carbonaceous iron can be used which, when heated, is hydrolyzed to form $Fe(OH)_2$, and then oxidized to $FeO \cdot Fe_2O_3$:

$$FeCO_3 + H_2O \rightarrow Fe(OH)_2 + CO_2, \quad (2.44)$$

$$3Fe(OH)_2 + 0{,}5O_2 \rightarrow Fe_3O_4 + 3H_2O. \quad (2.45)$$

Oxidation is carried out by heating, but even during heating process runs very slowly. According to some studies, oxidation can be significantly accelerated by the addition of small amounts of sodium nitrite or zinc chloride to $Fe(OH)_2$. Fe_3O_4, obtained by this method, has very high stability: it is not oxidized by oxygen and differs very high pigmentary properties.

To produce $FeO \cdot Fe_2O_3$ this technology iron sulfate dissolved in water by heating the solution to a solution of baking soda in an amount necessary to complete the deposition of carbon iron. A solution of iron sulfate should contain $FeSO_4$ 200-300 g/dm^3, and Na_2CO_3 100-150 g/dm^3 of soda solution. Adding soda immediately occurs deposition of carbon iron.

The resulting suspension is heated to 80-90 °C and then it is passed through a stream of air. Oxidation is very slow and lasts up to 20-30 hours. In this case, the formation of a mixed ferrous oxide is bluish-black color and high stability. The resulting pigment is washed to remove water- soluble salts and dried at 60-80 °C.

By preparation of coarse ferrous oxide, it is not possible to obtain pure $FeO \cdot Fe_2O_3$ containing the estimated FeO content ~31,03 %. The content of FeO in technical products is usually in the range of 17-25 %, and the more active

$FeO \cdot Fe_2O_3$ in the receiving stage, the less it contains FeO. As pigments should be used compounds, which contain at least 17-18 % of FeO.

2.4.4 Production of natural iron-containing pigments

Characterization of natural fermentation pigments. Yellow, natural iron–based pigments represent varieties of brown iron, having a pure color and a soft structure. By chemical composition, they are oxides of iron (III) hydrates with clay impurities, which are called marl. In addition to the ferric oxide (III), hydrate and clay in their composition may include an iron oxide (II), iron (II) and iron (III) oxides, manganese oxide, organic compounds. Due to the presence of these impurities, the yellow color of natural pigments based on marl may vary from pure yellow to pale-orange and brownish-red.

The pigment properties of the yellow natural pigments are higher, the more they contain the oxide of iron (III) hydrate. As pigments for the production of oil paints, minerals and ores containing at least 12 % Fe_2O_3 are used. Pigments with less content are used in construction. Yellow, natural iron-based pigments are called yellow ocher. Ohra it is the cheapest and strong pigments, due to this they have a wide range of uses: in lime, glue and oil paints, in the construction industry.

Like red (natural fermentation pigments) different types of hematite and iron oxides are used. Also, as red natural pigments use red iron and bauxite. According to the content of iron oxide (III), red natural pigments are divided into mummies (20-70% Fe_2O_3) and minerals (75-85% Fe_2O_3). Red natural fermentation pigments are highly resistant to light, atmospheric influences, and corrosive agents.

Mummies are divided into light (up to 35% Fe_2O_3) and dark (35-70% Fe_2O_3), normal and bauxite. Mummies are used to producing all kinds of paints: oil, glue, and facade.

Iron minium is a natural blend of ferric oxide (III) with clay substances and quartz. The color of iron minium varies from dark cherry to yellow-red and is used very widely: water and oil paints, first coats, etc. Like iron-sulfur, a number of iron ores that contain large amounts of Fe_2O_3 are used.

The representative of brown natural pigments is umber natural and roasted. The color of the umber is due to the presence of manganese iron ores and ranges from light reddish to brownish to greenish. According to the chemical composition of the umber is similar to ocher, which differs only in the content of manganese in it. The pigment characteristics of the umber are also similar to the pigmentary characteristics of ocher. Umbra is used in the manufacture of oil paints for oil and fresco painting. Umbra, roasted at low temperatures, changes its color to darker: from dark brown to black and brown. It is used for the same purposes as the natural ureter.

Technological operations of production of natural fermentation pigments.

Minerals and ores used as raw material for the production of natural fermentation pigments are subjected to mechanical processing in order to shred and remove impurities, and in the case of red pigments, also degradation. Mechanical processing consists of, grinding, defrosting, calcining, scattering, air separation, etc.

The grinding is carried out in the jaw or disk crusher (for grinding hard rocks), runners or rollers (for grinding not very hard rocks and soft rocks, respectively).

The grinding is carried out in the jaw or disk crusher (for grinding hard rocks), runners or rollers (for grinding not very hard rocks and soft rocks, respectively).

Grinding of Iron ores is carried out on ball and drum mills or in disintegrators.

Pouring is carried out in order to remove impurities from iron ores, for example, sand, stones, and other mechanical impurities. The equipment used for defrosting is quite varied: several tanks connected to each other; Shampoo– mixer with a dressing table, etc.

Natural pigments are poorly filtered, so dehydration is carried out in two stages. The first one is sold in settlers or thickeners, which separate the bulk of water.

To accelerate precipitation, the pigment is coagulated with a small amount of calcium chloride and aluminum sulfate. Next, a slurry containing up to 50-70 % dry matter is sent to further agglomeration on notch filters, filter presses, and drum filters. The final dehydration is carried out in dryers of different types at temperatures not exceeding 100-110 °C.

The calcining of iron ores is carried out in order to convert hydrated iron oxides into iron oxide, yellow and brown ores in red, as well as to destroy organic impurities. For calcining at low power, muffle or flame oven are used, rotary cylindrical furnaces with large capacity.

Grinding of the pigment is carried out in order to reduce the size of the large particles remaining after the melting and the destruction of the lumps formed during the calcination. In the first case, ball and tubular mills are used, in the second case is disintegrators.

The next step in the preparation of natural pigments is the dispersion or separation to produce a pigment of given dispersion.

The final product – natural iron – based pigments must comply with the conditions given in Table 2.11.

Table 2.11. **The main indicators of the quality of mineral pigments [25]**

Indicator	**Ocher of the highest quality**	**Ocher defective**	**Ocher no defective**	**Mummy bauxite**	**Mummy light**	**Mummy dark**	**Iron dry minium**	**Brown dry Umbrian**
Content of Fe_2O_3, %	18	18	12	77	20	35	75	48
The loss on ignition, not more %	10	10	10	–	–	–	–	1
Reaction of water extraction, pH	neutral							
Soluble salts, not more, %								
Soluble salts of iron, not more, %	–	–	–	–	trace	trace	0,0001	–
Moisture, not more, %	5	5	5	3	3	3	3	3
The residual on the screen, 4900 revs/cm^2, not more, %	–	0,5	2	2	2	2	3	2
The residue on the sieve, 10000 otv/cm^2, not more, %	0,1	–	–	–	–	–	–	–
Coverage, not more then, g/m^2	65	70	90	60	45	30	20	40

QUESTIONS AND TASKS FOR SELF-CONTROL

1. Give the general information about coagulants and coagulation. List the producers of coagulants in Ukraine and the types of coagulants they produce.

2. Describe the crude and purified of aluminum sulfate. Describe the aluminum-containing coagulants: aluminum oxychloride, sodium aluminate, and aluminum chloride.

3. Give the characteristic of iron sulfate (II) and iron (III)sulfate. Characterize iron-containing coagulants: iron (III) chloride, chlorinated aluminum sulfate, mixed alumina.

4. Bring the raw material base for producing of coagulants.

5. Identify and characterize the main stages of aluminum sulfate production from aluminum hydroxide.

6. Provide physicochemical bases for the production of aluminum sulfate from kaolin.

7. Describe the technological scheme for obtaining aluminum sulfate from aluminum hydroxide in a periodic method.

8. Describe the technological scheme of obtaining raw aluminum sulfate from kaolin.

9. Give chemistry and the essence of obtaining aluminum hydroxide by Bayer's method.

10. Give the functional scheme of production of alumina.

11. Describe Bayer's cycle.

12. Chemical transformation of existing raw materials in the Bayer process.

13. Describe the technological scheme for obtaining aluminum hydroxide by Bayer method.

14. Give a modern classification of pigments and give examples of basic pigments.

15. Describe and define the basic pigmentary properties.

16. Provide the physicochemical and pigment characteristics of titanium (IV) oxide.

17. Bring the raw material base for the production of white pigment (TiO_2). Give a comparative description of sulfate and chloride methods of producing TiO_2 from ilmenite concentrate.

18. Give a brief description of the production stages of white pigment (TiO_2) by sulfate method.

19. Describe the principle scheme for the decomposition of titanium–containing raw materials and restoration of the ferrule. Provide the physical and chemical bases of the hydrolysis stage in the production of TiO_2.

20. Describe the iron oxide materials and use them as pigments. The raw material base is iron-containing pigments.

21. Characteristics of yellow, red and black pigments. Getting the specified pigments in Ukraine.

22. Provide existing methods for obtaining yellow, red and black pigments.

23. Describe the method of obtaining yellow, red and black pigments in aniline production.

24. List the raw materials and methods for obtaining pigments from ferrous sulfate (II).

25. Give chemistry to the process of obtaining red pigment by firing methods.

26. Describe the technological scheme of obtaining red pigment by thermal decomposition.

27. Give the methods of chemical precipitation used to produce iron-based pigments.

28. Give a description of the scheme for the production of fermentation pigments by the Pennman’s method.

29. Bring the peculiarities of the ammonia synthesis of iron-containing pigments and a description of the receipt scheme.

CHAPTER 3 LABORATORY WORKSHOPS

3.1 DETERMINATION OF SORPTIVE PROPERTIES OF TITANIUM (IV) OXIDE

Objectives: to determine specific surface area of sorbent TiO_2 by desiccator method by adsorption of benzene vapors; to construct sorption isotherm of dye methylene blue on TiO_2 and to determine the specific adsorption of organic pollutant.

Brief theoretical information

In recent years, the focus has been paid of investigations of catalytic processes and usage of semiconductors as photocatalysts for removing of organic and inorganic pollutants from water or gas phase systems in processes of ecological catalysis, preparation of drinking water etc. Oxidation of pollutants is in the basis of this method of liquids purification, mainly, inorganic to nontoxic substances or fully mineralization. These processes are most widely used for discharging wastes, containing dyes.

Among many inorganic materials, are considered as photocatalysts, the most popular is titanium (IV) oxide (TiO_2). Firstly, Fudgishima and Honda had discovered its photocatalytic activity in 1972, at usage in photoelectrochemical process. Its effectivity didn't exceed 10 % [1]. Titanium (IV) oxide is different high photosensitivity and has acceptable width of the bandgap (E_g=3,2 eV). It has dominant position in photocatalysis, because it is also chemically and biologically inert and has low cost. It also belongs to the most often used photocatalysts [2].

Among other photocatalysts, TiO_2 is investigated the most active and widely used in practice by its powerful oxidation properties in processes of decomposition

of organic pollutants, increases chemical stability, durability, non-toxicity, relatively low cost and transparency in relation to visible light.

Titanium (IV) oxide exists in several modifications. Crystals of tetragonal (anatase, rutile) and rombic syngony (brookit) are found in nature. It is believed that anatase modification in photic stimulation catalytic and photoelectric reactions. Enhance of photo activity of anatase can be attributed higher position of Fermi level (by 0,1 eV) in compare with rutile. Besides, the difference in levels of hydroxylation of surface can also plays role. It is believed that rutile phase has weak photocatalytic properties. However, the rutile phase can be active and non– active, depending on the method of synthesis of sample.

Except photocatalytic properties, TiO_2 should have satisfactory sorption characteristics, determining by sorption and structural characteristics of powders. The last of them can be evaluated by specific surface area and activity related to methylene blue.

Experimental part

Devices, utensils, reagents

Desiccator with benzene, glass buckets, technic balances, analytic balances, vacuum drying cabinet. The flask measures a nominal volume 500 ml – 1, the flask measures a nominal volume 100 ml – 10, conical flask measures a nominal volume 250 ml – 5, rubber stoppers for conical flasks – 5, pipette measures a nominal volume 50 ml – 1, burette with nominal volume 100 ml – 1, spatula, device for shaking, centrifuge and metal ammunition for centrifuge, photoelectric colorimeter, set of ditch. Titanium (IV) oxide. Methylene blue. Distilled water.

Determination of the specific surface area

Samples of TiO_2 (1 g) weighed in glass buckets with stoppers, pre– dried and weighed on analytic balances. Then they are placed (with opened stoppers) into vacuum drying cabinet and dried at 378 K during 2 hours. After drying, buckets with samples of TiO_2 weighed with stoppers and placed into desiccator with benzene. Buckets with samples must be opened in desiccator. Exhaust cabinet with the desiccator with benzene must be switched off!

After 25 minutes' buckets with samples got out the desiccator. Then their weight is measured. The same operations conducted with interval 15 minutes. Measuring of the mass is conducted till the difference between weights of four last measurements isn't changed. Total sorption is determined after a day.

The specific surface area (S_{spec}, m^2/g) is calculated by the formula:

$$S_{spec} = \frac{m_{C6H6} \cdot N_A \cdot S_0}{m \cdot M_{C6H6}},$$

where m_{C6H6} – weight of absorbed benzene vapor, g; N_A – Avogadro constant ($6{,}02 \cdot 10^{23}$ mole^{-1}); S_0 – surface area, occupied by one molecule of benzene ($39 \cdot 10^{-20}$ m^2); m – weight of sample, g; M_{C6H6} – molecular weight of benzene (78 g/mole).

Construction of adsorption isotherm of dyes

Model solution of methylene blue is prepared (500 mg/L). The sample of dye (250 mg) is transferred into the flask (500 ml). The sample is weighed on analytic balances.

Working solutions of methylene blue are prepared (100, 200, 300, 400, 500 mg/L) by following way: appropriate quantity of model solution is transferred into flasks (100 ml).

Samples of TiO_2 (50 mg), weighed on analytic balances, are transferred into numbered conical flasks (250 cm^3). Then 50 cm^3 of working solutions are entered into conical flasks. Flasks are closed by stoppers and shook during 20 minutes for establishing of adsorption equilibrium.

For separation of particles of TiO_2 from solution of methylene blue, suspensions are transferred from conical flasks into metallic cartridge and centrifuged 30 minutes at 3000 min^{-1}.

The concentration of methylene blue is determined photometrical: the determination of optic density is conducted by photoelectric colorimeter at 660-670 nm and length of cuvette 1 cm with distilled water as solution of comparison. Heavily painted solutions are diluted with distilled water.

Construction of calibration graph

Firstly, solutions of methylene blue are prepared (5, 10, 15, 20, 25 mg/L) by following way: appropriate quantity of dye by burette is transferred into flasks (100 ml).

The determination of optic density of prepared solutions are conducted by photoelectric colorimeter at 660-670 nm and length of cuvette 1 cm with distilled water as solution of comparison.

Processing results

The specific adsorption of methylene blue (a) is calculated by the formula, mg/g:

$$a = (C_0 - C_p) \cdot V_{m/b} / m,$$

where C_0 and C_p – concentrations of methylene blue before and after sorption, mg/ml; $V_{m/b}$ – volume of solution of methylene blue, added to TiO_2, ml; m – weight of TiO_2, g.

Experimental data is noted in Table 3.1.1, and adsorption isotherm is constructed in coordinates a – C_p.

Table 3.1.1 **Experimental data**

C_0, mg/ml	V_{ts}, ml	C_p, mg/ml	m, g	a, mg/g

Safety

1. To perform rules of work with vacuum drying cabinet.
2. Do not leave the installation inoperative without supervision.
3. Caution should be exercised when treating all the chemicals used in the work.

Control questions

Access to work

1. The aim of work. Safety.
2. What is in the base of photocatalytic purification of liquids and gases?
3. What is the definition based on the specific surface area by desiccator method?

Defense of work

1. What is specific adsorption?
2. Give the characterization of TiO_2?
3. Bring the area of usage of TiO_2.

3.2 SYNTHESIS OF ACTIVATED CARBON

Objective: In this lab work students have to view the theory of synthesis of activated carbon and study in practice the activation, oxidation and nitrating processes. Three different modifications of one initial activated carbon will be obtained.

Brief theoretical information

Activated carbon is a kind of microcrystalline carbon, belongs to the group of graphite bodies and is a spatial polymer. The main structural element of all types of carbon is a system of condensed aromatic rings (an integral part of a crystalline lattice of graphite) and related chains of linearly polymerized carbon, which can carry various functional groups similar to organic (Fig. 3.1.1).

At the heart of the synthesis of this class of substances is the ability of hydrocarbons to oxidize in the air and decompose when heated. Actually, activated carbon can be obtained by pyrolysis of any mineral and organic carbonaceous raw materials. In this case, non– carbon elements are oxidized to volatile oxides and are removed, and free formed carbon atoms begin to be structured into elementary crystallites, chains and amorphous carbon.

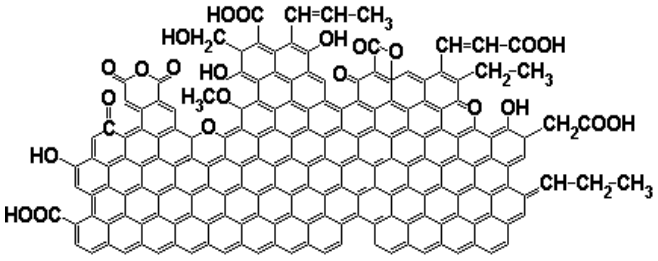


Fig. 3.1.1. **Fragment of the surface of activated carbon.**

Most known synthesis methods are only variants of a single process, the specific conditions of which affect the characteristics of the resulting activated carbon. Natural raw materials, which are used in industry for the production of activated carbon, are classified by their origin into mining, plant–animal and industrial waste. Phenol formaldehyde and vinyl pyridine resins, styrene, divinylbenzene, vinyl, polyvinyl, polyvinyl dichloride and their

copolymers, as well as a number of other organic substances, are used to produce synthetic activated carbon.

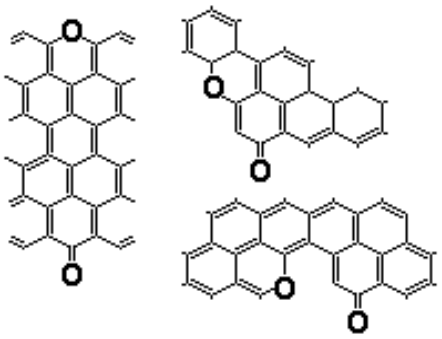


Fig. 3.1.2. Fragment of the surface of basic activated carbon.

Surface chemistry has a significant effect on the properties of carbon sorbents and determines their behavior in a variety of physical and chemical processes, including technological ones. The presence of even small amounts of certain surface groups or atoms can have a significant effect on the characteristics of the activated carbon and radically change the parameters of the processes by its participation. For example, anion-exchange ability, catalytic activity and adsorption capacity of carbon, when introduced into its composition no more than 2-3 % of oxygen or nitrogen, can be increased several times.

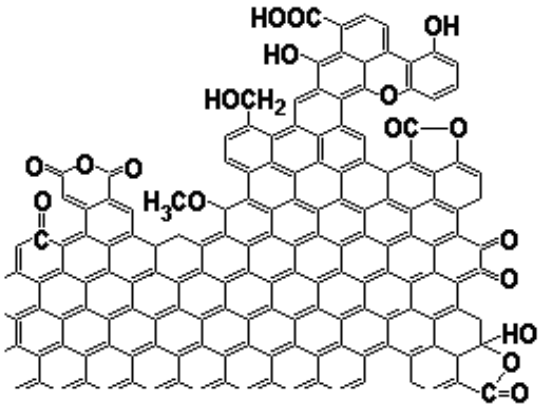


Fig. 3.1.3. **Fragment of the surface oxidized activated carbon.**

Carbon activation – a complex heterogeneous high-temperature process (800-1000 ˚C), in which under liquid or gas is formed activators developed porous structure, advanced oxidation and burning out of the unorganized carbon structuring elementary crystallites. When the carbon is activated in the inert atmosphere, the thermal decomposition of the surface ≡C– H, ≡C– C≡, =C=C= and other bonds and the formation of graphite-like crystallites of unsaturated valences on the finite portions occurs when the air is in contact with the oxygen (after

cooling Carbon to room temperature) form predominantly ether groups. The atoms of the ethereal type of oxygen in combination with thermally stable carbonyl groups, which do not decompose during pyrolysis, form the so-called pyrone structures (Fig. 3.1.2), which give the nature of the carbon of nature.

Oxidation is a recognized method for modifying the surface of activated carbon. The interaction of activated carbon with oxidants, both in the gas and in the liquid phase at room temperature or higher, leads to the formation of surface functional groups of acidic character – carboxyl, phenolic, alcohol, hydroxyl, quinone and others (Fig. 3.1.3).

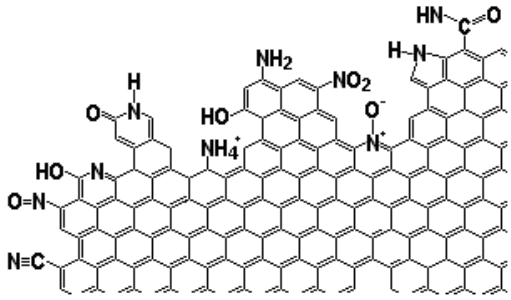


Fig. 3.1.4. **Detail of the nitrogen-doped surface of activated carbon.**

Modification with nitrogen is achieved by treatment of activated carbon with various nitrogen-containing substances of both organic and mineral origin. In this method, the atoms of the nitrogen are chemisorbed on the surface of the activated carbon in the functional groups, or embedded in the carbon matrix in the form of heteroatoms (Fig. 3.1.4). For example, the modification of activated carbon by melamine is a rather new method that has not yet been widely used.

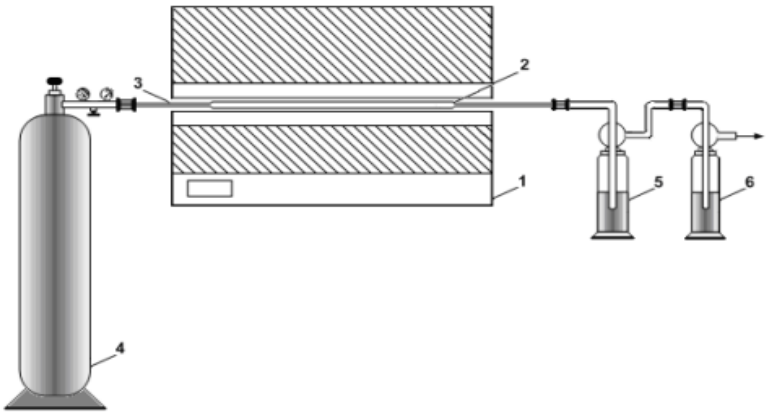
Experimental part

Devices, utensils, reagents

Muffle oven Drying cabinet. Electric tile. Shaking machine. Scales technical. Chemical-resistant glass with a capacity of 500 cm^3. Conical flask with a capacity of 250 cm^3. Glass sticks Nitrogen cylinder. The concentrated solution of H_2O_2. Melamine.

Description of installation scheme

For high-temperature syntheses, an installation (Fig. 3.1.5) consisting of a tubular muffle furnace 1, a quartz reactor 2 for calcination (length 1,2 m, internal diameter of the working zone 3 cm) is used, which, by means of the gas-duct tube 3 (internal diameter 12 mm) on one side is connected to the nitrogen cylinder 4, and on the other with the help of the same gas-discharge pipe, with the system of absorbers– absorbers. Traps 5, which is filled with a solution of sulfuric acid serves to absorb ammonia. The absorbent 6 containing sodium hydroxide (ω(NaOH) = 30 %), is used to absorb CO_2, H_2S and other acid gases.



1 – muffle furnace; 2 – quartz reactor; 3 – gas–duct tube;
4 – nitrogen cylinder; 5,6 – traps.

Fig. 3.1.5. **Scheme of laboratory installation.**

Activation

The weight of raw material weighing ~20 g, weighed on technical scales, transfer to a quartz reactor using a chemical funnel, which is connected to a gas–fired tube with a cylinder and placed in a muffle furnace. Plug on the heating of the furnace, open the tank and establish a constant flow of nitrogen ~1-2 bubbles per second, which is presented in the trap 5 (see Fig. 3.1.5). After reaching the oven temperature of 850ºC, which is further supported automatically for 1 hour pyrolysis

are carefully watching the flow of gases output from the reactor. At the end of the process without disabling nitrogen, the reactor very carefully (!) is removed from the oven, which then exclude (these operations cannot do by students and only by teaching staff). Quartz reactor and carbon in it is cooled to room temperature, continuing to continuously apply nitrogen in area Reactions and only after complete cooling of the system close the valve cylinder and disconnect the gas outlet. The resulting product is weighed on technical scales and replaced into a dry, clean, pre–signed capacitance that closes tightly. Calculate the loss of weight (Δ_{act}, %):

$$\Delta_{act} = (m_1 – m_2)/m_1,$$

where m_1 – mass output of raw carbon, g; m_2 – mass derived activated carbon, g.

Oxidation

Sample source raw carbon weighing ~20 g, taken on the technical balance, transferred to a beaker with a capacity of 500 $cm^{3,}$ in which small amounts (~25-30 cm^3) gradually adds 250 cm^3 of concentrated hydrogen peroxide solution. After the addition of each portion of the liquid mixture is mixed thoroughly with a glass rod until decomposition of H_2O_2; Remnants of the liquid are evaporated on an electric tile continuously mixing the mixture. After further the final drying in the oven (100-110°C) the product obtained weighed and lace in a dry, clean previously signed container tightly closed. Calculate the loss of weight (Δ_{ox}, %):

$$\Delta_{ox} = (m_1 – m_2)/m_1,$$

where m_1 – mass output of raw carbon, g; m_2 – weight of the resulting oxidized carbon, g.

Nitration

The original sample weight of activated carbon ~20 g, taken on the technical balance, transferred to a conical flask 250 cm^3 adds 5 g melamine and 150 cm^3 of

distilled water, close tightly and shake on the machine to shake for 30 minutes. After that, the flask is opened, placed on an electric tile, and, continuously mixing the mixture, evaporate the liquid. Thereafter the final dried at the temperature 100-110 ^{o}C material transfer to a quartz reactor, which gas pipe connecting the cylinder and placed in a muffle furnace.

Safety measures

1. Cylinder with nitrogen is operated only by lecturer or staff.
2. The switching on of the electric muffle furnace is carried out after examination by the training personnel of the correctness of connection of the elements of the installation.
3. During work, do not leave unattended laboratory installations and carefully monitor the flow of gases at the outlet of the reactor.
4. Follow the rules of working with chemicals and electrical appliances.

Quiz

Admission to work

1. What is activated carbon? The internal structure of activated carbon, its features.
2. The purpose of the work. Scheme of laboratory installation.
3. Methods of preparation of activated, oxidized and nitrated activated carbon.

Defense of work

1. Methods of synthesis of activated carbon.
2. Raw material for activated carbon.
3. Methods of modifying activated carbon.

4. Features of surface chemistry of activated, oxidized and nitrated activated carbon.
5. Ways of usage activated carbon.

3.3 DETERMINATION OF TOTAL PORE VOLUME AND BOUNDARY VOLUME OF ADSORPTION SPACE OF ACTIVATED CARBON

Objective: In this lab work students have to determine the total pore volume and limit the amount of activated carbon adsorption space.

Brief theoretical information

The porosity of adsorbents is determined on the basis of their true and apparent density, and expressed as a percentage of the volume of the adsorbent:

$$R = (d - \delta)\ 100/d,$$

where P – porosity, %; d – the true density g/cm^3; δ – apparent density, g/cm^3.

The degree of porosity adsorbent is characterized by a total pore volume V_Σ. In the scientific literature refer υ_Σ, and the terms «maximal (ad)sorbed volume», «volume of (ad)sorption (porous) space». The total porosity can be found as the difference between the volume v_1, which is 1 g adsorbent and its true volume of solid v_2:

$$V_\Sigma = v_1 - v_2.$$

The total specific volume $v_1 = 1/\delta$. The true volume v_2 can be found the true density of the substance, as $v_2 = 1/d$.

Imaginary density Is equal to the mass of the unit volume of the porous material. It can be determined by the Kubelka method, which is based on the assumption that the grain content remains virtually unchanged after the absorption of sorbent by paraffin, filling only its outer pores. The apparent density of activated carbon is also found in the volume of mercury, since mercury does not wet the carbon and at atmospheric pressure does not fill the pores of carbon, but only the voids between the samples of the sample.

To study the true density, it is necessary to use liquids or gases, the molecules of which are sufficiently small and can penetrate the narrowest pores. The preferred standard method for determining the true density of helium accepted method of filling the pores of the adsorbent that already has been evacuated (spherical molecules of helium are van der Waals diameter D=20 nm).

The relative complexity of the technique pledged to develop simpler – the approximate method of determining the total pore volume of activated carbon, followed by getting the value of V_{Σ}, which coincide with Values found by the helium method. Suitable for most practical purposes was the method of impregnating adsorbents with water during boiling. Under these conditions, water displaces from the pores of activated carbon, the air is quite full. Water from the spaces between grains is removed by filtration under vacuum 8×10^{-3} MPa.

Van der Waals diameter of the water molecule is 35 nm. Therefore, the use of water instead of helium eliminates from the total volume of adsorption space those pores whose diameter is ≤35 nm but> 20 nm. It might make some errors in the study of the adsorption of certain gases, such as CO or CO_2 (D=28 nm). However, for adsorption of the vast majority of gases, vapor or dissolved substances, pores of such sizes are not available and therefore they can be excluded from the total porosity of activated carbon.

Using a set of pycnometric liquids of different sizes of molecules (Table 3.2.1) and thus excluding, in a manner consistent with the total volume of pore pores with diameters smaller than the Van der Waals size of these molecules, one can differentiate the volume of the smallest pores by their effective radius. Then pore volume, which neglected the replacement pycnometric fluid 1 with fluid 2 having a molecule to make: $\Delta v = 1/d_1 - 1/d_2$.

Table 3.2.1. **Van der Waals diameters of molecules of pycnometric liquids**

Adsorbate	*D*, nm	Adsorbate	*D*, nm
Water	35	Dioxane	59
Methyl alcohol	46	Four-Carbon Carbon	61
Acetic acid	51	Toluene	63
Ethanol	52	*n*-Hexane	67
Acetone	56	Triethylamine	69
Benzene	58	*n*-Octane	73

Pore volume of activated carbon, which is filled with a relative pressure $p/p_s \approx 1$, represents a marginal amount (ad)sorption space, also called maximum (ad)sorption capacity. In some approximation, it can be characterized by the data of static activity under equilibrium conditions. The maximum amount of gas (vapor) absorbed by the unit mass of the sorbent at the equilibrium with the gas (vapor) contained in the air at a given temperature, and has a certain concentration, is called the equilibrium static activity of the adsorbent. At constant pressure, it is a function of temperature and concentration.

Static equilibrium activity expressed in cm^3 steam or gas (at NTP), which adsorbed 1 gram of adsorbent (a_s, cm^3/g); In mg of gas (vapor) per 1 g of sorbent (mg/g), as well as the ratio of the mass of adsorbed gas (vapor) to the mass of the initial sorbent in %. These expressions are related to each other:

$$a_s \text{ [mmole/g]} = 1/22{,}4 \cdot a_s \text{ [cm}^3\text{/g]},$$

$$a_s \text{ [mmole/g]} = 1/M \cdot a_s \text{ [mg/g]},$$

$$a_s \text{ [mmole/g]} = 1000/100\, M \cdot a_s \text{ [\%]} = 10/M \cdot a_s \text{ [\%]},$$

where M – molar mass of gas; 22,4 – volume of 1 mmole of gas (steam), cm^3.

Often the adsorption size refers to the mass of the adsorbent, which is contained in the unit volume of the layer of the sorbent. If Δ is mass of 1 cm^3 adsorbent layer (bulk density), the static equilibrium activity of 1 cm^3 adsorbent layer is:

$$a_s \text{ [mmole/cm}^{3]} = \Delta a_s \text{ [mmole/g]}.$$

The most common method for determining the static equilibrium activity porous solid materials is desiccator method.

Experimental part

Instruments, glassware, reagents

Oven. Analytical scales. Water jet pump. Manometer. Stopwatch. Buchner funnel. Bunsen flask. Conical flasks with a capacity of 250 cm^3, 2 pcs. The glass cylinder capacity of 10 cm^3. Wide glass cups with ground covers, 8 pcs. Desiccator capacity of 2 dm^3 of benzene. Desiccator capacity of 2 dm^3 of $CaCl_2$. Spatula porcelain. Clamp. Laboratory filter paper.

The total pore volume

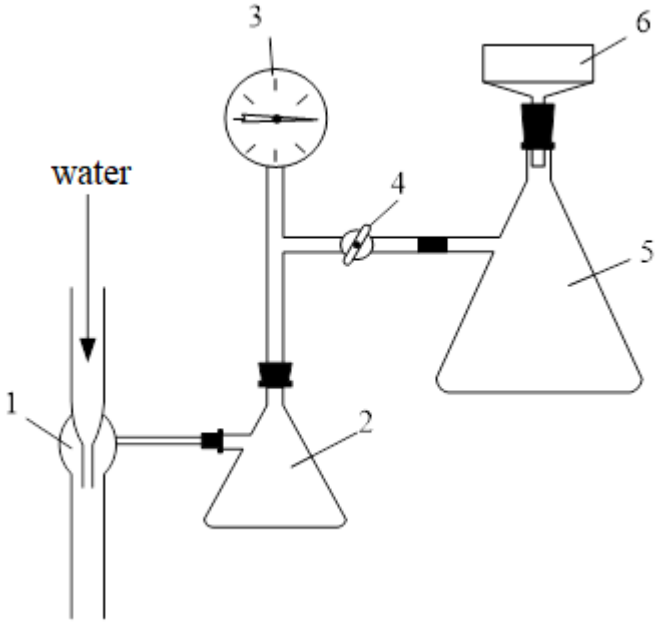
The method of determining the total pore volume on water– based water–filled pore size from 0,3 to 10^4 nm boiling carbon sample in water and remove excess water from the surface of grains by suction under certain conditions.

The circuit installation. To determine the total pore volume on water collecting device, a general view is shown in Fig. 3.2.1. When using water jet pump 1 by changing the flow of water faucets regulate the vacuum, which measure the pressure gauge bulb 3.2 serves as a buffer capacity. Gate valve 4 (glass hole diameter of 6-8 mm) adapted to disconnect the flask 5, which carries a porcelain Buchner funnel 6.

Analysis. Before determining the activated carbon has to be dried at 100-110 ^oC for 1 hour in a layer no more than 5 mm for 1 hour in a porcelain cup. From the dried sample is poured into a graduated cylinder with a weak shaking 10 cm^3 carbon and lace in pre-weighed weighing bottle, close lid and weigh with an accuracy of less than 0,01 g.

After weighing carbon quantitatively transferred to a conical flask, pour 100 cm^3 of water and mark the level. The contents of the flask were heated for 15 minutes, then adds cold distilled water to the original volume and the outer surface of the bulb cool water tap to room temperature.

At the bottom of porcelain funnel 6 put a paper filter and moisten it with water. When the tap closed 5 system creates negative pressure 8×10^{-3} MPa, then turn creates discharge valve 5 in the flask, then the flask is again disconnected. All the time closely monitoring so that when suction filter lies flat tightly to the bottom of the funnel and connecting hoses to crack.



1 – waterjet pump; 2 – intermediate buffer capacity; 3 – vacuum gauge;
4 – valve connecting glass; 5 – Buchner funnel; 6 – Bunsen bulb.

Fig. 3.2.1. **Scheme of laboratory installation.**

The contents of the Erlenmeyer flask lossless carefully transferred into a funnel extraction of carbon and spread over the surface of the filter spatula. Turn the tap start sucking while running stopwatch, and support for 3 minutes discharging 6 MPa.

After this time poured into carbon weighing bottle, which conducted the initial weight, which flask with funnel gently tilted at an open faucet being careful that no water got into the funnel. The grains remaining on the filter, gently remove with a spatula, transferred to a weighing bottle with no losses and close the lid. Cups of wet carbon are weighed with an accuracy of less than 0,01 g no later than 3 minutes after suctioning.

Valve overlap, remove the filter from the flask and pour water preparing plant for the next experiment. The results of two parallel experiments should not differ one from another by more than 5%. Calculation of total porosity is of the formula:

$$V_{\Sigma} = (m_p - m_o)/m_o \cdot d_{H2O},$$

where m_g – weight of wet activated carbon (without sample bottle), g; m_o – source supply activated carbon (without sample bottle), g; d_{H2O} – water density at a given temperature, g/cm^3.

Static equilibrium activity

Activated carbon sample weighing approximately 1 g, taken to the nearest 0,001 g, in a foster pre-weighted (with lid) glass weighing bottle, put in preheated to a temperature of 100-110 ^{o}C oven and open the door.

Every 30 minutes, closed cooled to room temperature in desiccator with $CaCl_2$ weighing bottle is weighed on an analytical balance. When the deviation between the results of two successive weighing does not exceed 0,5 % of carbon weighing bottle is left open in a desiccator with benzene per day.

After this time closing weighing bottle and weighed on an analytical balance. Adsorption space volume calculated using the formula:

$$a_s = (m_p - m_o)/m_o \cdot d_b,$$

where m_p – mass of carbon after contact with benzene (without a sample bottle) g; m_o – initial weight (dry cooled) activated carbon (without sample bottle) g; d_b – density of benzene at a given temperature, g/cm^3.

All experimental data are entered in the table. 3.2.2.

Table 3.2.2. **Experimental data**

Name of samples	**V_Σ, cm^3/g**	**a_s, cm^3/g**

Safety measures

1. When working on the laboratory facility must follow that when suction filter lies flat tightly to the bottom of the funnel (air should not «blow») and that the connecting hoses bend.
2. When wet carbon interspersed with funnel cups to prevent the loss of grains of adsorbent.
3. To prevent thermal burns when removing and hot cups of drying cabinets use the metal grip.
4. All work with benzene carried out in a fume hood.

Quiz

Access to work

1. The purpose of the work. Safety.
2. The concept of total pore volume and the adsorption limit amount of space, methods of determination in the laboratory.
3. Scheme of laboratory setup procedure and rules for safe work on it.

Defense of work

1. How does characterize porosity activated carbon?
2. What methods can determine the true and apparent density of the porous body?
3. What is called static equilibrium adsorbent activity? What does it depend on?
4. What is the difference between the total pore volume, the maximum amount adsorbed, the adsorption capacity of the porous space and volume space? What units of measurement are these values?
5. What is the limit adsorption amount of space, the maximum adsorption capacity? In what units they can be measured?

3.4 RESEARCH PORE VOLUME AND SPECIFIC SURFACE AREA OF ACTIVATED CARBON

Objective: In this lab work students have to determine the volume of micro– and macro–pores transitional and specific surface area of activated carbon sample.

Brief theoretical information

Most brands of activated carbon used in practice, has all three types of pores, which represent a single complex system in which the mesopores are an offshoot of macropores and micropores – the continuation of transitional pores. The nature of the activated carbon porosity determined by the properties of the source material, carbonization and activation conditions. The porous structure has a great influence on the course of adsorption, ion exchange, catalyst and other processes on the surface of adsorbents.

Activated carbon has a very high value of specific surface area (500-1000 m^2/g or more). These sorbents generally have developed polydisperse structure and synthesis of specific samples can be obtained with a narrow distribution of pore radii required size.

The value of the total pore volume of the adsorbent does not provide information about its activity and the maximum amount of material that can absorb the solution with steam or this adsorbent. Part of the total number of pores can be quite large sizes (macropores), so that it is not completely filled with capillary condensation of steam even at a relative pressure close to unity. Adsorption on the surface of the pores is also negligible, as was their surfaces.

Transition pore volume plays an important role in the absorption of the substance. This amount can be estimated by the number of capillary condensed vapor at $p/p_s \approx 1$ (measurements are usually at $p/p_s \approx 0{,}9$). Adsorption capacity at

relative transition pore pressure is insufficient to start the capillary condensation of vapor on them can be characterized by the value of specific surface area (S_{spec}).

In heterogeneous porous bodies share of the total porosity attributable to micropores, sometimes exceeding the amount of the remaining pores. Rate of porosity which attributes to micropores is filled with vapor adsorption volume at pressure capillary condensation beginning. Adsorption capacity of the adsorbent structure of the most uniquely determines the volume of micropores.

Thus, porous adsorbents to be described that least four parameters: the total volume of pore volumes and macro transitional and micropores. More detailed description of the structure of porous adsorbents is possible only if the information on the distribution volume of each of these main groups according to their pore radius (r).

The largest directly visible pores increase from macropores with r>50 nm. Mesopores are a large variety; their radius is in the range 2-50 nm. When vapor sorption at high relative pressures (up to the saturation pressure) in the pores of the capillary condensation occurs – condensation of vapors by reducing the elasticity of the vapor concave meniscus fluid. Micropores – the smallest pore size of the molecular order (r<2 nm). They will almost entire surface at which the adsorption.

The share of total macropore pore 1 g of activated carbon typically account for 0,2-0,5 cm^3/g mesopores – 0,02-0,1 (in special cases – carbon, intended for adsorption of large molecules to 0,7 cm^3/g) of micropores 0,15-0,60 cm^3/g. Specific surface of carbon adsorbents are provided a major way macro- and mesopores, as by theory of volume filling of micropores by gases and steam, the concept of surface micropores has no physical meaning.

Experimental part

Instruments, glassware, reagents

Oven. Analytical scales. Refractometer. Pycnometer at 10 cm^3, 6 pcs. Volumetric flasks with rubber stoppers with a capacity of 100 cm^3, 6 pcs. Glass tubes with rubber stoppers with a capacity of 50 cm^3, 8 pcs. Glass ampoules with tightly graded ground stoppers with a capacity of 25 cm^3, 6 pcs. Glass ampoules are not graded with dense ground stoppers with a capacity of 10 cm^3, 6 pcs. Graduated pipettes chemical capacity of 5 cm^3, 1 pcs, and a capacity of 25 cm^3, 3 pcs. Graduated Pipettes chemically capacity of 5 and 25 cm^3 1 pc. Glass rod. Filter paper. Isopropanol. Toluene. Isooctane.

The volume of macropores

Macropore volume (V_{macro}, cm^3/g) of carbon are the difference between total porosity V_Σ (p. 2.2.2.) and the limit adsorption amount of space a_s (p. 2.2.3.):

$$V_{macro} = V_\Sigma - a_s.$$

The volume of micropores and transition pores

Building of calibration graph. In the six numbered volumetric flasks of 100 cm^3 with a tight six ground stoppers prepared stock solution of isopropyl alcohol in water concentration c_o = 0,5; 1,5; 2,5; 3,5; 4,5; 5,5 mole/dm^3. To this flask pipette poured 3,8; 11,5; 19,1; 26,7; 34,4; 42,0 cm^3 of isopropanol and dilute with water to the mark. The contents of the flasks and mix thoroughly measure the refractive index of output solutions ($n^{20}_{D(r)}$).

The data are entered in the table 3.1 and build a calibration graph – the dependence of the refractive index ($n^{20}_{D(r)}$) the concentration of the initial solution of isopropanol (c_o, mole/dm^3).

Analysis. Before determining the activated carbon has to be dried at 100-110ºC for 1 hour.

In the six numbered glass test tubes with 50 cm^3 with rubber stoppers weigh 1 g of activated carbon to within 0.01 g and poured in 25 cm^3 prepared solution of alcohol (p. 3.2.3.1). The contents of vials thoroughly mixed simultaneously prepare two capsules (control) – parallel and idle experiments.

Then the content of ampoules quickly filtered through dry ash freed filter (wetting of filter is unnecessary, discard the first portion of the filtrate!) And determine the refractive indices of equilibrium solutions ($n^{20}_{D(eq)}$).

Processing and presentation of results. Build isotherm of alcohol adsorption on the sample (Fig. 3.3.1).

To do this, value of the equilibrium concentration of isopropyl alcohol solution c_p lay on the horizontal axis that found by calibration schedule, and the vertical axis – corresponding value of adsorption a of isopropanol, calculated using the formula:

$$a = (c_o - c_p) \cdot V/1{,}000 \cdot m,$$

where V – volume of solution of isopropanol, cm^3; m – sample mass of adsorbent, g.

All data are entered in the table 3.3.1.

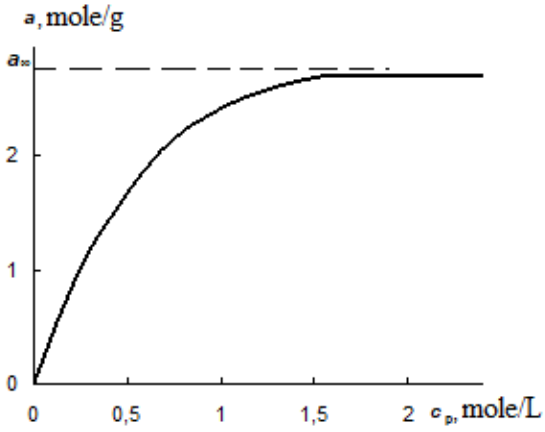


Fig. 3.3.1. Adsorption isotherm of isopropyl alcohol on activated carbon birch.

Table 3.3.1. **Data analysis and initial equilibrium solution of isopropanol**

Flask number	**1**	**2**	**3**	**4**	**5**	**6**
c_o, mol/dm^3	0,5	1,5	2,5	3,5	4,5	5,5
$n^{20}{}_{D(r)}$						
$n^{20}{}_{D(eq)}$						
c_p, mol/dm^3						
a, mmol/g						

It is necessary to determine the adsorption limit value ($a_{s\infty}$, mol/g), calculate the volume of micropores (V_{micro}, cm^3/g) and transition pore (V_{tran}, cm^3/g):

$$V_{micro} = a_\infty \cdot V_m,$$

$$V_{tran} = a_s - V_{micro},$$

where V_m – molar volume of isopropyl alcohol cm^3/mole.

Accordingly, build the received structural curve of investigated activated carbon. It is necessary to build the dependents of calculated volume species from the porous radius. In the built dependents each maximum suggests to the radius of micropores at 10^{-8} cm, mesopores 10^{-6} cm macropores 10^{-2} cm.

Specific surface area

The method of adsorption liquid phase of toluene solution in isooctane is suitable for rapid determination of high specific surface area adsorbents. However, unmeasured remains a small part of the surface that occur in the fine pores that are not available for molecules of toluene. The immediate problem of this method – determine the maximum adsorption toluene (it is proportional to the specific surface area).

Preparation of solutions of toluene. In the six numbered graduated glass vials with a capacity of 25 cm^3 of thin sections and tight ground stoppers prepared stock solution of toluene six Isooctane in different concentrations (*C*). To do this using a cylinder ampoule poured volumes of toluene ($V_{toluene}$) and isooctane ($V_{isooctane}$) as indicated in the table 3.3.2. The contents of vials and mixed thoroughly measure the refractive index $n^{20}_{D(r)}$ and the density (d_{20}) obtained solutions.

In case the measured value of n_D^{20} differs from the set (see Table. 3.3.2) more than 0,0003, the concentration of the solution corrects by adding the necessary components and then measure the refractive index.

***Table 3.3.2.* Indicators of output solutions of toluene in isooctane**

Flask number	**1**	**2**	**3**	**4**	**5**	**6**
C, % vol.	27,1	30,0	32,8	35,7	38,5	41,4
$V_{toluene}$, cm^3	5,4	6,0	6,6	7,1	7,7	8,3
$V_{isooctane}$, cm^3	14,6	14,0	13,4	12,9	12,3	11,7
$n^{20}_{D(s)}$	1,4200	1,4230	1,4260	1,4290	1,4320	1,4350
d_{20}, m^2/g						

Analysis. Before determining the activated carbon has to be dried at 100-110°C for 1 hour.

Six numbered glass vials are not calibrated capacity of 10 cm^3 of thin sections and tight ground stoppers weighed on an analytical balance (m_1). In each vial is made equal to 1 g of activated carbon with an accuracy of 0,01 g (*m*), poured 4,5 cm^3 prepared toluene solution in isooctane 1-2 ml above the adsorbent and then weighed (m_2). All experimental data are entered in Table 3.3 and calculate the mass toluene solution, which is filled in each vial (m_t). The contents of vials and mixed thoroughly measure the refractive index of equilibrium solutions ($n^{20}_{D(eq)}$).

If the temperature in the laboratory is different from 20°C, refractive index ($n^{20}_{D(r)}$ and $n^{20}_{D(eq)}$) to transfer the current temperature:

$$n = n^{20} + (20 - t) \cdot 0{,}0002.$$

Based on the data calculated adsorption of toluene, activated carbon, using the following formula and the results obtained are entered in Table 3.3.5.

$$a = m_t \cdot (n^{20}_{D(r)} - n^{20}_{D(eq)}) \cdot 10^4/m \cdot d_{20}.$$

Table 3.3.3. **Data analysis of equilibrium solutions in toluene/isooctane**

Flask number	**1**	**2**	**3**	**4**	**5**	**6**
m_1, g						
m_2, g						
m_t, g						
$n^{20}_{D(p)}$						
a, m^2/g						

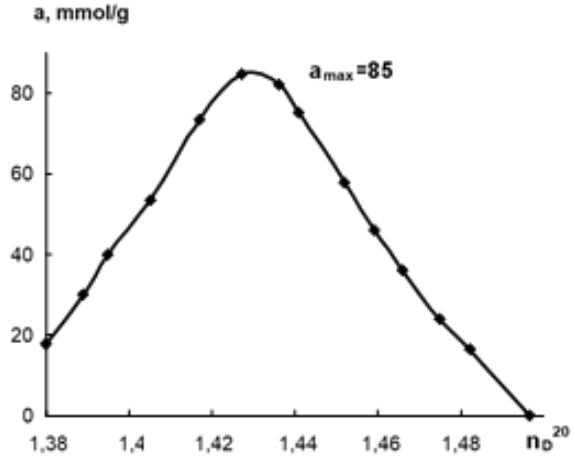


Fig. 3.3.2. Depending the adsorption of toluene in isooctane of the change in refractive index $n^{20}D$.

Processing and presentation of results. The build graph of the refractive index of equilibrium solutions in toluene from isooctane calculated values of specific adsorption of the scale: 1 cm abscissa corresponds to 0,01 units ($n^{20}_{D(eq)}$), and 1 cm ordinates – 10 units as well. The refractive index of 100% solution of toluene is 1,4964 (Fig. 3.2.2).

Define a_{max} from Fig. 3.3.2 and calculate a specific surface area of the studied activated carbon (m^2/g): $S_{sp} = 3,2\ a_{max}$.

Results of investigation obtained in laboratory work put in Table 3.3.4.

Table 3.3.4. **Experimental data**

Type of carbon	V_{Σ}, cm^3/g	a_s, cm^3/g	V_{macro}, cm^3/g	V_{meso}, cm^3/g	V_{micro}, cm^3/g	S_{sp}, m^2/g

Safety measures

1. To carry out the work necessary under specified herein consistency. If there are doubts about the performance of any procedure, contact the teacher.
2. Before you start, check the installation of zero-point refractometer.
3. The amount of liquid that is poured into the refractometer, in all cases, measurements should be the same.
4. All works of toluene and isooctane carried out only in a fume hood using samples.

Quiz

Access to work

1. Purpose and consistency of its implementation. Safety.
2. What kinds of pores present in the activated carbon, their size and proportion of the total volume of pores?

3. In processes where porous structure of activated carbon is crucial? Explain why.
4. List and expand the core methods for measuring the porosity of solids.

Defense of work

1. What determines the nature of the porosity of activated carbon?
2. What value has a specific surface area of the activated carbon?
3. What is the fate of the specific surface area of activated carbon is necessary for every kind of far?
4. What kinds of pores provided the bulk surface activated carbon? Why?
5. What are the dimensions of the micro, meso and macropores?
6. On the surface pores which are almost all adsorption?

3.5 STUDYING SURFACE PROPERTIES OF ACTIVATED CARBON

Objective: In this lab work students have to learn the basic physical and chemical properties of activated carbon. To do this, they determine static exchange capacity, functional surface composition and its pH dependence and carbon exchange capacity of pH.

Brief theoretical information

Oxygen activated carbon systems, so-called surface oxides, greatly affect the polar properties of carbon surface and its adsorption capacity, which is important from a practical point of view. The polarity of the surface oxygen-containing activated carbon adsorption causes intensive steam from wet gas atmosphere and at the same time slows the absorption of other vapors and gases. In liquid phase, selective adsorption capacity of activated carbon is relatively different polar substances also depends on the surface of these compounds.

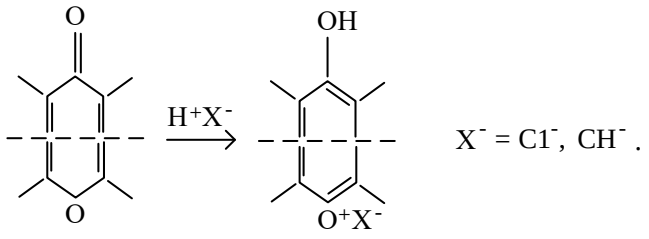


Fig. 3.4.1. **Structure of alkaline surface oxides by Böhm.**

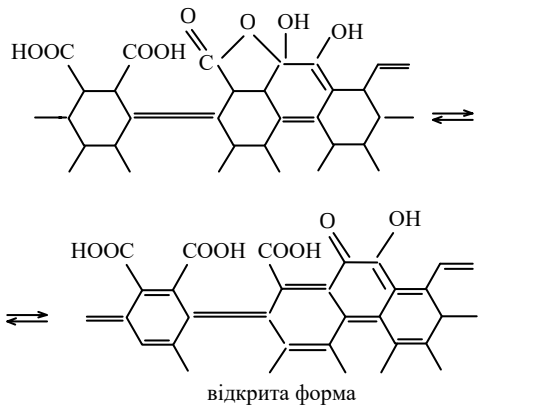


Fig. 3.4.2. **Structure of acidic surface oxides by Böhm.**

Activated carbon, which was calcined at 1000 °C in vacuum, adsorbs the oxygen at room temperature. In the presence of water or aqueous solutions of acids

neutralized acid amount equivalent to the amount of oxygen that was adsorbed. The surface oxides formed under these conditions are alkaline in nature (Fig. 3.4.1). However, much more frequently observed surface acidic oxides formed during the interaction with carbon or oxygen at elevated temperatures (300-500 °C) or with oxidizer such as chlorine, ozone, nitric acid, potassium permanganate, etc. in aqueous solution (Fig. 3.4.2).

The dotted line in Fig. 3.4.1 means that the carbonyl group and the group of pyronic type located in more than one benzene ring and connected via a resonant system electrons graphite layers arranged one above the other or in different layers of graphite.

The ability of surface functional groups of activated carbon to dissociation and ion exchange allows the use chemistry to analyze the surface of standard analytical methods. Thus, the definition of one of the most important characteristics of carbon sorbents – static exchange capacity, based on the neutralization and implemented by acid-base titrimetric.

The interaction of a strong base with the carbon surface in aqueous solution occurs to neutralization of alkali cations of carbons and the anions formed as a result of the dissociation of precursors, according to the reaction: $H^+ + OH^- = H_2O$. After titration received and the source of alkali acid determines the amount of OH^- ions react. It is equivalent to the concentration of H^+ on the surface of carbon and describes the overall content of acid groups (mmol/g). The interaction with the acid is neutralized surface basic character centers, whose number is set as the acid– base titration.

Similarly, conduct an analysis of the functional structure of the surface of carbon. The distribution of surface functional groups according to the degree of acidity titrated based on various carbons NaOH, Na_2CO_3, $NaHCO_3$ and HCl. This method is designed by renowned German scientist HP Boehm and is based on the

assumption that sodium bicarbonate neutralizes the strongest acid sites, bicarbonate – their own and weakly acidic carboxyl groups Alkali – in addition of phenol, whereas the acid can interact only with surface groups of basic type.

The study of functional capacity ion exchange of material in depending on the pH of the solution could be made by the method of pH potentiometric titration. It is building two titration curves substances that can exchange ions with activated carbon in his presence and without it. If the resin is in the H^- form (dissociated to form hydrogen ions exhibits acidic properties), then the titration of the electrolyte solution in the presence of his liquor consumption will be higher than the titration of the same solution without cations. Consequently, the titration curve in the presence of cations will be shifted toward the growth of the alkali (Fig. 3.4.3).

In the study of ion-exchange properties of activated carbon quantity and quality of certain types of surface groups capable of exchanging ions estimate based on an analysis of titration curves. In view of these curves (pH as a function of the added amount of alkali or acid dependent quantity absorbed ions – absolute or relative – pH) can be about, but usually quite accurate for practical purposes, to judge the nature of the ion exchanger (mono- or multifunctional) the type of active groups, their ability to dissociate, the most suitable for pH range and others.

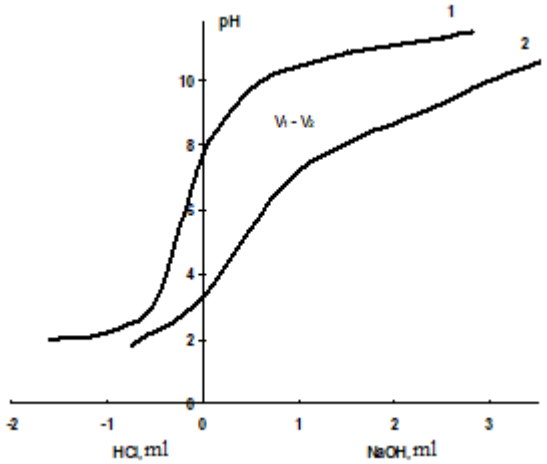


Fig. 3.4.3. **Titration curve in the absence (1) and presence (2) of activated carbon.**

The difference abscissa two points lying at different titration curves at the same pH makes it possible to calculate the amount (in mmol) of ions H^+, which supplanted with cations at a given pH. Knowing this number is, you can count the number (in mmol) of other cations *a* that the exchange of ions H^+ resin (expressed in mg/g of dry cations). By measuring the difference in the graph abscissa at different pH values are dependent *a* pH:

$$a = c\,(V_1 - V_o)/m, \qquad (4.1)$$

where *c* – concentration acid solution (alkali) mmol/dm^3; V_1 – volume of volumetric solution of alkali that corresponds to the pH of the solution in the presence of cations, dm^3; V_o – the same without cations, dm^3; *m* – weight of dry cations, g.

If titration curves divided into several sections and determine the average ionization constants for each type of functional groups on Griesbach method, assuming that pH=*pK* at the point corresponding to 50 % neutralization type groups that represented this area, you can more or less approach to calculate the dissociation constant of multifunctional resins. Thus, for example, it became known that carboxylic and phenolic groups on the surface of oxidized carbon active function in the pH range 1-8 and 8-10, respectively. The dissociation constant of carbon functional groups that has been oxidized by nitric acid, which were calculated by the Henderson-Haselbach equation for carboxyl groups were $4{,}2\cdot10^{-5}$, and for phenol – $4{,}7\cdot10^{-10}$.

Experimental

Instruments, glassware, reagents

Muffle. Apparatus for shaking. Balance analytical. Electric oven. pH meter. Porcelain mortar and pestle. Burettes for titration capacity of 25 cm^3, 4 pc. Conical

flasks with a capacity of 100 cm^3, 30 pcs. Conical flasks with a capacity of 250 cm^3, 5. Watering glass, 6 pcs. Pipettes with a capacity of 5 cm^3. Volumetric solution of 0,2 M NaCl; 0,1 M NaOH; 0,1 M HCl; 0,05 M NaOH; 0,05 M HCl; 0,05 M Na_2CO_3; 0,05 M $NaHCO_3$. Indicators: 1,0% methyl red, 1,0% methyl orange, 1,0 % phenolphthalein.

Static exchange capacity

In a conical flask of 100 cm^3 on an analytical balance weighing ~0,25 g activated carbon, poured 25 cm^3 of 0,1 M solution of NaOH, tightly and shaken for 4 hours, or leave without shaking daily.

Then filter, discarding the first portion of filtrate selected 5 cm^3 of filtrate and transfer to a flask for titration. Dilute with distilled water and 50 cm^3 and titrate with 0,1 m HCl in the presence of methyl orange to the color from yellow to red. In this way determine the equilibrium concentration of alkali (c_p, mmol/dm^3).

Similarly, analyzed stock solution NaOH, specifying the initial concentration of alkali (c_o, mmol/dm^3). Static exchange capacity (*SEC*, mmol/g) of the analyzed carbon determined by the formula:

$$SEC = V\,(c_o - c_p)/m, \qquad (4.2)$$

where V – volume solution of NaOH, taken for the reaction dm^3; m – mass of activated carbon source, g.

Functional surface composition

Four samples (~0,25 g) of activated carbon are on an analytical balance numbered in conical flasks (100 cm^3). In each flask poured 50 cm^3 0,05 M HCl, NaOH, Na_2CO_3 and $NaHCO_3$, tightly and shaken for 4 hours or leave without shaking daily. Then, discarding the first portion of the filtrate, selected 5 cm^3 of filtrate in flasks for titration.

Determination of the equilibrium concentration of solutions and refine their initial concentration. For titration the acid use 0,05 M NaOH solution and phenolphthalein indicator. Hydroxide, carbonate and sodium titrate by 0,05 M HCl in the presence of methyl orange.

Using the formula, the amount of total acidic (C_{acid}, mol/g), carboxylic (C_{carb}, mol/g), phenolic (C_{phen}, mol/g) and alkaline (C_{alk}, mol/g) of functional groups on the surface investigational activated carbon have calculated. For this based on the assumption that sodium bicarbonate neutralizes the strongest acid sites, bicarbonate – their own and weakly acidic carboxyl groups Alkali – in addition phenolic and while the acid can interact only with surface groups of basic type. All data are entered in the table 4.3.

The pH of the surface of carbon

A porcelain mortar and grind to powder small amount of activated carbon source. On an analytical balance and conical flask 250 cm^3 weigh 0,2 g obtained powder and pour 100 cm^3 of distilled water, close tightly and shaken for 4 hours or leave without shaking daily. Then boil for 5 minutes, rapidly cooled under running water and filtered through ash freed filter, discarding the first portion of filtrate. Water extraction pH measured pH meter with continuous stirring, and the data are entered in the Table 3.7.

The dependence of the exchange capacity of pH

Before determining the activated carbon has to be dried at 100-110 ^oC for 1 hour.

On an analytical balance 12 numbered conical flask of 100 cm^3 are 12 activated carbon samples 0,5 g in each flask poured 25 cm^3 of 0,2 m sodium chloride and sodium hydroxide (0,1 M) and hydrochloric acid (0,1 M) in amounts

indicated in Table 3.7. To each flask add distilled water so that the total volume of liquid in each glass composed of 50 cm^3 (thus the equilibrium concentration of NaCl in all cups are the same and is 0,1 M) tightly and shake on the machine to shake for 4 or leave hours a day, and then determine the pH of each solution.

Table 3.4.1. **The data for the preparation of a series of initial solution**

Flask number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
NaCl, cm^3	25,0	25,0	25,0	25,0	25,0	25,0	25,0	25,0	25,0	25,0	25,0	25,0
NaOH, cm^3	0	0,5	1,0	1,5	2,0	2,5	3,0	3,5	0	0	0	0
HCl, cm^3	0	0	0	0	0	0	0	0	0,5	1,0	1,5	2,0
H_2O, cm^3	25,0	24,5	24,0	23,5	23,0	22,5	22,0	21,5	24,5	24,0	23,5	23,0

The schedule is plotted, in which on the horizontal axis is the number of cm^3 alkali (acid) of added to each glass, and the vertical axis is measured pH. The dates are entered in Table 3.4.2. This curve is obtained by 2 (Fig. 3.4.3).

To get curve 1 hold so- called «idle» experiment – an experiment similar to the previous one, but without carbon. For this, 12 conical flasks are filled with 25 cm^3 of sodium chloride, added a similar amount of NaOH or HCl and dilute each cup to 50 cm^3, as in Table 3.4.1. Then flick on the machine to shake for 4 hours, or leave a day, and then determine the pH of each solution, the data are entered in Table 3.4.2.

Using the built curves, calculate the difference abscissa for given values of pH and formula (4.1) is calculated a_s. The resulting values are entered in the Table 3.4.2 and build on them in tracker coordinates pH – but figuring out the type of test material according to the Nikolsky classification.

Table 3.4.2. **Results of pH-metric titration**

Number of flask	V_1	**pH with carbon**	V_{at}	**pH without carbon**	$V_1 - V_o$	**pH difference** $V_1 - V_o$	***c*, mmole/dm^3**	***a*, mmole/g**
1								
2								
3								
4								
5								
6								
7								
8								

Table 3.4.3. **Experimental data**

Name of sample	***SEC*, mmole/g**	**pH of surface carbon**	C_{acid}**, mmole/g**	C_{carb}**, mmole/g**	C_{phen}**, mmole/g**	C_{alk}**, mmole/g**	***a*, mmole/g**

Safety measures

1. In carrying out the work must comply with the rules of conduct in the chemical laboratory and the rules of safe handling of chemicals, glassware and electrical appliances.

2. Strictly follow the rules of safe handling of acids, alkalis, set out in the general safety instructions in the chemical laboratory.

Quiz

Access to work

1. Purpose and consistency of its safety implementation.

2. Methods of static exchange capacity, functional structure of the surface and its pH, and also depending on the exchange capacity of carbon from the pH of the solution.

Defense of work

1. How are formed alkaline or acidic surface oxides of activated carbon? What is the impact they have on the course of physical and chemical processes involving activated carbon?
2. What analytical methods may investigate surface properties and chemical composition of activated carbon?
3. What is the SEC value of activated carbon?
4. What information about the composition and surface properties of activated carbon provides a method pH-potentiometric titration?

3.6 TEST METHOD ACTIVATED CARBON

Objective: In this lab work students have to learn the basic methods of testing industrial activated carbon. For this the activated carbon is tested on adsorption activity toward to methyl orange and iodine and also discoloration to methylene blue.

Brief theoretical information

Determination of specific surface area and porosity sorption materials are often conducted using monoionic dyes. Depending on the charge, which takes in water sorbent surface, Dyes are divided into anionic and cationic. Most powder and granular adsorbents that are of interest to the industry, such as silica, titanium illuminating, activated carbon, water charged negatively, because on the surface adsorbed anionic dyes.

Since the pore size of many industrial adsorbents compared to the size of dye molecules and can be used as molecular sieves and, assessing the selectivity installed specifics porous structure. The results obtained in this way generally agree with relevant data from other methods.

Isotherm of dye adsorption can be determined by measuring adsorption at room temperature. Usually this area is characterized isotherm, which is almost parallel to the horizontal axis. It is believed that the plateau isotherm reflects the completion of the formation of condensed monomolecular coverage of the adsorbent. If you know the cross-sectional area of adsorbed molecules of dye per isotherm can calculate the surface area of the adsorbent.

According to calculations, dye adsorbed in the form micelles, in which molecules are arranged in several layers, and the average number of molecules in a cubic micelle increases depending on the ion mass coloring dye molecule. It was also established that the adsorbent surface micelles are flat, so each micelles takes

the same platform as the dye molecule is isolated. Adsorption of methylene blue gives a picture of the surface of activated carbon, formed by pores with a diameter of 1,5 nm. Titer of methylene blue is considered the number of cm^3 of uncolored solution.

Activated carbon depending on the application areas is divided into three groups. The whitening activated carbon intended for adsorption coloring admixtures of large molecules or particles of colloidal dispersion degree. Carbon gas type used for adsorption of gases, steam (at low concentrations), and dissolved substances whose molecules are close in size to the molecules vaporous substances. Recuperated activated carbon used to capture and return to steam volatile solvents (at high concentrations).

The first group of activated carbon is A, B, AGS-4, OS, MD et al. The types the whitening activated carbon A and B is made of carbon-containing source by activation followed of grinding into powder; it is used to bleaching the food, pharmaceutical and other products. Granulated active carbon AGS-4 is used for bleaching sugar syrups in sugar industries. Active Carbon MD is intended to illuminate dirty and stained solutions and for the removal of various substances from solutions and vapor (gas) air mixtures. The types the whitening activated carbon are used for cleaning liquids from high-tar and coloring agents.

Activated carbon gas type designed for fine purification and separation of gases, adsorption of solutes with small molecular size at relatively low concentrations, water treatment to remove odors as catalyst and base of catalyst. Sorption activity by iodine (iodine index, Iodine number, iodine adsorption) is the amount of iodine in mg, which can be adsorbed 1 gram of powdered activated carbon with a diluted water solution is one of the most important parameters of this type of carbon.

Carbon gas types such as SCT, DAC, KAD and others are widely used. Active carbon type SCT is used to capture a pair of organic solvents to clean the water and aqueous solutions of different additives. Activated carbon of the SCT is adapted to remove oil from the steam condensate to the heating power stations, for adsorption emulsion type «oil in water», for the removal of various substances from solutions. KAD activated carbon is used in industry to remove iodine from mineralized drill water absorption of various substances from solutions and vapor (gas) air mixtures. KAD are used in the flotation of ore minerals.

Experimental part

Instruments, glassware, reagents

Apparatus for shaking. Photoelectrical colorimeter. Cuvettes of 10 mm. Centrifuge. Burettes for titration capacity of 25 cm^3, 2 pcs. Measuring flask with a capacity of 100 cm^3, 11 pcs. Conical flask with a capacity of 100 cm^3, 5 pcs. Pipettes capacity of 1 and 10 cm^3. Methyl orange solution 150 mg/dm^3 and 0,15% methylene blue. A solution of 0,1 M iodine and 0,1 M sodium thiosulfate. Indicator starch.

Adsorption activity toward methyl orange

Construction of calibration graph. To construct a calibration graph solutions are prepared. For this 10 volumetric flask of 100 cm^3 each injected 0,5; 1,0; 2,0; 3,0; 4,0; 5,0; 6,0; 7,0; 8,0; 9,0 cm^3 of working solution of methyl orange concentration of 150 mg/dm^3, and then bring the volume of water to the mark. The resulting solutions are contained in 1 dm^3 respectively 0,75; 1,50; 3,00; 4,50; 6,00; 7,50; 9,00; 10,50; 12,00; 13,50 mg/dm^3 of methyl orange.

Absorbance reference solution are performed in photoelectric measuring with a filter (wavelength (λ) of 390 to 410 nm) in cuvettes. As a control solution using distilled water.

According to the data of the calibration graph building as the dependence of optical density of the initial concentration from reference solution (c_o, mg/dm^3).

Analysis. Before determining the activated carbon has to be dried at 100-110 ^oC for 1 hour. On an analytical balance in conical flask 100 cm^3 weigh 0.1 grams of activated carbon. Poured 25 cm^3 solution of methyl orange concentration of 150 mg/dm^3, close and shake to shake apparatus for 30 minutes. Then the carbon slurry is transferred to a centrifuge tubes and centrifuged for 15 minutes. Selected 1 cm^3 lit solution in a volumetric flask of 100 cm^3, dilute to the mark with distilled water and measure the optical density.

According to the absorbance value using the calibration graph, find a final concentration of methyl orange in dilute solutions. Adsorption activity indicator carbon (X, mg/g) is calculated using the formula:

$$X = V\,(c_0 - Kc_p)/m,$$

where V – volume indicator solution that is taken for lighting, dm^3; m – weight activated carbon sample, g; c_0 – the initial concentration of methyl orange, 150 mg/dm^3; K – coefficient of dilution equal to 100; p_p – The final concentration of methyl orange in dilute solution, mg/dm^3.

Perform 2-3 parallel definition; the difference between them should not exceed 5%.

Adsorption activity by iodine

Before determining the activated carbon has to be dried at 100-110 ^oC for 1 hour.

On techno-chemical scales in conical flask 100 cm^3 weigh 1,0 g activated carbon. Poured 100 cm^3 of 0,1 M solution of iodine closed and shaken on the machine to shake for 30 minutes. Then pipette select 10 cm^3 lit solution and titrate with 0,1 m sodium thiosulfate in the presence of starch indicator that rushes at the end of titration. Similarly specify the initial concentration of iodine solution.

Adsorption activity by iodine (F, %) is calculated using the formula:

$$F = (V_o - V_p)\ 0{,}0127 \cdot 100 \cdot 100/10 \cdot m,$$

where V_o – the volume of sodium thiosulfate solution, which went on titration stock solution of iodine cm^3; V_p – the amount of sodium thiosulfate solution, which went on titration of iodine solution after lighting investigational active carbon cm^3; m – weight activated carbon sample, g; 0,0127 – iodine, corresponding to 1 cm^3 0.1 M solution of sodium thiosulfate, g

Perform 2-3 parallel definition; the difference between them should not exceed 5%.

Brightening capacity for methylene blue

Before determining the activated carbon has to be dried at 100-110 ^oC for 1 hour.

On techno-chemical scales in conical flask 100 cm^3 weigh 1,0 g activated carbon, poured 10 cm^3 0,15% methylene blue solution, tightly closed and shaken for 10 minutes. After bleaching added 10 cm^3 continue to add methylene blue solution 1 cm^3 to the blue color of the solution persists for 5 minutes. If the first 10 cm^3 dye does not fade for 10 minutes, repeating the experiment, since fewer methylene blue.

Brightening the ability of activated carbon (E, %) expressed as a percentage of the value of conventionally illuminating capacity of the sorbent, 1 g of which discolor 20 cm^3 0,15% aqueous methylene blue (conventionally taken as 100 %):

$$E = 5\,n,$$

where n – the amount of methylene blue solution, which discolors 1 g of activated carbon, cm^3; 5 – factor 100/20.

Perform 2-3 parallel definition; the difference between them should not exceed 5%.

Results of the test of activated carbon enter in Table 3.6.1.

Table 3.6.1. **Experimental data**

Name of sample	***X*, mg/g**	***F*,%**	***E* %**

Safety measures

1. In carrying out the work must comply with the rules of conduct in the chemical laboratory and the rules of safe handling of chemicals, glassware and electrical appliances.
2. Before you start, check the setup of zero-point refractometer.
3. The amount of liquid that is poured into refractometer for measurement in all cases must be the same.

Quiz

Access to work

1. What groups are divided activated carbon, depending on the scope of application?
2. What anionic dyes you know?
3. What are the reasons for some of sorbent surface adsorbed anionic dyes?

Defense of work

1. What kind of gas type active carbons do you know?
2. In what area is used actively active carbon of AGS-4?
3. What is called adsorption activity indicator for iodine? How else can it be called? What does it mean the number 5 in the formula for calculating the adsorption activity for methylene blue?

3.7 DESIGNING THE SORPTION ISOTHERM OF CARBOXYLIC ACID

Objective: In this lab work students have to investigate the adsorption monobasic carboxylic acid on activated carbon, to build isotherm of adsorption and to calculate the value of specific adsorption.

Brief theoretical information

The researching adsorption systems «liquid– solid» hold by static and dynamic methods. The latter belongs chromatographic method in which the solution is passed continuously through a layer of adsorbent chromatographic column until saturation amount of adsorbed adsorbent material. However, adsorbents with a specific surface developed, which include activated carbon, cause tangible adsorption from solutions that change the concentration of adsorbed substance in a volume sufficient to determine its conventional analytical methods.

It is well known that the adsorption depends on the surface area of the adsorbent, temperature, concentration of the solution, and the nature of the adsorbent, adsorbate and solvent. The adsorption increases with increasing solution concentration. The dependence of adsorption (at constant temperature) from the equilibrium concentration of adsorbate expressed by the equation is called adsorption isotherm.

In Fig. 3.6.1 presented typical adsorption isotherm, which expresses the dependence of the number of adsorbate that swallowed 1 kg of adsorbent (a = x/m) of the equilibrium concentration of adsorbate (c_p). At low concentrations, the adsorption equilibrium is proportional to the concentration shown a straight course isotherm at the site AC. The horizontal section of the CD shows that despite a further increase concentration, growth stops due to saturation adsorption surface molecules adsorbent material that adsorbs, that reached the threshold value of specific absorption so-called specific adsorption, a_∞.

Construction of the adsorption isotherm monobasic carboxylic acids activated carbon classic static method is as follows. If the solution of known concentration put in contact with the adsorbent after adsorption equilibrium measure establishing the equilibrium concentration of the solution, the amount of adsorbed substance solution is determined by the difference between the concentration of the solution before and after adsorption.

In order to determine the shape of the adsorption isotherm choose one of the accepted equation and transform it into linear. Having thus straight line one can be sure in correctness or falsity selection equation to describe the adsorption isotherm obtained. In the latter case, choose another equation. In this paper, adsorption isotherm is satisfactorily described by Langmuir.

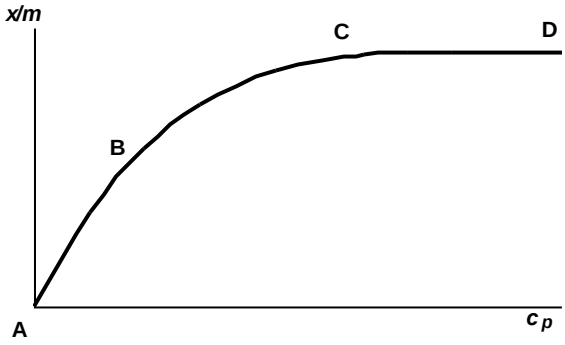


Fig. 3.6.1. **Adsorption isotherm.**

In order to determine the shape of the adsorption isotherm choose one of the accepted equation and transform it into linear. Having thus straight line one can be sure in correctness or falsity selection equation to describe the adsorption isotherm obtained. In the latter case, choose another equation. In this paper, adsorption isotherm is satisfactorily described by Langmuir.

Experimental

Instruments, glassware, reagents

Apparatus for shaking. Conical flasks with a capacity of 100 cm^3, 12 pcs. Graded glass chemical dropper capacity of 25 cm^3, 1 pc. Burettes to titration, 3 pcs. A solution of 0,1 M sodium hydroxide. Formic acid, acetic acid, propionic acid. Phenolphthalein indicator. Filter paper.

Preparation of initial acid solutions

To prepare initial acid solutions of carboxylic acids (formic, acetic, propionic), specify its concentration, which 5 cm^3 acids 2-3 titrate with 0,1 M sodium hydroxide, in the presence of phenolphthalein ($c_{init} \approx$ 0,2 mmole/dm^3).

Then six numbered conical flasks of 100 cm^3 prepared six of the acid solutions of different concentrations. For this purpose, from a burette rush off acid solution (V_{acid}, cm^3) set the concentration, the other – distilled water (V_{in}, cm^3), in amounts specified in the table. 3.6.1.

Table 3.6.1. **The data for the preparation of initial solution series**

Flask number	**1**	**2**	**3**	**4**	**5**	**6**
V_{acid}, cm^3	50	40	30	20	10	5
V_{in}, cm^3	10	20	30	40	50	55
c_o, mmole/dm^3						

Calculated as follows prepared concentration of all solutions (c_0, mmol/dm^3) and enter the data in the Table 3.6.1:

$$c_0 = (V_{acid} \cdot c_{in})/60,$$

where V_{acid} – the amount of initial carboxylic acid filled in the corresponding flask, cm^3; c_{in} – initial concentration of carboxylic acid, mmol/dm^3; 60 – the total amount of carboxylic acid solution in each flask, cm^3.

Adsorption experiment

Before determining the activated carbon has to be dried at 100-110 ^oC for 1 hour.

In each of the six numbered flasks with prepared solutions to enter ~1 g of activated carbon, weighed to within 0,01 g flasks tightly and shaken for 4 hours, or

leave without shaking, then filtered in a dry flask throw folded paper filters. The first 5-7 drops of the acid filtered have to be waste.

Processing and presentation of experimental results

After the adsorption process determine the equilibrium concentration of solutions of carboxylic acid. To this flask from each selected sample volumes analyzed (V_{al}), as indicated in the Table 3.6.2, and titrated with sodium hydroxide (c_{NaOH} = 0,1 mmol/dm^3) to obtain matching results.

Table 3.6.2. **The analysis of equilibrium solutions carboxylic acid**

Flask number	**1**	**2**	**3**	**4**	**5**	**6**
V_{al}, cm^3	5	10	20	20	25	25
V_{NaOH}, cm^3						
c_p, mol/dm^3						

The equilibrium concentration of carboxylic acid (c_p, mol/dm^3) is calculated using the formula:

$$c_p = (V_{NaOH} \cdot c_{NaOH})/V_{al},$$

where V_{NaOH} – the amount of alkali, which went on titration V_{al}, cm^3.

All experimental data are entered in the Table 6.2. To build isotherm adsorption and calculated adsorption specific amount (a_{exp}, mmol/g):

$$a_{exp} = x/m = V\,(p_o - p_p)/m,$$

where V – volume of acid solution (in this case, V = 60 cm^3 = 60 × 10^{-3} dm^3);

m – weight activated carbon, g.

Safety measures

1. All actions to perform in compliance with safety regulations at work in the chemical laboratory.
2. In the performance of bound by the terms and rules of safe handling of acids, alkalis and other chemicals, as well as glassware and electrical appliances.
3. Work done in accordance listed her in this text sequence. With a presence doubts about the performance of any procedure to contact the teacher.

Quiz

Access to work

1. Purpose and consistency of work.
2. What method will we use for adsorption processes investigating?
3. What is typical sorption isotherm by solid adsorbent?

Defense of work

1. How could determine the value of adsorption?
2. What types of sorption isotherms do you know?
3. What ways do perform for determination the shape of sorption isotherm?
4. What equations do describe the adsorption isotherm? How do they differ?

3.8 SYNTHESIS OF FINE SORBENT – NICKEL (II) FERROCYANIDES

Objective: In this lab work students have to carry out the synthesis of finely dispersed sorbent – nickel (II) ferrocyanide in aqueous solution and establish optimal conditions for its receipt.

Brief theoretical information

It is known that the most effective sorbents with respect to, for example, ions of cesium (potentially radioactive element) are ferrocyanides transition metals. In this case the formed low soluble ferrocyanides characterized by a considerable capacity and behave as ion exchangers.

Most often, ferrocyanides use after fixing them on the matrix, for example, particles of zeolite, the size of which is equal to more than 1 mm. Thus, mass fraction obtained ferrocyanide complex on the carrier is approximately equal to 10-12 %. Consequently, the amount of radioactive waste that must be buried increases in 8-10 times. Thus, the prospect of ferrocyanides obtaining in an aqueous solution with radioactive ions, particularly cesium ions, is obvious.

It is known that the stability of ferrocyanides of heavy metals depends on the pH. In a very alkaline environment ferrocyanides dissolve with the formation of hydroxides of the metals included in their composition. The nickel (II) ferrocyanide is most stable in alkaline environment, significant solubility which is achieved only at a pH of 10,0-10,5. Thus, nickel (II) ferrocyanides can be used both in acidic and in alkaline solutions.

Light green precipitate of normal nickel (II) ferrocyanide $Ni_2[Fe(CN)_6]\cdot xH_2O$ formed by the interaction of salt solutions of nickel (for example, nickel (II) chloride) and salts of ferrocyanides alkali metals (for example, potassium ferrocyanide). Free from alkali metal or normal nickel (II) ferrocyanide is formed only when an excess of nickel ions, or by using $H_4[Fe(CN)_6]$, or its lithium salt.

Depending on the conditions of dewatering the $Ni_2[Fe(CN)_6]\cdot xH_2O$ precipitate contains different amount of hydration water . Dehydration of the precipitate in the presence of oxygen leads to oxidation of this salt to ferricyanides, and the color changes to yellow-brown. A similar effect has also bromine water.

Normal nickel (II) ferrocyanide soluble in water ($2{,}7\cdot10^{-5}$ mol/dm^3 at 298 K) and in dilute acids. And thus, it is fairly stable in water in the range of pH 2-3 and, as noted above, to a pH of 10,0-10,5. Freshly precipitated nickel (II) ferrocyanide is soluble only in solutions of salts of oxalates and phosphates of alkali metals. Under the action of mineral acids, it is a partial decomposition with the formation of $H_2Ni[Fe(CN)_6]$.

Normal nickel (II) ferrocyanide quite prone to reactions with ferrocyanides of alkali metals with forming mixed salts. The formation of mixed nickel (II) ferrocyanide can occur not only due to the accession of alkali metals ferrocyanides, but also due to displacement of a part of nickel ions from lattice of normal nickel (II) ferrocyanide by scheme:

$$3Ni_2[Fe(CN)_6] + 4K^+ = K_4Ni_4[Fe(CN)_6] + 2Ni^{2+}.$$

The ability of the mixed nickel (II) ferrocyanide to exchange the alkali ions is in the following order:

$$Cs^+ \geq Tl^+ > Rb^+ > K^+ > Na^+ > Li^+.$$

Thus, it is obvious prospects of using normal and mixed ferrocyanides for the removal of alkali metal ions, particularly cesium ions.

Experimental

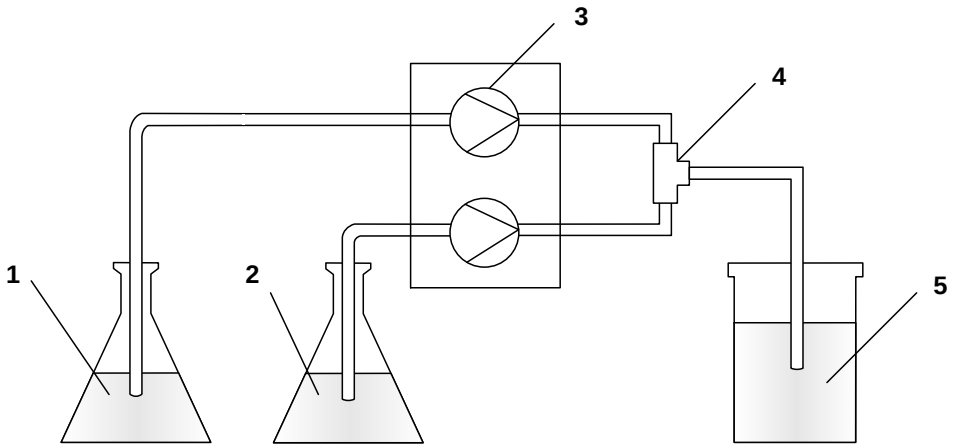
Instruments, glassware, reagents

Oven. Peristaltic pump. Centrifuge. Technical and analytical balances. Waterjet pump. Buchner funnel. Bunsen flask. Volumetric flask 1 dm^3, 1 pc.

Volumetric flask of 100 cm^3, 1 pc. Volumetric flask of 50 cm^3, 5. Not graded glass tubes, 5 pcs. A solution of iron (III) chloride. Nickel (II) chloride. Potassium ferrocyanide. Alcohol solution dimethylglyoxime (Chuguev's reagent). Ammonia solution 10%. Laboratory filter paper.

The circuit installation

To obtain finely dispersed nickel (II) ferrocyanides used laboratory setup (Fig. 3.7.1) consisting of 1 and 2 cups of initial reagents for sorbent; peristaltic pump 3, which delivers reagents with a specified flow rate; mixer 4 to form the sorbent and receiving cup 5 to the fine sorbent.



1, 2 – glass; 3 – peristaltic pump; 4 – mixer, 5 – receiving socket.

Fig. 3.7.1. **Scheme of laboratory installation.**

Synthesis finely dispersed sorbent and determination of its release

Synthesis finely dispersed sorbent is carried out as follows. The first write reaction equation for obtaining normal nickel (II) ferrocyanide. Calculate the concentration of potassium ferrocyanide and nickel (II) chloride in solution to obtaining normal nickel (II) ferrocyanide concentration under the instruction of a

teacher in g/dm^3. Calculate the concentration of potassium ferrocyanide and concentration of nickel (II) chloride referred to above, to obtain a ratio of ions $[Fe(CN)_6]^{4-}/2[Ni]^{2+}$, listed in Table 3.7.1.

Table 3.7.1. **Experimental data**

Value $[Fe(CN)_6]^4/2[Ni]^{2+}$	**The concentration of potassium ferrocyanide in solution, g/dm^3**	**The concentration of nickel (II) chloride in solution, g/dm^3**	**Qualitative reaction to ferrocyanide ions**	**Qualitative reaction to nickel ions**
0,7				
0,8				
0,9				
1,0				
1,1				
1,2				

Prepare solutions – potassium ferrocyanide in 100 cm^3, nickel chloride in 1 dm^3 by calculated concentration. By using peristaltic pump sorbents obtained in amount 50 cm^3 at relationships listed in table and to determine the ratio of reagents when qualitative reactions will be negative. The resulting suspensions are centrifuged, and the filtrates analyze for ions of nickel and ferrocyanide.

The data on qualitative analysis are entered in the Table 3.7.1. The remaining precipitate is filtered using water jet pump to funnel Buchner and dried at 100-110 ^{o}C at least one hour.

Determination of sorbent yield

The resulting sorbent slurry at a ratio of 1:1 to 50 cm^3 is filtered on Buchner funnel using water jet pump (to pre– weighed filter), then the residue dried at 110 ^{o}C for 1 hour and weighed on an analytical balance. According to the obtained data calculate of yield sorbent using the formula:

$$F = \frac{m_1 - m_2}{m_3},$$

where m_1 – mass of resulting precipitate with filter, g; m_2 – mass filter, g; m_3 – mass of the sorbent, which must be formed by the reaction equation in 50 cm^3.

Qualitative determination of ions nickel and ferrocyanide in solution

Determining the presence of nickel ions carried out as follows: in a test tube with 2-3 drops of nickel solution add 3-5 drops of ammonia solution and 2-3 drops of alcohol solution of dimethylglyoxime (reagent of Chuguev). If nickel ions are present, then a bright red precipitate of complex compound of nickel dimethylglyoxime.

Ferrocyanide ions detected by ions of iron (III). For this in a test tube with ferrocyanide solution add a few drops of iron (III) chloride. If ferrocyanide ions are present, formed a bright blue precipitate of $Fe_4[Fe(CN)_6]_3$, called Prussian blue.

Safety measures

1. In carrying out the work must comply with the regulations and rules of safe handling of chemicals, glassware and electrical appliances.
2. To carry out the work necessary under specified herein sequence if doubts about the performance of any procedure to contact the teacher.

Quiz

Access to work

1. What are the sorbents? What is their purpose? What materials can be used as sorbents?

2. The purpose of the work.

3. Methods of obtaining finely dispersed sorbents.

Defense of work

1. Methods of obtaining ultra and nano disperse materials. Give examples of obtaining fine sorbents from aqueous solutions.
2. Methods of removing ultra/nano disperse materials from aqueous solutions.
3. The use of adsorbents in wastewater treatment. What are kind pollutants removed fine disperse sorbents?

3.9 BIOSORPTION OF HEAVY METALS FROM WATER SOLUTIONS

Objective: In this lab work students have to study the process of adsorption from aqueous solutions of heavy metals (the example copper ions) by biosorbents (dry biomass of different origin).

Brief theoretical information

The basis of the biosorbtion process or extraction of metal ions from aqueous solutions using biosorbents, are processes of interaction with surface structures of cells and their exopolymer metabolites. The biosorbtion process or extraction of metal ions from aqueous solutions using biosorbents based on the interaction with surface structures of cells and their exopolymer metabolites. Biosorbents include various biologically active cells are alive and dead such as bacteria, algae, plants, fungi, yeast and so on. The mechanism linking metals by biosorbent determined by the following main types of interactions: ion exchange reaction, complexation, sorption, precipitation.

The first and second type similar processes that occur on ion exchange resins. That is, they behave similarly to ion exchange resins, natural zeolites and others. The third type of interaction involves the binding of metal cations as well as simultaneous precipitation of insoluble compounds on the particles and inside the particles of biosorbent. Biosorbent also able to selectively accumulate on its surface the metal ions.

Biosorbtion could be active and passive. Active biosorbtion runs through metabolic processes including metal structures in cells. The rate of ion exchange is quite low. Passive biosorbtion is on the surface of cells and explains the physical and chemical interactions of metal ions from the ion-exchange membrane cell groups. The process is relatively fast: it occurs within a few hours.

The ability of biosorbent to accumulate metals is characterized by the so-called the sorption capacity of biomass. Sorption capacity of biomass is the number of adsorbed metal in mg or mmol, which accounts for 1 g of biomass. Of course, it averaged value as the actual value of capacity may vary widely.

Thus, the most famous and widely used in biological treatment processes are activated sludge. It has a large sorption capacity toward to heavy metals. As well as promising to use waste biosorbent biotech industries, such as the production of yeast and others.

The choice of natural biosorbents or biosorbents based biotech industries for waste water purification from heavy metal ions causes the following advantages: availability and cheapness biosorbents and low-cost energy and clean technology.

Experimental part

Instruments, glassware, reagents

Apparatus for shaking. Photoelectric colorimeter. Conical flask 250 cm^3, 9 pcs. Volumetric flask 100 cm^3, 6 pcs. Burette capacity of 25, 50 and 100 cm^3, 1pc. Measuring cylinders with a capacity of 10, 25 and 50 cm^3, 1 pc. Chemical funnels, 9 pcs. Standard copper sulfate solution (1 mg Cu in 1 cm^3). Ammonia 5 %. Copper sulphate. Yeast, dry biomass.

Determination of the biosorption kinetics

Prepare 2 dm^3 model solution containing copper ions concentration as directed by the teacher in mg/dm^3. Calculate weight the biosorbent to prepare a solution with a concentration of 1 g/dm^3, if the volume of water that is purified, 0,2 dm^3.

Hold biosorption process and determine the kinetics of the process. For this to 5 flasks 250 cm^3 add 200 cm^3 model solution and enter calculated portion of the sorbent. All flasks shake at 15, 30, 45, 60 and 75 minutes.

After the mixing time solutions with biosorbent were filtered and analyzed for content of copper ions. Calculate the degree of heavy metals extraction (x, %) from model solution by the formula:

$$x = [(c_o - c_a)/c_o] \times 100\%.$$

where c_o and c_a – initial and final concentration of copper ions, respectively, mg/dm^3.

The results enter in Table 3.8.1 and build on their base graph of the degree of extraction of biosorption duration $x = f(\tau)$.

Table 3.8.1. **Experimental data**

No	c_o**, mg/dm^3**	τ**, min.**	s_a**, mg/dm^3**	x **%**
1				
2				
3				
4				
5				

Determination of biosorbent sorption capacity

Prepare four flasks with model solutions containing various concentrations of copper ions as directed by the teacher in mg/dm^3. Calculate mass of biosorbent for its concentration of 1 g/dm^3, if the water volume that is purified, equal to 0,2 dm^3.

Put the flasks into the apparatus for shaking. After the mixing time of solutions with biosorbent filter and analyze their content of copper ions. Determine the initial concentration of copper ions in model solutions.

Calculate the adsorption of copper ions from model solutions by the formula:

$$a = (c_o - c_p)\, V/(1000\, m),$$

where c_o and c_p – initial and equilibrium concentration of copper ions, respectively, mg/dm^3; V – the volume of treated solution, cm^3; m – mass of the sorbent sample, g.

According to the calculated data to construct a graph of adsorption of copper ions from solution by sorbent $a = f$ (s).

Analysis of solutions for content of copper ions

Determination of copper ions in solution is carried out by ammonia. As result the action of ammonia in the solution with copper appears intense blue coloration due to the formation of complex ions: $Cu^{2+} + 4NH_3 = [Cu(NH_3)_4]^{2+}$.

Construction of calibration graph. In a volumetric flask with a capacity of 100 cm^3 made 1, 3, 5, 7, 9, 10 cm^3 standard solution $CuSO_4$. In each flask poured 25 cm^3 ammonia solution and made up to mark. Define absorbance at the selected wavelength and layer thickness and build the calibration chart. To determine the copper content solution was treated as above. Determine the optical density and build calibration schedule for determining copper content in the test solution.

Safety measures

1. In carrying out the work must comply with the regulations and rules of safe handling of chemicals, glassware and electrical appliances.

2. To carry out the work necessary under specified herein sequence if doubts about the performance of any procedure to contact the teacher.

Quiz

Access to work

1. What is biosorbtion? What biosorbtion different from conventional adsorption? What are its advantages?
2. The purpose of the work.
3. Method of determining the sorption kinetics of biosorbent and its sorption capacity.

Defense of work

1. What types of sorption do you know? What is their nature?
2. In what forms can be heavy metal ions in aqueous solutions?
3. Give the types of biosorption. To give a comparative description.
4. Give examples of existing systems in which bio sorption of heavy or radioactive metals occurs.
5. As quantitatively evaluate the effectiveness of sorbents?

3.10 PREPARATION OF SILICA GEL BY SOL-GEL METHOD

Objective: In this lab work students have to synthesize the silica gel by sol-gel method, to determine its specific surface and explore adsorption of water vapor by synthesized silica from the air.

Brief theoretical information

One of the most common practices in industrial mineral sorbent is silica, which is known, has a well-developed surface. Silica gel is solid hydrophilic adsorbent obtained by drying gel polysilicon acid.

Depending on the process for receiving they are divided into fine porous or coarse porous silica gel. Finely porous silica is used to absorb water vapor, vapor alcohol, acetone, benzene and others. Coarse porous silica serves as a carrier for many catalysts, including those for platinum, palladium.

The main method used to produce silica gel is sol-gel method. Sol-gel process is usually carried out in two stages: initially obtained sol, and then sol converted into a gel. In the first stage of the sol-gel process occurring hydrolysis and polycondensation reactions that lead to the formation of colloidal solution, and sol particle size does not exceed a few tens of nanometers. Increasing the volume concentration of the particles or the change in external conditions (pH, solvent replacement) leads to the formation of intensive contacts between the particles and to obtain a gel in which the solvent molecules are bound in a flexible, but sufficiently stable three-dimensional grid of particles. The resulting gel is then dried or calcined.

Silica sol can be obtained in several ways: by reacting alkali silicate with acids or acidic salts, alkalis or alkaline salts, hydrolysis of silicon (IV) chloride, the

saponification of methyl or ethyl esters of silica acid and so on. In industrial scale silica obtained by the action of sulfuric acid on soluble glass.

The first step, regardless of method of preparation is really the formation of soluble SiO_2. Further carry out the condensation in which the molecular weight silicates gradually increasing. The polymerization process leads to the formation of colloidal solution:

$$n\ Si(OH)_4 \rightarrow (SiO_2)_n + H_2O.$$

The resulting molecule $nSi(OH)_4$ become larger by condensation before the formation of a gel. The rate of gelation of silica hydrogel acid depends on several factors: the concentration of SiO_2 in the ash, temperature, pH and the nature of the mineral acid or alkali.

With increasing concentration of SiO_2 in the ash gelation rate increases significantly. Also, similarly affects heating in case of acid sols of silica and in highly alkaline coagulation of sols. A special impact on forming silica gel have pH. The gelation accelerating as ions H^+ and OH^-. That there is a certain pH region, where resistance silica sol minimum; it is a range of 5 to 8.

Significantly affect the rate of gelation concentration of hydrogen ions and hydronium. The fastest way is the formation of a gel when added nitric acid, more slowly is with the addition of sulfate, and the slowest is while adding phosphoric acid. That is, the rate of gelation depends on the strength of attached acid or alkali.

Experimental part

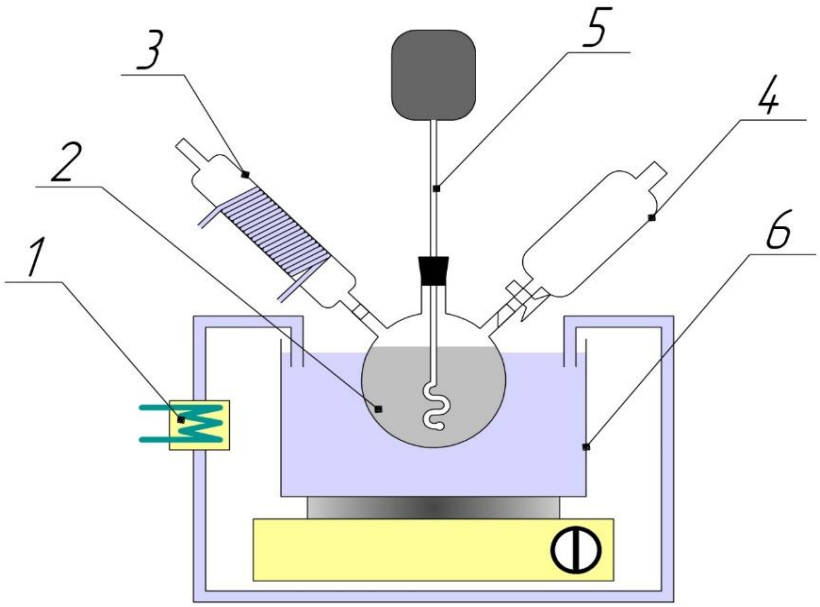
Instruments, glassware, reagents

Thermostat. Mixer with motor. Refractometer. Reverse refrigerator. Water jet pump. Bunsen flask. Buchner funnel. Flask round heat-resistant by capacity of 500 cm^3. Separating funnel. Test tube with ground glass stopper by capacity of

25 cm^3, 4 pcs. Measuring flask with a capacity of 250 cm^3. Measuring flask with a capacity of 25 cm^3, 3 pcs. Pipette capacity of 2 cm^3. Pipette graduated 10 cm^3, 3 pcs. Liquid glass (solution of Na_2SiO_3). Silver nitrate solution (10 %wt.). Ammonium chloride. Cobalt chloride. Toluene. Isooctane.

The circuit installation

Laboratory installation consists of round – bottom flask with a capacity of 500 cm^3, reverse refrigerator, separating funnel, 5 and thermostatic mixer with a current source.



1 – current source; 2 – round heat– resistant flask; 3 – reverse refrigerator; 4 – separating funnel; 5 – stirrer; 6 – thermostat.

Fig. 3.9.1. **laboratory installation to produce silica:**

Preparation of silica gel

In a reactor with a capacity of 500 cm^3 pour 100 cm^3 of distilled water, added 10 grams of ammonium chloride and stirred until complete dissolution (heated to a temperature as directed by the teacher). After dissolution of ammonium chloride with vigorous stirring 70 cm^3 sodium silicate (concentrations in% by weight as

directed by the teacher) add for 15 minutes. The resulting suspension hydrated silicon oxide is cooled, filtered on a Buchner funnel, washed with distilled water until negative reaction filtrate to chloride ions and dried at a temperature of 200°C for 2 hours. The dried silica weighed, determine its specific surface area, tested for indicator properties.

Determination of silica gel yield

Theoretically possible mass (m_{theor}) silica calculated from the equations of the reaction. The yield (F, %) is calculated using the formula:

$$F = (m_{pr}/m_{theor}) \cdot 100.$$

Determination of the specific surface area of silica gel

Up to 0,01 g weigh 0,5-1 g of silica gel and placed in a test tubes with ground glass stopper, add 2 cm^3 of solution consisting of 40% toluene and 60% vol. isooctane (refraction factor must be within 1,4328-1,4330). Adsorption equilibrium is established after about 2-3 hours. Next, determine the coefficient of refraction of the solution. In parallel experiments carried out 2-3.

Specific surface area (S_{pit}, m^2/g) determined by the formula:

$$S_Q = a_m \cdot N_A \cdot \omega_m \cdot 10^{-20},$$

where a_m – amount of adsorbed benzene mol/g; N_A – Avogadro's number, mol^{-1}; ω_m – area of the benzene molecule, which is 53 $Å^2$.

Number of adsorbed toluene (a_m, mol/g) can be calculated using the formula:

$$a_m = (V \cdot (n^{20}_D(a) - n^{20}_D(p)) \cdot \rho_T) / (g \cdot 100 \cdot C\,(1 - \omega) \cdot M),$$

where V – volume 40% solution add to the investigated sample, cm^3;
$n^{20}_D(s)$ and $n^{20}_D(p)$ – coefficients of refraction the initial solutions and after sorption;
ρ_t – density of benzene at the temperature experiment, g/cm^3;

g – mass of sorbent sample, g;

ω – the volume fraction of benzene in the solution;

M – molar mass of benzene, g/mole.

Formula for determining the specific surface area takes the following form:

$$S_Q = 47400 \cdot (V/g)\ (n^{20}_{D(a)} - n^{20}_{D(eq)}).$$

Table 3.9.1. **Experimental data**

Results	Samples		
	1	**2**	**3**
The weight of sodium silicate, g			
The theoretical mass of silica, d			
Practical weight of silica, grams			
Exit silica%			
The volume mixture of toluene and isooctane to determine the specific surface area silica, cm^3			
Silica sample to determine the specific surface g			
Refractive index stock solution of toluene and isooctane, $n^{20}_{D(s)}$			
Refractive index equilibrium mixture of toluene and isooctane, $n^{20}_{D(p)}$			
The specific surface area silica, $m^{2/}g$			
Color output indicator silica gel			
The color indicator silica gel after absorbing water vapor from the air			

Getting silica gel indicator

Up to 0,01 g sample weighed silica (as directed by the teacher) and placed in a test tube with ground glass stopper. Add 25 cm^3 solution of cobalt chloride concentration of 5 % by weight. and leave for 20 minutes. Then filtered and dried at a temperature of 170-180 °C for 1-2 hours. The dried silica gel is divided into two parts: one left in the desiccator, the second – in the air. The changes notes.

Safety measures

1. Perform the rules of heaters.
2. Do not leave the installation and running unattended.

Quiz

Access to work

1. The objective of the work. Safety.
2. What is silica gel? In some processes using silica gel?
3. What method used for determination of the specific surface area?

Defense of work

1. What is the sol-gel technology?
2. Describe the chemistry changes that occur during the obtaining silica gel.
3. What other methods of producing silica you know?
4. What parameters affect reception quality silica gel by sol–gel method?

REFERENCES

1. Novy spravochnik khimika [Эlektronnыi resurs]. – Rezhym dostupa: http://chemanalytica.com/book/novyy_spravochnik_khimika_i_tekhnologa/05_syre_i_produkty_promyshlennosti_organicheskikh_i_neorganicheskikh_veshchestv_chast_I/5941
2. Karnaukhov, A.P. Adsorbtsyia. Tekstura dyspersnykh y porystykh materyalov / A.P. Karnaukhov. – Novosybyrsk: Nauka, Syb. predpryiatye RAN, 1999. –470 P.
3. Tolmachev, A.M. Adsorbtsyia hazov, parov y rastvorov: Monohrafyia / A.M. Tolmachev. – Moskva, Yzdatelskaia hruppa «Hranytsa», 2012. – 241 P.
4. Davydov, S.Iu. Dyffuzyia i adsorbtsyia v heterohennykh systemakh: Ucheb. Posobye SPb / S.Iu. Davydov, L.P. Efymenko, A.Y. Mamykyn, V.A. Moshnykov. – Yzd–vo SPbHETU «LETY», 2001. – 48 P.
5. Keltsev, N.V. Osnovyi adsorbtsionnoy tehniki / N.V. Keltsev. – M.: Himiya, 1984. – 592 p.
6. Greg, S. Adsorbtsiya. Udelnaya poverhnost / S. Greg, K. Sing; perevod s angl. A.P. Karnauhova. – M.: Mir, 1984. – 310 p.
7. Kinle, H. Aktivnyie ugli i ih promyishlennoe primenenie / H. Kinle, E. Bader; perevod s nem. T. B. Sergeevoy. – L.: Himiya, 1984. – 216 p.
8. Fenelonov, V.B. Poristyiy uglerod / V.B. Fenelonov – Novosibirsk: In–t kataliza, 1995. – 518 p.
9. Tarkovskaya, I.A. Okislennyiy ugol / I.A. Tarkovskaya – K.: Nauk. dumka, 1981. – 200 p.
10. Koganovskiy, A.M. Adsorbtsiya rastvorennyih veschestv / A.M. Koganovskiy, T.M. Levchenko, V.A. Kirichenko. – K.: Naukova dumka, 1977. – 222 p.
11. Koganovskiy, A.M. Adsorbtsiya rastvorennyih veschestv / A.M. Koganovskiy, T.M. Levchenko, V.A. Kirichenko. – K.: Naukova dumka, 1977. – 222 p.

12. Kolyishkin, D.A. Aktivnyie ugli: Sprav / D.A. Kolyishkin, K.K. Mihaylova. – M.: Himiya, 1972. – 57 p.
13. Serpionova, E.N. Promyishlennaya adsorbtsiya gazov i parov: ucheb. posob. dlya stud. himiko–tehnologich. spets. vuzov / E.N. Serpionova. – M.: Vyisshaya shkola, 1969. – 416 p.
14. Leon y Leon, C. A. Interfacial chemistry and electrochemistry of carbon surfaces Chapter in book: Chemistry and Physics of Carbon / C.A. Leon, L.R. Radovic. – New York, Basel, Hong Kong: Marcel Dekker, 1994. – P. 213–310.
15. Kiselev, V.Ya. Adsorbtsiya na granitse razdela tverdoe telo – rastvor: Uchebnoe posobie / V.Ya. Kiselev, V.M. Komarov. – Moskva, MITHT im. M.V. Lomonosova, 2005. – 81 s.
16. Dzhessi, R. Adsorbtsiya / R. Dzhessi, K. Ronald. – VSD, 2015. – 54 p.
17. Kuprin, V.P. Adsorbtsiya organicheskih soedineniy na tverdoy poverhnosti / V.P. Kuprin, A.V. Scherbakov. – Kiev: Naukova dumka, 1996. – 162 p.
18. Kirovskaya, I.A. Adsorbtsionnyie protsessyi / I.A. Kirovskaya. – Irkutsk: Izdatelstvo Irkutskogo universiteta, 1995. – 304 p.
19. Parfit, G. Adsorbtsiya iz rastvorov na poverhnostyah tverdyih tel / G. Parfit, K. Rochester. – M.: Mir, 1986. – 488 p.
20. Koganovskiy, A.M. Adsorbtsiya organicheskih veschestv iz vodyi / A.M. Koganovskiy, N.A. Klimenko, T.M. Levchenko, I.G. Roda. – L.: Himiya, 1990. – 256 p.
21. Dunken, H. Kvantovaya himiya adsorbtsii na poverhnosti tverdyih tel / H. Dunken, V. Lyigin. – M: Mir, 1980. – 288 p.
22. Skomoroha, V.N. Proizodstvo dvookisi titana pigmentnoy sulfatnim sposobom / V.N. Skomoroha, V.G. ZarechennIy, I.P. Vorobeva, S.V. Vakal. – Sumi: ATZT «Arsenal– Press», 2002. – 204 p.

23. Shabanova, N.A. Himiya i tehnologiya nanodispersnI oksidov / N.A. Shabanova, V.V. Popov, P.D. Sarkisov. – Moskva: IKTs «Akadem– kniga», 2006. – 301 p.
24. Belenkiy, E.F. Himiya i tehnologiya pigmentov / E.F. Belenkiy, I.V. Riskin. – L.: Nauchnoe izdatelstvo, 1949. – 624 p.
25. Hazin, L.G. Dvuokis titana / L.G. Hazin. – L.: Himiya, 1970. – 239 p.
26. Goroschenko, A.Ya. Himiya titana / A.Ya. Goroschenko. – Kiev: Naukova dumka, 1972. – 218 p.
27. Zhang, H. Preparing single–phase nonacristalline anatase from amorphous titania with particles sizes tailored by temperature / H. Zhang, M. Finnegan, J.F. Banfield // Nano Letters. – 2001. – № 2. – P. 81-85.
28. Mishin, D.D. Magnitnyie materialyi / D.D. Mishin. – M.: Vyissh. shk., 1981. – 355 p.