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THE INVESTIGATION OF THE STRUCTURE ALUM-COAGULATION SLUDGE BY ADSORPTION METHOD

The importance of surface phenomena, despite the role they perform in all the processes of alum-coagulation sludge neutralization is either not mentioned or neglected in many investigations, even in the basic ones. In the paper presented theoretical and experimental bases of one of the method for testing the parameters characterizing the intensity of those phenomena occurring in sludge have been dicussed. Isotherms of carbon dioxide and benzene sorption on the sludge investigated have been determined by means of high vacuum gravimetric apparatus. The analysis of the results obtained made it possible to determine the distributions of volume and area of the sludge pores. Both the methods of investigations and their interpretation have been adapted to the sludge structure. The results were analyzed by employing the Dubinin-Raduszkiewicz's and BET theories. It has been shown that besides technological tests of dehydration processes, basic methods have to be also applied to study surface phenomena occurring in sludge. The interpretation of effects of dehydration of sludge by its structural properties will allow to know better mechanism of these phenomena as well as it will enable their optimization.

DENOTATIONS

SPIS SYMBOLI I OZNACZEŃ

a — amount of the substance adsorbed at the given pressure P, in mmol/g,
ilość substancji zaadsorbowana przy danym ciśnieniu P,

a_m — amount of the adsorbate necessary to cover the adsorbent surface with a monomolecular layer, in mmol/g,
ilość adsorbatu potrzebna do pokrycia powierzchni adsorbentu warstwą monomolekularną,

l — adsorption layer thickness at the given relative pressure P/P_0,
grubość warstwy adsorpcyjnej przy danym ciśnieniu względnym P/P_0;

g — density in g/cm^3 at temperature T,
gęstość w g/cm^3 w temp. T,

r_k — so-called Kelvin's radius of the pore,
tzw. kelvinowski promień poru,

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$\bar{r}_n$ — mean real (effective) radius of pores emptying in the n-th desorption stage,
średni rzeczywisty (efektywny) promień porów opróżniających się na n-tym etapie desorpcji,

A — Avogadra number,
liczba Avogadra,

B — constant of Dubinin-Raduszkiewicz's equation given by the formula
stała równania Dubinina-Raduszkiewicza równa

$$B = \frac{D}{0{,}4343\, T^2},$$

T — temperature, K,
temperatura ,

C — constant of the BET equation,
stała równania BET,

D — constant of Dubinin-Raduszkiewicz's equation,
stała równania Dubinina-Raduszkiewicza,

M — molecular mass,
masa cząsteczkowa,

P — pressure of vapour concave liquid meniscus with the radius of curvature r_k at temperature T,
prężność pary nad wklęsłym meniskiem cieczy o promieniu krzywizny r_k przy temp. T,

R — gas constant,
stała gazowa,

S — area ,
powierzchnia,

U — hydration of aluminium coagulation sludge,
uwodnienie osadów pokoagulacyjnych,

W — amount of substance adsorbed at the given pressure P of adsorbate in cm^3/g,
ilość substancji zaadsorbowana przy danym ciśnieniu P adsorbatu,

W_0 — limiting volume of adsorption space in cm^3/g,
graniczna objętość przestrzeni adsorpcyjnej,

V — volume,
objętość,

Y — constant occurring in formula (12) and (13),
stała,

β — so-caled convergence coefficient of characteristic curves, approximately equal to the ratio of the parachors of the given and standard adsorbates, respectively,
tzw. współczynnik zbieżności krzywych charakterystycznych, w przybliżeniu równy stosunkowi odpowiednich parachor adsorbatu danego i standardowego,

$\delta_{C_6H_6}$ — surface tension of benzene at temperature T,
napięcie powierzchniowe benzenu w temperaturze T,

ε — adsorption potential,
potencjał adsorpcyjny,

η_{os} — apparent viscosity,
lepkość pozorna,

σ_{CO_2} — area of carbon dioxide molecule, assumed after Toda [12] as equal to 0.185 nm^2,
powierzchnia cząsteczki CO_2, którą przyjęto wg Tody [12] jako równą 0,185 nm^2,

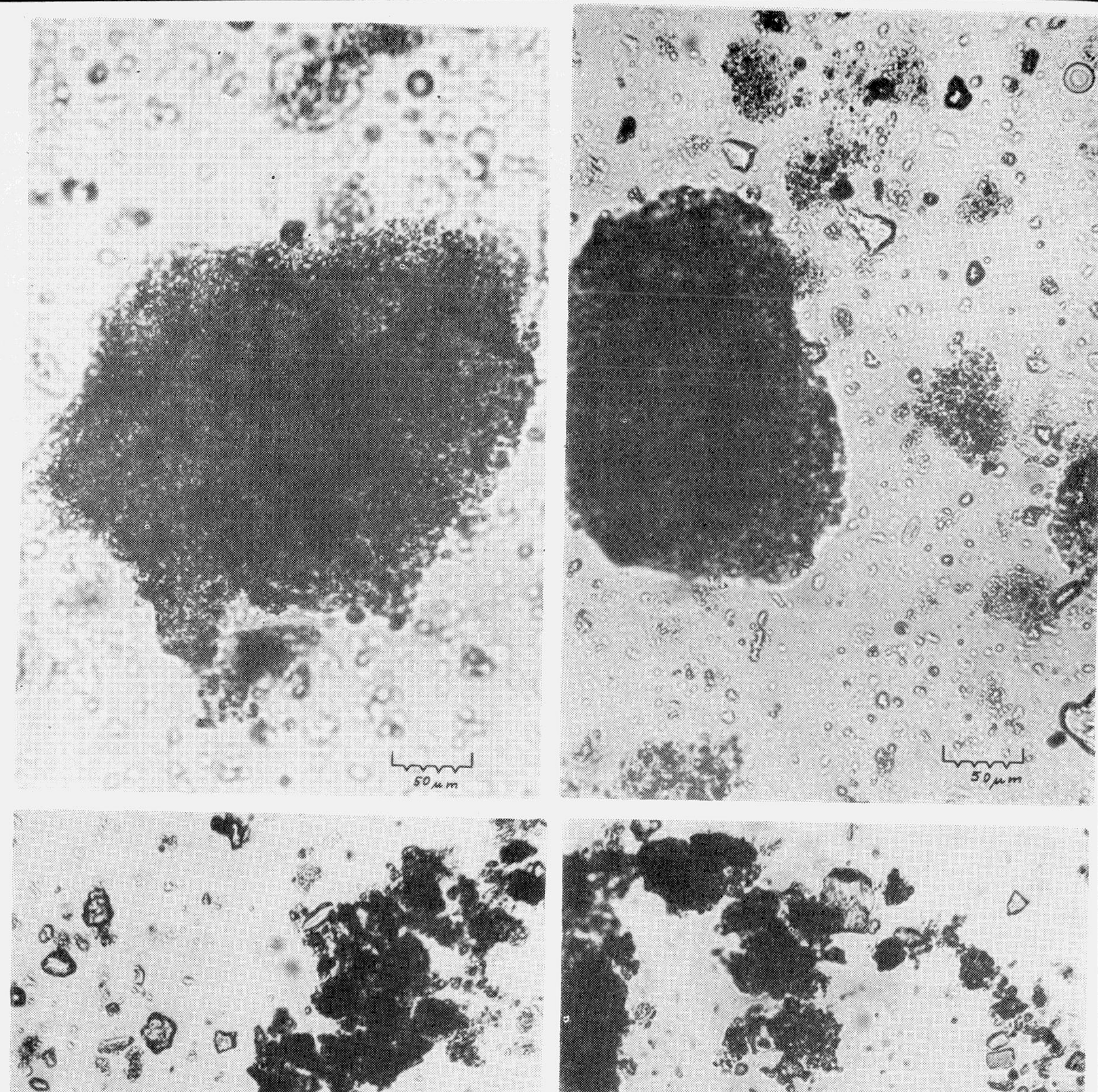
1. INTRODUCTION

Utilization processes, removal, and neutralization of sludge formed during coagulation, are closely connected with the development of the water treatment technology and protection of natural environment. Owing to the fact that coagulation process is generally applied in treatment of surface water, alum-sludge is one of basic problems faced by big contemporary waterworks. The volumes of sludgeds and unitary energy consumptions accompanying mechanical and thermal processes of their dehydration are the basic data indispensable for the solution of this problem in practice. The size, kind and shape of solid particles of sludge exert an essential influence on the kinetics of basic processes of their neutralization. The surfaces of alum-sludge may strongly bind water, and it adsorbs many organic and inorganic substances dissolved, colloidal, and suspended ones. First phenomenon makes it difficult to the sludge dehydration, while the second one has been for a long time utilized in the technology of water treatment. Structural properties and specific surface of alum-sludge are the subject of intensly developing investigations of a great importance from theoretical and practical viewpoints. Basic problems of these experiments is the application of a sufficiently accurate methods to investigations of structural properties of this sludge. On such a method depends the success in investigations aimed to find complex and simplified generalizations enabling a better knowledge of the principles of technology of utilization and neutralization.

2. SIZES OF PARTICLES IN ALUM-SLUDGE

The measurement of the sizes of solid phase particles occurring in alum-sludge is a much complex problem. The difficulties are due to both the character of the particles and a great variety of their sizes and shape. Flocculation process leads to the changes in the composition of the sludge with respect to the size of its components. These changes are difficult to determine, since the sizes of the floccules are not constant, depending among other on hydration and velocity gradient. Sizes and shape of granular particles can be determined by a microscopic method, whose choice depends on both the grains sizes, and on the possibilities of performing the measurements in can two-dimensional system. A distinct image of particles can be obtained if the examined samples of alum-sludges are sufficiently hydrated, and placed in special flat glass chambers preventing the evaporation of water during the observations.

Some results of microscopic investigations of grains composition of alum-sludges taken from several settling tanks of large waterworks in Poland are presented in fig. 1. Photographs of particles have been made by means of Zeiss microscope NfpK coupled with a photocell and luminescence dosimeter. Microscopic investigations have shown the presence of fine grains of minerals and of floccules which had been formed during flocculation. Granular particles are isometric and irregular with respect to the shape and degree of their surface smoothness. Maximal size of most grains present in sludges examined did not exceed 30, only sporadically this size reached 50 microns.


50 μm
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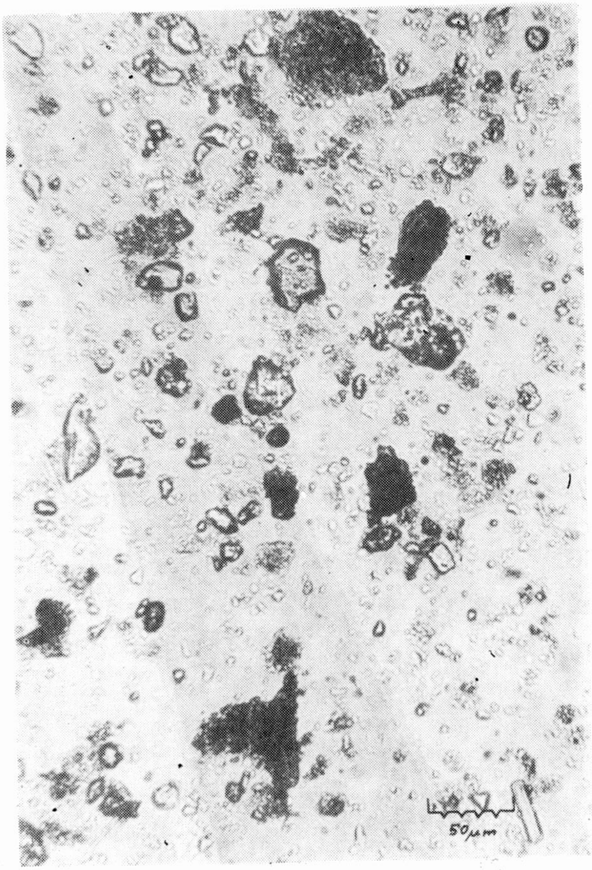


Fig. 1. Microscopic photograph of aluminium coagulation sludge particles from water treatment plant:

a — Tomaszów Mazowiecki, *b* — Goczałkowice, *c* — Rzeszów, *d* — Kraków "Dłubnia", *e* — Kraków "Rudawa"

Rys. 1. Zdjęcia mikroskopowe cząstek osadu pokoagulacyjnego z Zakładów Oczyszczania Wody z:

a — Tomaszowa Mazowieckiego, *b* — Goczałkowic, *c* — Rzeszowa, *d* — Krakowa "Dłubni", *e* — Krakowa "Rudawy"

The observations allowed to state that quartz was a dominant component of grains. This was verified by chemical composition of the solid phase of sludges. The content of SiO_2 in the sludge examined was as high as 31.15–67.07% of their dry weight. The sizes of grains occurring in sludges allowed to classify them to quasi-homogeneous dispersion systems. The floccules observed in the microscope were approximately round in shape, and their size exceeded many times 300 microns. The size of floccules like that of granular particles is often determined by their diameter. This does not seem to be justified since the results are inaccurate, ambiguous, and have solely a formal character. The size and shape of floccules as well as their sorption properties can be measured appropriately by the specific surface of sludges. In practice a precise and univocal determining of specific surface and other parameters characterizing the structure formed in hydrated sludges by solid phase is much difficult. These quantities, however may be much accurately measured in dry weight of sludges. The results obtained appeared to be very useful in interpretation of many processes related to flow and neutralization of hydrated sludges.

3. GENERAL CHARACTERISTICS OF THE STRUCTURE OF POROUS SLUDGES

Capillary structure of the dry weight of alum-sludges is constituted by a system of pores and small ducts filling the substance and forming a kind of a microscopic sponge. The type of porosities appearing in the sludges investigated is determined by the sizes of pores and the mode of their interconnections.

The investigations conducted on many highly porous substances allowed to state the presence of three kinds of pores, namely:

a) micropores, i. e. pores whose radii are smaller than 1.5 nm,

b) transiental pores — whose radii range from 1.5 to 100 nm,

c) macropores, whose radii are greater than 100 nm.

Macropores, because of their relatively large dimensions, perform the role of arterial roads for the transportation of gas molecules diffusing inside the grain. Usually their area does not exceed a few square meters.

In the present paper the authors have been confined to description of basic parameters characterizing the mentioned above types of porosity. Capillary system of alum-sludges has been characterized on the basis of carbon dioxide and benzene sorption isotherms determined in high vacuum gravimetric apparatus (fig. 2).

4. METHOD AND RESULTS OF THE MEASUREMENTS OF THE AREA AND VOLUME OF THE PORES IN ALUM-SLUDGE DEPOSITS

4.1. EXPERIMENTAL APPARATUS

The method used to investigate the sorption is one of gravimetric methods, in which the absorbed amount of the substance (adsorbate) is measured from the increase in the mass of the adsorbant investigated. The simplest apparatus for the measurement of the adsorption isotherms by gravimetric method is quartz spiral (the McBain-Bakr's balance [2].) Although the usage of quartz spirals because of their fragility is not easy, nevertheless their resistance to the vapours of sorbed compounds is a factor deciding on their superiority over other materials.

The method developed by McBain-Bakr is of a special importance for comparative investigations, since several balance cells can be connected with the same manometer, so that the adsorption properties of a number of substances may be measured under identical conditions. This system has been applied in the present work since 4 balance chambers have been interconnected.

The scheme of the apparatus is shown in fig. 2. The main element is constituted by quartz spirals (*1*) on which the samples of sludges are hanged in special baskets (*2*). The spirals are placed in glass pipes (*3*) and (*4*). The pipes with spirals are connected through a system of cocks with the container with absorbate (*5*) and differential mercury manometer with the measurement range $0–10^5 N/m^2$ (*6*). The apparatus is also equipped with

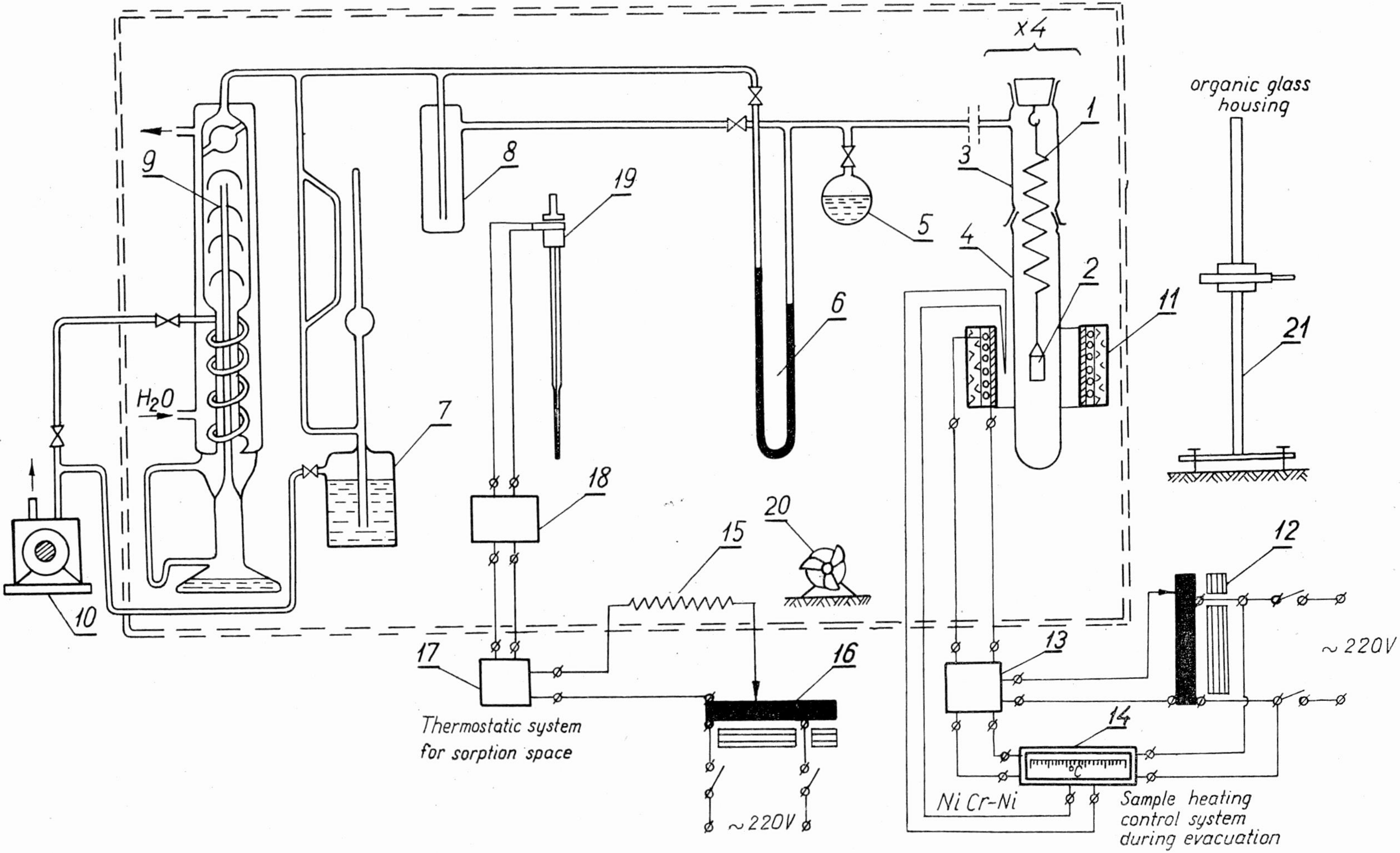


Fig. 2. Scheme of experimental sorption apparatus (description in text)

Rys. 2. Schemat doświadczalnej aparatury sorpcyjnej (opis w tekście) a McLeod manometer (*7*), frezer (*8*), three-stage diffusion pump (*9*) to obtain a high vacuum, and oil pump (*10*) to obtain preliminary vacuum.

Before the sorption measurement the samples were dried and degassed at 523 K and at vacuum of the order 10^{-2} — 10^{-3} N/m^3 in order to clean their surfaces. Degassing time amounted to 2 hrs. Each sample was heated with electric resistance heater (*11*) fed by means of autotransformer (*12*). Thermoelement was placed outside the pipe and connected with thermoregulator system (*13, 14*) which allowed to keep a constant degassing temperature.

After degassing the space of the apparatus, encaused in organic glass was thermostatized for sorption measurements using a thermo-ventilator (*20*) with a variable heating range (*15*), fed by means of autotransformator (*16*) and connected by means of a contactor (*17*) and transmitter (*18*) with contact thermometer (*19*).

The amounts of carbon dioxide or benzene absorbed at the given pressure were calculated from the elongation of quartz coil, previously calibrated.

Elongation of spirals and equilibrium pressure for each point of the isothermal line were read by means of a kathetometer (*21*).

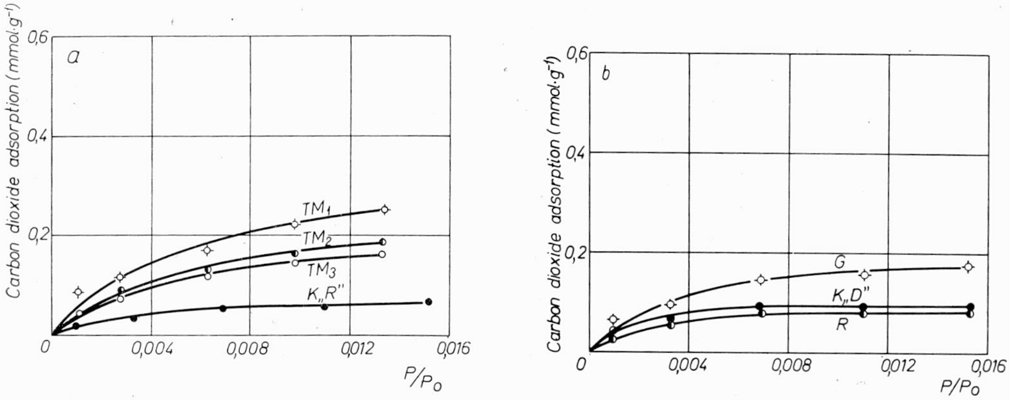
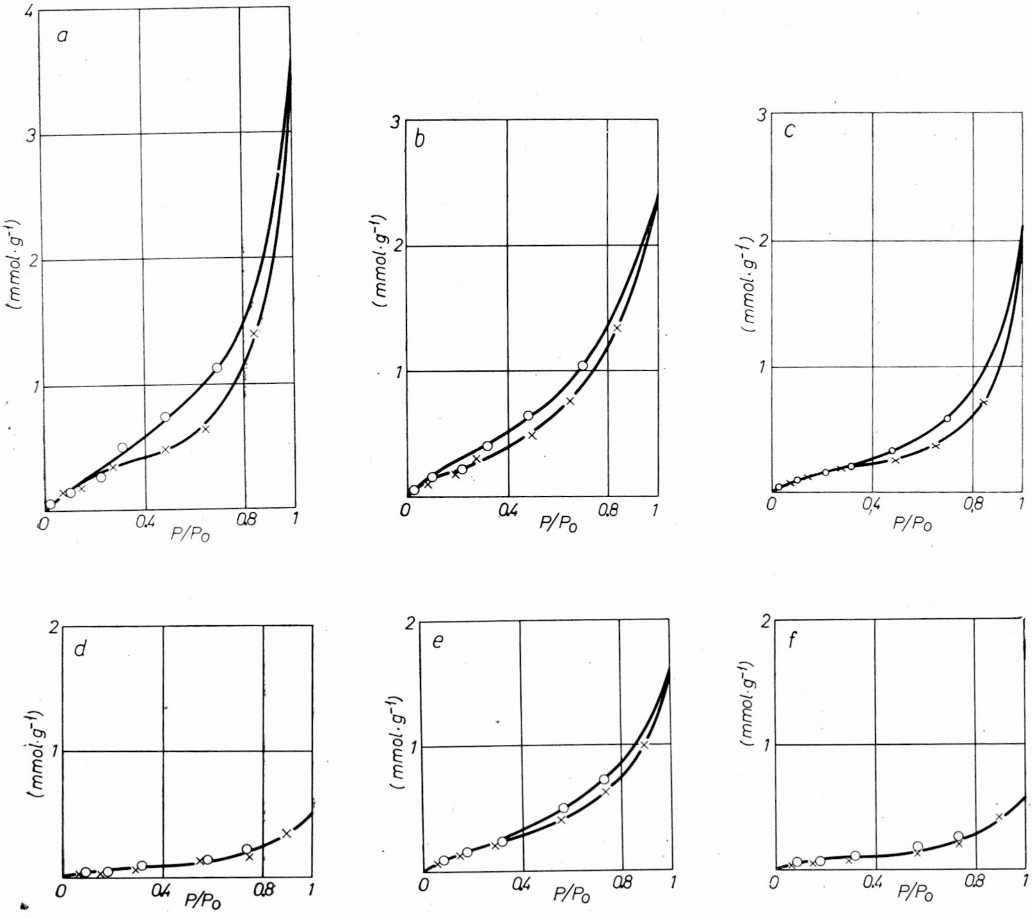


Fig. 3. Isotherms of carbon dioxide adsorption on aluminum coagulation sludge specimens

a — comprises the sludges
TM_1 washings from Tomaszów Mazowiecki taken in 1973,
TM_2 sludge from Tomaszów Mazowiecki taken in 1973,
TM_3 sludge from Tomaszów Mazowiecki taken in 1974,
K,,R'' sludge from Kraków ''Rudawa'',
b — comprises the sludges:
G — sludge from Goczałkowice,
K,,D'' — sludge from Kraków ''Dłubnia'',
R — sludge from Rzeszów

Rys. 3. Przebieg izoterm adsorpcji dwutlenku węgla na próbkach osadu pokoagulacyjnego

a
TM_1 — popłuczyny z Tomaszowa Mazowieckiego z 1973 r.,
TM_2 — osad z Tomaszowa Mazowieckiego z 1973 r.,
TM_3 — osad z Tomaszowa Mazowieckiego z 1974 r.,
K,,R'' — osad z Krakowa ,,Rudawy''
b
G — osad z Goczałkowic,
K,,D'' — osad z Krakowa ,,Dłubni'',
R — osad z Rzeszowa



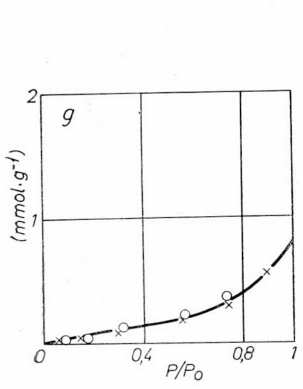


Fig. 4. Isotherms of benzene adsorption and desorpion on aluminium coagulation sludge samples

a — washings from Tomaszów Mazowiecki taken in 1973,
b — sludge from Tomaszów Mazowiecki taken in 1973,
c — sludge from Tomaszów Mazowiecki taken in 1974,
d — sludge from Kraków "Rudawa",
e — sludge from Goczałkowice,
f — sludge from Kraków ,,Dłubnia"
g — sludge from Rzeszów

Rys. 4. Przebieg izoterm adsorpcji i desorpcji benzenu na próbkach osadu pokoagulacyjnego

a — popłuczyny z Tomaszowa Mazowieckiego 1973 r.,
b — osad z Tomaszowa Mazowieckiego z 1973 r.,
c — osad z Tomaszowa Mazowieckiego z 1974 r.,
d — osad z Krakowa ,,Rudawy",
e — osad z Goczałkowic,
f — osad z Krakowa ,,Dłubni",
g — osad z Rzeszowa

The obtained experimental points were used to draw isothermal lines for carbon dioxide absorption in function of the amount of CO_2 absorbed in milimoles (gram of alum-sludge) on relative CO_2 pressure at 298 K (fig. 3), and isothermal lines of adsorption and desorption of benzene in function of the amount of adsorbed C_6H_6 (minimoles/gram of sludge) on relative pressure of saturated benzene vapour at the temperature of measurements (fig. 4).

4.2. INTERPRETATION OF EXPERIMENTS

4.2.1. The method for calculation of volume and area of micropores according to Dubinin-Raduszkiewicz

The calculation method of micropore volume is based on a potential theory of vapours adsorption, developed by DUBININ and cow. [3]. This theory is applied to adsorption systems in which dispersion forces are the main component of the adsorbent-adsorbate reaction, and the vapour adsorbed in micropores at low relative pressures (e. g. for benzene at $P/P_0 \geqslant 0.1$) is transformed into liquid in due to compression resulting from superposition of fields of opposite walls.

The assumptions of the Dubinin's theory allows to present the sorption isotherm in form of a straight line

$$\log W = \log W_0 - B\frac{\varepsilon^2}{\beta^2} \text{ or } \log W = \log W_0 - D(\log P_0/P)^2. \tag{1}$$

In the system of coordinates

$$\log W = f\left(\frac{\varepsilon^2}{\beta^2}\right)$$

the sorption isotherm is a straight line, and its intersection point with the ordinate cuts off the segment corresponding to the value W_0. In case of benzene sorption W_0 is equal to the volume of micropores accessible for the C_6H_6 molecules at 298 K. These values are presented in table 1 (column 3).

Sorption isotherms of carbon dioxide in the Dubinin's system of coordinates are presented in fig. 5.

In case of the sorption of carbon dioxide the value of W_0 does not define the volume of micropores but the amount of carbon dioxide (in cm^3g^{-1}) necessary to cover the surface of pores with a monomolecular layer [7]. The fact that CO_2 does not fill the volumes of micropores but is adsorbed on their surface is due to the specific properties and structure of carbon dioxide molecules (small dimensions, oval shape, the absence of dipole moment). Hence, from the value of W_0 we may compute the area of micropores

$$S_{\text{mic}} = W_{0_{CO_2}} \frac{A \cdot \sigma_{CO_2} g}{M}, \tag{2}$$

where S_{mic} — surface of micropores.

Table 1

Distribution of pore volume in dry weight of aluminum-sludges

No of sludges sample	Source		Volume and kind pores, cm^3/g					
			Micropores $V_{mic} = W_0$ C_6H_6 C_6H_6	Transitional pores				$V_{mic}+V_p$ C_6H_6
				$V_{1.5-3.0}$	$V_{3.0-30.0}$	$V_{30.0-100.0}$	V_p	
1	Water Treatment Plant	Tomaszów Mazowiecki	0,024	0,037	0,182	0,065	0,284	0,308
2			0,025	0,030	0,143	0,029	0,202	0,227
3			0,012	0,011	0,111	0,040	0,162	0,174
4		Goczałko-wice	0,013	0,019	0,096	0,021	0,136	0,149
5		Rzeszów	0,004	0,008	0,050	0,011	0,069	0,073
6		Kraków na Dłubni	0,006	0,004	0,036	0,007	0,047	0,053
7		Kraków na Rudawie	0,002	0,004	0,032	0,007	0,043	0,045

sludges from washing

By inserting suitable numerical values we get

$$S_{mic} = W_{0_{CO_2}} \cdot 2627, \ m^2/g. \tag{3}$$

The calculated values of S_{mic} are presented in table 2, column 3.

4.2.2. Calculation of the distribution of volume and area of transitional pores

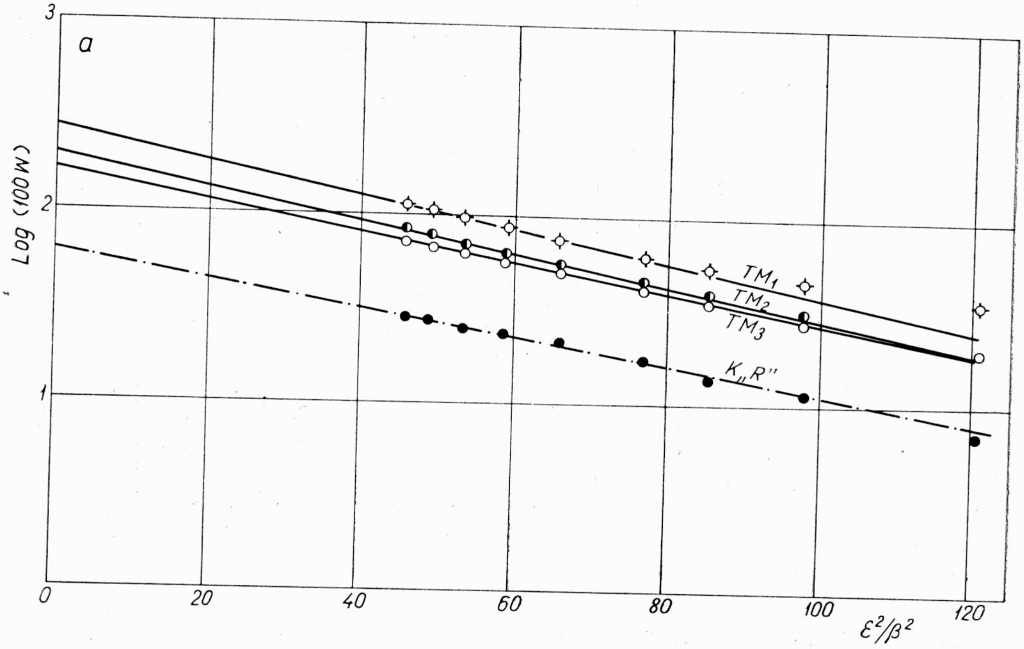
Desorption curves of sorption isotherms of benzene vapours (fig. 4) at relative pressure P/P_0 ranging from 0.98 to 0.16 were the basis for the calculation of the distributions of volume and area of transitional pores. The calculations were performed by the PIERCE'S method [9] modified by ORR and DALLAVALLE [8].

Within the above range of relative pressures one observes the process of capillary condensation occurring in transitional pores, since the dimensions of these pores are relatively large and the space between the adsorption layers present on their wall surfaces is large if compared with the dimensions of the molecules of the sorbed substances.

To carry out the required calculation the full desorption process (from $P/P_0 = 0.98$ to $P/P_0 = 0.16$) was divided into 28 stages, assuming that desorption takes place in steps, the pores have a cylindrical shape, and their sizes changes also in steps.

The sizes of pores on each step of benzene desorption have been calculated from the Kelvin's equation [11].

$$r_k = \frac{2\delta_{C_6H_6} \cdot M_{C_6H_6}}{RT \cdot g_{C_6H_6} \cdot \ln P_0/P}. \tag{4}$$


a
Log (100 W)
3
2
1
0
20
40
60
80
100
120
ε^2/β^2
TM1
TM2
TM3
K„R"

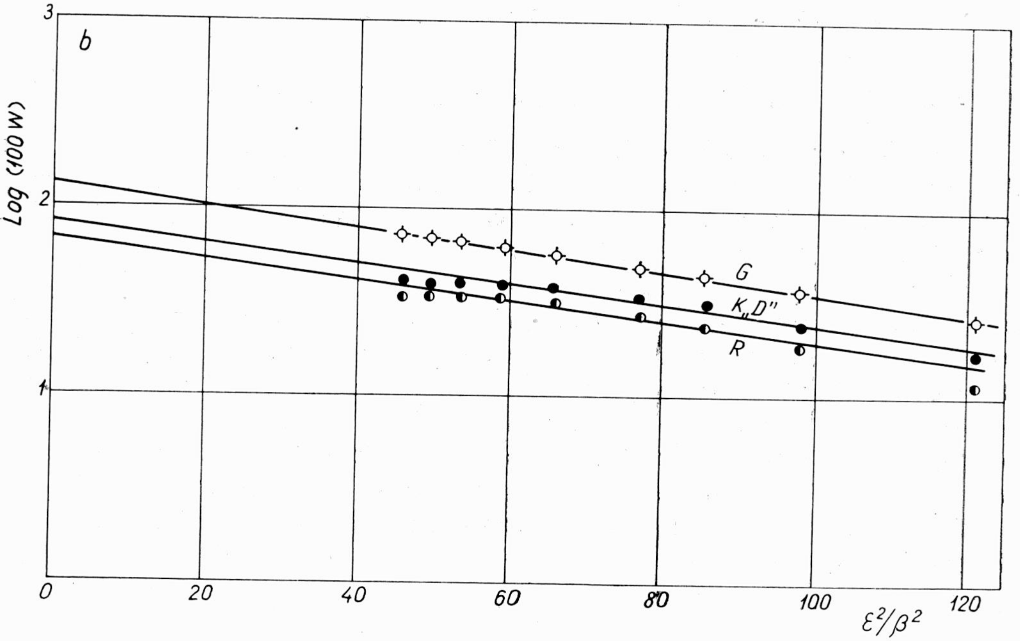

b
Log (100 W)
3
2
1
0
20
40
60
80
100
120
ε^2/β^2
G
K„D"
R

Table 2

Distribution of area pores in alum-sludge dry weight

No of sludges sample		Source	Area of pores, cm^2/g						
			Micro-pores S_{mic}	Transitional pores (S_p)				$S_{mic}+$ $+S_p$	Area of pores calculated by the BET method
				$S_{1.5-3.0}$	$S_{3.0-30.0}$	$S_{30.0-100.0}$	S_p		
1	Water Treatment Plant	Tomaszów Mazowiecki	68,3	33,6	45,1	2,0	80,7	149,0	93,2
2			52,3	27,6	39,1	0,9	67,4	119,7	63,0
3			42,5	9,9	26,1	1,3	37,3	79,8	50,4
4		Goczałko-wice	35,5	17,0	25,1	0,7	42,8	78,3	59,6
5		Rzeszów	17,4	7,5	12,2	0,3	20,0	37,4	30,9
6		Kraków na Dłubni	21,8	3,7	8,7	0,2	12,6	34,4	23,1
7		Kraków na Rudawie	15,8	4,4	7,2	0,2	11,8	27,6	22,0

Real radius of pore is equal to Kelvin's radius the thickness of adsorption layer; the latter was accepted for calculations from the literature data [5].

After having taken into account the correction for the adsorption layer thickness and correction for the changes in the thickness of this layer depending on the consecutive desorption stage, the final formula for the volume of pores within the given interval of the

Fig. 5. Isotherms of carbon dioxide adsorption in Dubinin-Raduszkiewicz system

a — comprises the sludges

*TM*1 — washings from Tomaszów Mazowiecki taken in 1973,
*TM*2 — sludge from Tomaszów Mazowiecki taken in 1973,
*TM*3 — sludge from Tomaszów Mazowiecki taken in 1974
K,,R" — sludge from Kraków ,,Rudawa",

b — comprises the sludges

G — sludge from Goczałkowice,
K,,D" — sludge from Kraków "Dłubnia",
R — sludge from Rzeszów

Rys. 5. Izotermy adsorpcji dwutlenku węgla w układzie Dubinina-Raduszkiewicza

a

*TM*1 — popłuczyny z Tomaszowa Mazowieckiego z 1973 r.,
*TM*2 — osad z Tomaszowa Mazowieckiego z 1973 r.,
*TM*3 — osad z Tomaszowa Mazowieckiego z 1974 r.,
K,,R" — osad z Krakowa ,,Rudawy",

b

G — osad z Goczałkowic,
K,,D" — osad z Krakowa ,,Dłubni",
R — osad z Rzeszowa

pore radii takes the form

$$\Delta V_n^* = \left[\Delta V_n - \Delta l_n \sum_{i=1}^{i=n-1} \frac{2\Delta V_i}{\bar{r}_{k,i}}\right]\left(\frac{\bar{r}_n}{\bar{r}_{k,n}}\right)^2 \tag{5}$$

where

ΔV_n — volume of pores emptying in the n-th desorption stage,
Δl_n — change in adsorption layer thickness in n-th desorption stage,
$\bar{r}_K$ — mean Kelvin's radius of pore

the value of the adsorption layer thickness being calculated from the relation [5]

$$l = 5.2 - 2.43 \ln(\ln P_0/P). \tag{6}$$

and the mean real radius of pores on the n-th stage of desorption expressed by the formula

$$r_n = r_{k,n} + \bar{l}_n.$$

where

$\bar{l}_n$ — mean thickness of adsorption layer of pores emptying in the n-th desorption stage.

On the other hand, the area of pores within a given interval of their radii (assuming a cylindrical shape of pores) as given by the formula

$$\Delta S_n^* = \frac{2\Delta V_n^*}{\bar{r}_n}. \tag{7}$$

If the adsorption isothermal line consists of $i = n$ stages and comprises the range of relative pressures corresponding to the whole region of capillary condensation, then the volume of transitional pores V_p is equal to

$$V_p = \sum_{i=1}^{i=n} \Delta V_i^* \tag{8}$$

and the total area of transitional pores S_p amounts to

$$S_p = \sum_{i=1}^{i=n} \Delta S_i^*. \tag{9}$$

4.2.3. Total area of sludges pores determines by the BET method

In the investigated alum-sludges, besides the mentioned above parameters of capillary system, a total area has been also determined by a standard method developed by BRAUNERR, EMMETT and TELLER [1], the so-called BET area (table 2).

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* The mentioned above parameters of capillary system have been calculated on computer ODRA 1204, according to the programme developed in the Department of Chemistry and Technology of Brown Coal of the Institute of the Chemistry and Technology of Petroleum and Coal of the Wrocław Technical University.

The calculations of the area by the BET method were based on benzene adsorption curves within the range of relative pressures P/P_0 0.05–0.25. The employed BET equation had the form

$$\frac{P}{a(P_0-P)} = \frac{1}{a_m C} + \frac{C-1}{a_m \cdot C} \cdot \frac{P}{P_0}. \tag{10}$$

In the system of coordinates

$$\frac{P}{a(P_0-P)} = f(P/P_0)$$

the isotherm is a straight line and from its intersection point with the coordinate and tangent of the inclination angle of the straight line we can compute the value a_m, i. e. the amount of benzene minimoles in the monolayer covering the surface of pores.

Then, assuming that under measurement conditions a benzene molecule occupies the area of 0.4375 nm^2 [6] the total area of pores can be calculated from a more detailed formula

$$S_{BET} = a_m \cdot 263.5, \ m^2g^{-1} \tag{11}$$

in which the value a_m is determined in minimoles g^{-1}.

4.3. PARAMETERS OF CAPILLARY STRUCTURE OF THE SLUDGES INVESTIGATED

The investigated alum-sludges came from the surfaces water treatment plant in which aluminium sulphate has been used for coagulation. Sludges from waterworks in Tomaszów Mazowiecki and Goczałkowice are characterized by a well developed porous structure. The area of pores determined as the sum of areas of micropores and transitional pores ranges from 149.0 to 27.6 m^2g^{-1}, and their volume ranges from 0.3 to 0.15 cm^3g^{-1}, respectively. In general, these are substances with a well developed transitional porosity. The contribution of transitional pores to the total volume of pores amounts to about 70%. The area of transitional pores ranges within 43–80 m^2g^{-1}, while the area of micropores ranges from 26 to 48 m^2g^{-1}.

Sludges coming from waterworks in Rzeszów and Kraków are characterized by considerably lower values of volume and area of pores. Total area of micropores and transitional pores does not exceed 30 m^2g^{-1}, and their volume reach at most 0.07 cm^3g^{-1}.

Sludges in which capillary structure was better developed contained relatively high amounts of Al_2O_3 in dry weight, ranging from 35–40% aluminium hydroxide, while the remaining samples contain about 10% of $Al(OH)_3$. Hence, this compound is responsible for the porosity of samples.

The calculations performed allowed also to state the differences between the values of specific surface computed by the BET method (table 2, column 9) and the values of area calculated as the sum of areas of micropores and transitional pores (table 2, column 8). These differences result from general assumption that every calculation method is based on a certain theoretical model, and that only the values of parameters calculated by the same method are comparable. In our case summary area of micropores and transitional pores being a parameter which illustrates more precisely the structure, these values were assumed for further considerations, hence S_{BET} may be treated as a complementary parameter of the structure characteristic.

5. USABILITY OF THE GRAVIMETRIC SORPTION METHOD IN THE INVESTIGATIONS OF ALUM-SLUDGES

The size of specific surface of sludges from alum-sludge settling tank ranges within 27.6–119.7 m^2g^{-1}, whereas sludges from washings have a larger area equal to about 150 m^2/g. The amount of aluminium oxide influences significantly by the value of the specific surface. The relation between specific surface and the content of aluminium oxide derived for the investigated alum-sludges settling tanks has the following linear form

$$S_{mic}+S_p = 8.25+2.9\,[Al_2O_3] \tag{12}$$

where Al_2O_3 is per cent of aluminium oxide in dry weight of sludge.

The particles of solid phase of other substances appearing in the sludges investigated give them the area equal to 8.25 m^2g^{-1}. Such an area is stated for monodispersion suspension of quartz particles ranging about 3.0 micrometers in size. Since the sludges investigated comprise larger quartz particles (fig. 1). hence the area of 8.25 m^2g^{-1} is caused not only by quartz but also by fine particles of other substances, mainly iron oxides and clayey minerals.

It has been many times stated that a high content of aluminium oxide and the increase in dispersion degree in sludges reduce considerably the effects of sedimentation and condensation, and induce the increase of the specific resistance of sludges and the decrease of dehydration effects during filtration and centrifugation. The relation between the specific surface, determined by the gravimetric method from the measurements of adsorption, content of aluminium oxide and size distribution of alum-sludges, as well as a high accuracy of the measurement method are very essential in interpretation of the investigations on condensation and mechanical dehydration technologies.

Another example of the usability of the presented method for the measurement of sludge structure is its application in the interpretation of investigations on rheological and hydromechanical properties of alum-sludges [10]. Within a wide range of hydrations rheological properties of sludges are described by one parameter — viscosity. The dependence of viscosity on the hydration of such sludges has a linear character and may be presented by the known equation of Einstein

$$\eta_{os} = \eta_w[1+Y\notin(100-V_s)], \tag{13}$$

η_w — dynamic water viscosity, V_s — volume of state phase where Y is a constant parameter. It has been stated that the values of the constant Y and specific surface of micropores in the investigated sludges (within the range of hydration 100% — U_{cr}) is described by the formula [10]

$$Y = 1.92\times10^{-3}\times S_{mic}^{1.46}. \tag{14}$$

It has been observed that when the hydrations of sludges are smaller than the critical one ($U < U_{cr}$) their specific surface influences essentially the values of rheological parameters, i. e. flow limit and plastic viscosity [10]. In alum-sludges with the specific surface larger than 80 m^2/g the flow limit appears at hydrations equal to 98% and at lower hydrations its value increases considerably. In sludges characterized by a smaller surface not exceeding 40 m^2/g critical hydration was lower (94%) and a rapidly increasing values of rheological parameters were observed at hydrations lower than 87%.

The essential importance of the measurements of structure of sludges is seen by the authors also in basic research on the sludge drying process. The application of experimental method determining the distribution of volume and area of pores in dry weight of sludges allows to make precise the mechanism of sludge drying, as well as to optimize the method of preparation of sludges by controlling the changes in their structure at which the drying process is quicker and more efficient. Finally, the knowledge of the sizes of pores and capillaries present in sludge gives the possibility to interprete mathematically the experiments on the drying of sludges and to construct adequate models, based on such parameters as capillary and surface forces causing water displacement, and on the law of steem diffusion.

CONCLUSIONS

1. Sludges resulting from coagulation surface impurities with aluminum sulphate have specific surface ranging from 27 to 149 m^2g^{-1}. The values of the areas of sludges taken from different waterworks depended on different content of aluminum sulphate with respect to impurities occurring in surface water. The porosity of sludges was chiefly (in about 70%) due to the pores whose radii ranges from 1.5 to 100 nm.

2. It has been stated that the parameters of capillary structure of the investigated alum-sludges influences their rheological properties. The increase of specific surface induces the intensification of non-newtonian properties in sludges, at hydrations amounting to 98%.

3. Parameters of the sludge structure determined by the gravimetric sorption method can constitute a basic criterion allowing both to determine quickly the direction at which the structure of sludges is changing, and to estimate the sludges from the viewpoint of optimal effects of gravitational and mechanical dehydration and drying.

4. A high contribution of micropores to the total porosity of alum-sludges indicates that their dehydration meets great difficulties, and that an appropriate change of the structure of sludges in the process preparing to their dehydration should increase the number of micropores and decrease both the porosity and the number of transient pores, and consequently reduce the specific area.

BADANIE STRUKTURY OSADÓW POKOAGULACYJNYCH METODĄ ADSORPCJI

Znaczenie zjawisk powierzchniowych, pomimo ważnej roli jaką odgrywają we wszystkich procesach unieszkodliwiania osadów pokoagulacyjnych, jest przemilczane lub pomijane w wielu badaniach o charakterze podstawowym. W przedstawionej pracy omówiono podstawy teoretyczne i doświadczalne jednej z metod badania parametrów charakteryzujących intensywność tych zjawisk w osadach. Wyznaczono izotermy sorpcji i desorpcji dwutlenku węgla i benzenu na badanych osadach, posługując się wysokopróżniową aparaturą grawimetryczną. Przeprowadzona interpretacja wyników umożliwiła ustalenie rozkładu objętości i powierzchni porów osadów. Tak sposób prowadzenia badań jak i ich interpretację dostosowano do struktury osadów. Przeanalizowano wyniki doświadczeń posługując się teorią Dubinina-Raduszkiewicza oraz metodą BET. Wskazano na konieczność stosowania podstawowych metod badania zjawisk powierzchniowych w osadach obok technologicznych badań procesów ich odwadniania. Uwzględnienie struktury osadów w interpretacji efektów odwadniania pozwoli na lepsze poznanie mechanizmu tych zjawisk oraz ich optymalizację.

ERMITTLUNG DER STRUKTUR VON FÄLLSCHLÄMMEN MITTELS ADSORPTIONSVERFAHRENS

Oberflächen-Effekte spielen bei der Behandlung von Koagulationsschlämmen eine wesentliche Rolle. Unverständlich ist, daß sie oft (auch in Grundlagen-Forschungen) verschwiegen oder vernachlässigt werden.

Im vorstehenden Bericht, geben die Verfasser die theoretischen Grundlagen und Versuchsbedingungen einer solchen Untersuchungsmethode an, die die Intensität dieser Effekte in Schlämmen gut charakterisiert. Die Isothermen der Sorption und Desorption wurden mit Hilfe eines gravimetrischen Hochvacuumapparates bestimmt.

Die Auswertung dieser Versuche ermöglichte die Bestimmung der Streuung des Poren volumens und der Porenfläche solcher Schlämme. Die Versuchsführung und Auswertung wurde der Struktur der Schlämmen angepaßt und untergeordnet. Zur Analyse der Ergebnisse wurden die Theorien von Dubinin und Raduszkiewicz sowie die von BET herangezogen. Die Verfasser weisen mir Nachdruck auf die Notwendigkeit solcher Untersuchungen in Schlämmen hin — parallel zu technologischen Entwässerungsversuchen.

Unter Zugrundelegung der Struktureigenschaften ist eine Interpretation des Entwässerungsvorganges möglich; man bekommt auch eine bessere Kenntniss der Mechanismen der erwähnten Effekte wovon eine Prozeßoptimierung resultieren kann.

ИССЛЕДОВАНИЕ СТРУКТУРЫ КОАГУЛЯЦИОННЫХ ОСАДКОВ МЕТОДОМ АДСОРБЦИИ

Значение новерхностных явлений, несмотря на важную роль, какую играют они во всех процессах обезвреживания осадков от коагуляции, либо замалчивается, либо не принимается во внимание — даже в исследованиях, носящих фундаментальный характер. В представленной работе обсуждены теоретические и экспериментальные основы одного из методов изучения параметров, характеризующих интенсивность этих явлений в осадках. В ходе исследований были определены изотермы сорбции и десорбции двуокиси углерода и бензола на исследуемых осадках, для чего использовалась высоковакуумная гравиметрическая аппаратура. Расчет результатов позволил установить объем и поверхности пор осадков. Способ произведения испытаний и расчет их результатов были приспособлены к структуре осадков. Проанализированы результаты опытов с использованием теории Дубинина-Радушкевича и BET. Указана необходимость применения фундаментальных методов исследования поверхностных явлений в осадках рядом с технологическими исследованиями по процессам их обезвоживания. Истолкование результатов обезвоживания осадков с помощью их структурных свойств позволит точнее изучить механизм этих явлений и возможность их оптимизации.

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