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THE THEORETICAL BASES OF CHEMISTRY AND WATER PREPARATION TECHNOLOGY

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who study in specialty 161 «Chemical technology and engineering»,
specialization "Chemical technologies of inorganic substances and water purification"

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INTRODUCTION

The discipline «The theoretical bases of chemistry and water preparation technology» belongs to the cycle of academic disciplines by free choice. It is administrated for depth education of students by the specialty «Chemical technologies of inorganic substances and water treatment»

Academic material bases on main regularities of water properties by different origin; knowledge of requirements, nominated for treated water.

Teaching of academic discipline «Theoretical bases of chemistry and water preparation technology» occupies important place in formation of future specialists. Its strategy is in approach on deep relation to theoretical postulates with its perfective embodiment due to choosing of real, rational scheme of water preparation.

Water is necessary condition of life existence on Earth. It is much necessary everywhere and always for economic and social development of society. It's difficult to overstate its value and in modern state of hi-tech. Because the problem of water resources, its complexing using, protection and playback is effectual for majority countries of the world.

Tutorial administrated for education students of future professional effectivity, related to water preparation and purification.

SECTION 1 GENERAL CONCEPTS AND DEFINITIONS

1.1 Natural waters classification

Hydrosphere – oceans, seas, rivers, lakes, swamps, atmospheric wet consist $1{,}385 \cdot 10^9$ km^3 of water or $1{,}4 \cdot 10^{19}$ t.

All of water can be classified on natural and waste (WW).

Natural water is surface, underground waters and atmospheric fall-out.

Surface water – rivers, lakes, seas, oceans, channels, ponds, swamps. Among surface origins rivers are the most often usable. Season fluctuations of expenses and quality water composition are appropriate for rivers. Composition of surface water determines by:

1) climate, geo morphological and anthropogenic effects (relief, form and size of pool, flora, fauna);

2) soil and geological conditions (state of soil and rocks);

3) agro- and hydro technical steps.

Underground origins – soil, artesian, underchannel, mine, between-layers, bleak, crack, karst.

Composition of underground waters determines, mainly, by conditions of its formation. Important feature of underground waters: the temperature constant (5 – 12 ºC), absence of color, muddy, relatively high sanitary reliability, increased mineralization, often increased content of dissolved gases, and also Fe, F, Mn, Al etc.

The following conditions of underground waters forming can be classified:

1) water with mineral content, formed in process of rocks leaching;
2) water trapped in sedimentary rocks in process of forming this rocks on bottom of seas and oceans, they are close by the composition to ocean waters;
3) water, formed by transition of water from bound state into free under the impact of high temperature and pressure.

Several classifications of natural water existed [1-4]:

- by mineralization degree (for underground and surface waters – different values of mineralization);
- by pH value;
- by general hardness;
- by degree of bacterial pollution.

Often surface and underground water connected with each other; it impacts considerably on its chemical composition. This primary relates to bleak and soil water.

Large storages of water are ices, focused to 2,1 % of world stocks of water. If all of ices melted, the level of water on Earth would be increased to 64 m, and approximately 1/8 of land would be completed by water (table 1.1).

Table 1.1 – Water inventories (by UNESCO materials) [1]

Name	**Water inventory, % from overall quantity**
Surface waters:	
fresh lakes	0,009
salty lakes, inside seas	0,008
rivers	0,0001
Underground waters:	
soil waters and swamps	0,005
underground shallow waters	0,31
depth waters	0,31
Ices and ice hats	2,15
Atmosphere	0,001
Oceans	97,2

Ukraine is one of the least provided countries by water in Europe: 1000 m^3 per 1 citizen, at the same time in Russia 31000 m^3 of water is responsible by 1 citizen, in Germany – 1900 m^3, in the US – 7400 m^3, in Poland – 1600 m^3.

1.2 Wastewaters classification by different features

Waters after using – wastewaters (WW). The composition of WW is very diverse (impurities, its concentration etc.). There are signs, assigned into the classification. The most common sign is – by the place or conditions of WW forming [4-5]:

1) household (HWW);
2) industrial – (IWW);
3) atmospheric or fall-out (AWW, FWW).

Household wastewaters formed as a result of household business (kitchens, hospitals, laundries etc.). HWW, usually, have strongly determined outgoings, related with norms of using (200 – 700 L/day · person). All of HWW have a very akin composition. Substances of natural origin effect in quality of pollutant. Wash means dramatically worsen of WW.

Industrial wastewaters – differ by uneven of outgoing, variety of composition, at the same time mixtures, its assortment include all known elements of Mendeleev’s table.

Fall-out (atmospheric) WW – waters, assigned from territories of industrial enterprises and residential massifs as a result of atmospheric fall-outs falling. They are distinguished: no-constant outgoing, they can be polluted by all that substances take place on the enterprise territory, and can be conditionally clear.

1.3 Downhill conditions of wastewaters into canalization and ponds. MPC of bad substances in ponds

WW should have subjected to purification. The cheapest way of WW disinfection is downhill to ponds. For all components MPC should be established – maximal permission concentration – minimal concentrations, in which long using (consumption) of water by person doesn’t lead to deterioration in health and depressing of its self-filling. Currently MPC established for more than 700 substances – but this is for individual compounds. The difficult question is: what Figure can have observed at their joint presence.

Downhill conditions of WW into ponds regulated by regulations of surface water defenses from contaminations. All ponds can be classified into three categories:

- household-drinking appointment (used for water selection, water composition is the most reliable from the point of view of sanitary safety);
- cultural-community appointment (used for aims of bathing, swimming, washing, but not for water selection);
- fish-business (ponds used for cultivation of different varieties of fish).

For example, after downhill of WW into pond the quantity of suspended substances should increase not more than 0,25 mg/L for ponds of the 1st category and not more than 0,75 mg/L for the 2nd category. For ponds of the 3rd category – depending on fish's variety and 0,25 mg/L, and 0,75 mg/L. The temperature of water shouldn't increase more than 3 ºC compared with an average temperature by last 10 years of the hottest month. These norms listed for the estimated target.

Target is the complex of hydro technical buildings, on ground of which water intake and spillway carried.

For flow ponds downhill can be made at the distance no less than 1 km to intake (fig. 1.1).

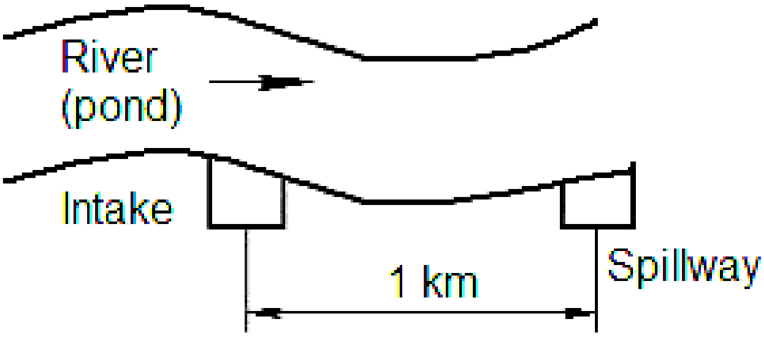


Figure 1.1 – WW downhill into pond

If pond isn't flowing – at the distance no less than 11 km into both directions [6-7].

1.4 Principles and systems of wastewaters canalization. Types of treatment plants

All of formed WW should be outgoing (canalizing).

Canalization – the complex of engineering buildings and sanitary events provides collection and drainage of WW from the territory of settlements and industrial enterprises, its purification, disposal and disinfection.

At the canalization of WW 3 main principles should be followed:

1) different flows of WW should have close dimension of mineralization, i.e. the total number of dissolved salts. This caused by the condition of using general purification methods;
2) flows allocated separately can contain different valuable components;
3) the combination isn't allowed, in which pollutants can react between each other to form explosive or toxic compounds.

Following kinds of WW canalization systems existed [3,7]:

1) general floatable;

2) separate: complete and incomplete, half-separate.

Besides, the combine canalization systems can exist.

General floatable canalization system – if all kinds of WW assigned by one overall collector. It allowed when all types of WW have one-type pollutions (fig. 1.2).

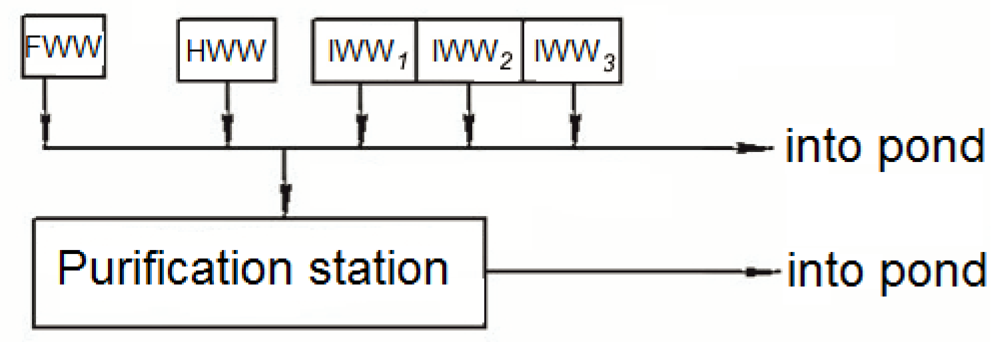
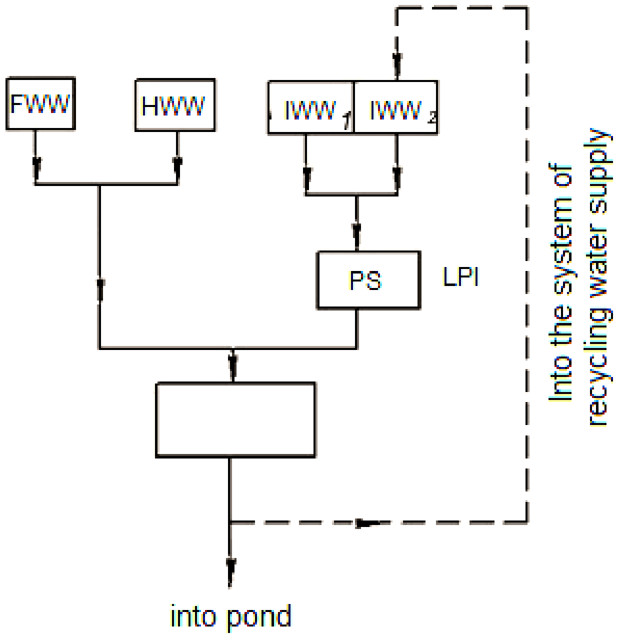


Figure 1.2 – General floatable canalization system

Separate canalization system includes at least two separate networks or all three networks, namely, wastewaters assigned at 2 water networks, for example (fig. 1.3):

HWW + FWW → 1 network;

IWW + HWW→ 2 network.



PS – purification station

Figure 1.3 – separate canalization scheme with 2 networks

If system contains 3 networks, this is completely separate canalization (fig. 1.4).

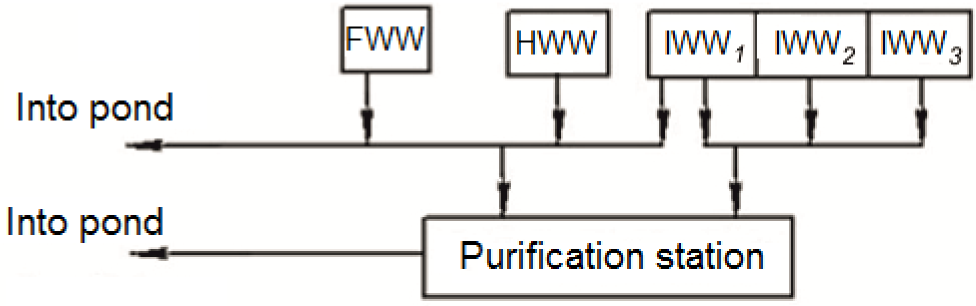


Figure 1.4 – Completely separate canalization system

Half-separate canalization system contains 2 networks: the first – for FWW, the second – for the mixture of HWW and IWW.

Currently separate canalization system used in chemical enterprises.

Types of treatment plants [4, 8]

There are treatment plants at their place of finding:

1) shop or local (LPI);
2) plant's (generally plant's);
3) regional or city.

Shop or LPI (local purification installations) situated directly in shop and are its continuing. Purpose – to comply necessary concentration of substances before its dropping into general collector. As a rule, valuable components removed from WW in local purification installations and returned into the producing cycle. Recuperation purification methods used.

Plant's treatment plants carry all of WW purification of industrial enterprise. The purification of also city WW currently conducted in generally plant's treatment plants. The main purification method is biological purification (mixture of HWW and IWW, organic compounds pollutions).

Regional or city treatment plants are always aeration stations.

In large cities, where industrial enterprises of different profile situated, IWW assigned together with HWW in city biological buildings of purification (in Kyiv – Bortnitska aeration station).

In this case following requirements nominated to IWW:

1) shouldn't violate of networks and buildings work;
2) content of suspended substances – no more than 500 mg/L;
3) shouldn't contain explosive and flammable substances;
4) strictly standardized substances, adversely impact on biological purification conditions.

They (WW) shouldn't contain oils. It's forbidden to dump waste residues, residues of raw materials and finished products.

All of these norms should performed according to rules of IWW reception into the canalization system of settlement. Currently WW after purification used in recycling water supply.

1.5 Wastewaters – reserve of industrial water supply. Producing principles of creating of water supply closed cycles

Repeating using of WW in industries keeps to create closed cycles of water supply. This keeps decrease of fresh water using 10 – 50 times.

Necessity and expediency of creating of industrial water supply closed systems due by three main factors:

-fresh water deficit. Continuous increase of water consumption and degradation of water quality of natural water origins impact on increase of fresh water deficit as a result of wastewaters earning into it.

- exhaustion of ponds ability to self-purification, in which wastewaters dump;

- economic benefits compare with wastewaters purification to relevant norms, keep its dumping into opened ponds.

The main principles of creation of closed water recycling systems.

Creation of economically proving closed water economy systems is sufficiently difficult task. The complex physically-chemical composition of wastewaters, variety of compounds, contained in it, and its possible interaction, make impossible selection of universal structure of non-wastes schemes, suitable for using in different branches of economy.

The question of primary necessity at creation of closed water recycling system is designing of scientific-prove requirements to water quality, use in all technological processes and operations.

In majority of technological operations, the necessity of using drinking quality water is absent. That's why, it's necessary to evaluate permissible edges of main water quality indices, determined by following factors:

- shouldn't worse of the obtained product quality;

-should provide non-accident work of equipment; it shouldn't destroy because of corrosion; deposits shouldn't show on walls etc.;

- no impact on health of attendants by changing of toxic or epidemiology water characteristics.

Historically, at designing of technological schemes attention doesn't paid on water quality. Drinking and even technic water in most cases satisfied technologists, and used water simply dumped into ponds and only later it became to direct in purification facilities.

Common tasks at designing of closed water recycling system for all branches of economy are following:

- maximal implementation of air cooling instead of water: in many enterprises to 70 % of all usable water spent for cooling;
- placing of the complex of industries on industrial playground by the way for making possibility of using water in technological industries by many times (cascade);
- consistent, many-time using of water in different branches or identical industries should cause to forming of large volume of maximal polluted wastewaters, for disposal of it relatively effective (and, as a rule, expensive) purification methods can be picked up;
- using of water for gas purification only in cases, when valuable components removed from gases and used; using of water for gas purification from solid particles allowed only in case of closed cycle;
- necessity regeneration of waste acids, alkaline and salty technological solutions by using recoverable products in quality of recycled materials.

At creating of closed water recycling systems of industrial enterprises water preparation and purification of wastewaters should have considered as one system.

Designing of closed systems conducted at the same time with designing of the main production.

a)

b)

Figure 1.5 – The general form of Kyiv water purification station “Bortnichi”

Questions for self-control to the section 1

1. Name the factors cause surface waters formation.
2. What origins related to underground?
3. Add the features of underground waters.

4. For what features can wastewaters be classified?
5. Give the principles of wastewaters canalization.
6. Compare the existing systems of wastewaters canalization.
7. Explain the principles of creating closed water recycling systems of water economy.
8. Name the main origins and distribution of water reserves on Earth.

SECTION 2 INDICES OF WATER QUALITY AND IMPURITIES CAUSE IT

1. Physical indices of water quality.
2. Chemical indices of water quality.
3. Bacteriological indices of water quality.

Quality of water determines by physical, chemical, bacteriological and technological indices.

2.1 Physical indices of water quality

At evaluation of water quality from origin it is, firstly, necessary to acquaint with its physical indices, its stability and season fluctuations [9,10].

Temperature, transparency, muddy, smell, taste, color related to the physical indices of water quality. Often these indices called organoleptic.

2.1.1 Temperature

The temperature of natural waters depends on, first of all, its origin. Waters of underground origins different by temperature constant, moreover, with increasing of depth season temperature fluctuations decreased. The temperature of waters in opened ponds experiences significant season changes. In Dnipro river – average winter temperature of the water – 0,1 º C, and the highest in year – +28 º C. The temperature of water can increase as a result of dumping of warm WW (power plants etc.). The optimal temperature of drinking water considered 7 – 10 º C.

2.1.2 Transparency and muddy of water

Natural waters, especially surface, rarely can be transparent because of presence in it suspended particles of clay, sand, sludge, organic substances, fito- and zooplankton etc. The content of suspended particles in different ponds fluctuates very high from several (10 – 15) g to (30 – 10000) mg/L. In Dnipro river the average content of suspended substances ≈ 25 mg/L (in winter) and increases to (70 – 80) mg/L in summer. In Desna river the quantity of suspended substances is much higher.

Water transparency determined by «the type» or by «the cross».

Water poured into the cylinder of some diameter and liquid column height measured, through which the type or the cross can be viewed.

For the determination of transparency by «the type» Snellen apparatus used – glass cylinder graduated through 1 cm, H (cil.) = 30 cm, d = 2,5 – 3 cm. The ceramic disk placed on the bottom of the cylinder, water is shacked, poured into the cylinder and dumped (or added) to appearance the type in the field of view (fig. 2.1).

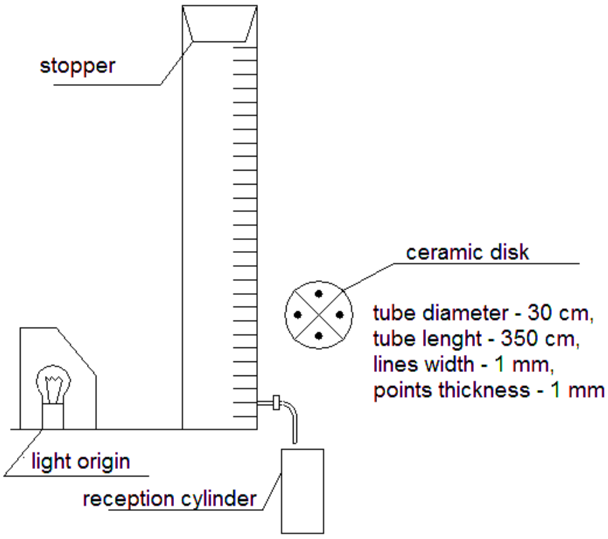


Figure 2.1 – Snellen apparatus for the determination of transparency by «the type» [5].

For drinking water, the transparency by «the cross» should be 35 cm, this responds the content of suspended substances – 1,5 mg/L; water for vapor producing should have the transparency – 50 cm.

When WW characterized, it isn't told about the transparency, but about the muddy.

The muddy of water determined by comparison at the same lightening of the sample of tested water with the same volume of artificial samples (muddy distilled water).

The muddy measured visual by the scale, composed of the set of special glasses, imitated different muddy (muddy-meter by Beilis). The dimension of muddy – mg/L. There are tables exist for transformation of the water's transparency by «the cross» to its muddy.

The muddy also measured by helping of the apparatus «muddy-meter».

2.1.3 The color of water (C)

The clear water in little volume – colorless, in thick layer it has bluish shade. Natural waters have the color from light-yellow to brown. At «flowering» of ponds water, depending on the kind of microorganisms, gets different shades – blue, green, emerald-green etc.

The color of water expressed in degrees of the platinum-cobalt or dichromic-cobalt scale. The etalon dichromic-cobalt scale contents solutions ($K_2Cr_2O_7$ + $CoSO_4$ + H_2SO_4). It determined colorimetric (comparing with calibration timetable).

2.1.4 The taste and smell of water

Sometimes it can be called «flavor» of water. This indices norm for drinking water. 4 tastes of water can be differed: salty, bitter, sweet and sour.

The intensity of the taste and flavor, as and smell, established by 5-mark scale (table 2.1).

Table 2.1 – 5-mark scale of the taste, flavor and smell intensity

Marks	**Characteristic**	**Using**
0	The taste and smell not felt	drinking water
1	Feeling only by experienced taster	
2	Filling by consumer	Can used as drinking in agreement with sanitary-epidemic station
3	Filling easily	
4	Make water unpleasant	
5	Has such intensity taste and smell, in which water doesn’t suitable for consumption	Not used as drinking

The qualitatively characteristic of flavors expressed descriptively: chlorine, fish etc.

The following smells can be differed: aromatic, swamping, decaying, wooding, soiling, molding, fishy, grassy, not-determined, hydrosulfide, phenol, oiling, acetic etc.

The edge of human tastes sensations is enough high (for example, phenol chloride revealed tasty at the concentration $4 \cdot 10^{-6}$ mg /L).

2.2 Chemical indices of water quality

2.2.1 pH — the effective reaction of water

The pH of the natural water (6,5 – 8,5). Wastewaters shouldn't have dumped into pond in not-treated state.

The permanence of water's pH determined by carbon dioxide equilibrium:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}.$$

At pH > 10 CO_3^{2-} ions are primarily in water.

2.2.2 COD — chemical oxygen demand

The presence in water organic and inorganic compounds, easily oxidizing (H_2S, sulfites, Fe^{2+} compounds etc.), caused a value of water oxidizing.

COD (or oxidizing) – the quantity of oxygen, necessary for oxidation of impurities, contented in 1 L of water (namely mg O_2/L).

The lowest value of COD is for artesian water – to 2 mg O_2/L; in ponds COD ≈ (3 – 4) mg O_2 / L (in winter (5 – 6) mg O_2 / L), COD of rivers – to (10 – 60) mg O_2 / L, swamping waters – to 400 mg O_2 / L [4-7].

For the determination of COD powerful oxidant added to water sample: potassium permanganate or dichromate, that's why permanganate and dichromate water oxidizing can be differed.

The prevailing is dichromate oxidizing (more accurate analyze of organic substances content), because it keeps to oxidize even hard soluble compounds to 90–95 %.

2.2.3 BOD — biological (biochemical) oxygen demand

BOD – the quantity of oxygen spent (consumed) by aerobic microorganisms for processes of its life for some time: BOD – 2 (2 days); BOD – 5 (5 days); BOD full – until the beginning of nitrification, namely $NH_3 \rightarrow NO_3^- \rightarrow N_2$ (as a result of albumen degradation).

2.2.4 The total salt content

The total salt content determined as dry residue at the calcination. The water sample filtered, evaporated and dried at (100 – 110) º C – dry residue (mg/L), then calcined in muffle at 600 º C during 1 hour.

The dry residue characterized the content in water of dissolved mineral salts and non-volatile organic compounds. The organic part of dry residue of water determined by the value of loss at the calcination.

2.2.5 The hardness of water

The hardness of water caused by the content of salts Ca^{2+} and Mg^{2+} in water. The carbonate (temporary or eliminated) and not-carbonate (constant), their sum – total hardness.

The dimension: mg-eq./L or mmole/L.

Drinking water has H ≈ 7 mg-eq./L.

In Kyiv region H ≈ 4 mg-eq./L.

UNESCO has proposed to cancel the term «hardness» of water, and to use the term «total salt content».

Table 2.2 – Units of water hardness measurement in some countries:

Units of hardness					
mg-eq./L	German degree, Hº	French degree, tº	American degree	English degree	ppm (mg-eq./L) $CaCO_3$
1,0	2,804	5,005	50,05	3,51	50,05

2.2.6 The alkalinity

The alkalinity caused by presence in water OH^-, HCO_3^- and salts of weak acids (silica, phosphate, humic etc.).

2.2.7 Sulfates, chlorides

Sulfates, chlorides normed in all waters, because they do negative destroying action on iron-concrete constructions. For drinking water, the norm of Cl^- - 350 mg/L, SO_4^{2-} –500 mg/L. The content of Cl^- i SO_4^{2-} is usually (60–100) mg/L.

2.2.8 Iron, alumina, manganese

Iron, manganese and alumina normed in water. At the excess in water Fe, Mn, Al, iron bacteria grown very quickly and the overgrown of pipelines placed. The content of Fe in drinking water norms at the lvel less than 0,3 mg/L, Mn – to 0,1 mg/L, Al – to 0,5 mg/L.

2.2.9 Radioactive substances

Currently in natural waters the norm is 10^{-8} – 10^{-10} Cu / L. 1 curie = $3{,}7 \cdot 10^{10}$ decays/s. Radioactive substances, getting to ponds, can be natural and artificial origin.

2.2.10 Microelements

Microelements I, F, Br normed in drinking and in WW. It’s lack or excess cause to the dysfunction of the thyroid, dental diseases, changes in bone tissue.

2.2.11 Toxic substances

They are absent in natural water. They income from WW or purposely. The content of Pb, Zn, Cu, As etc. and also organic toxic substances normed.

2.2.12 The content in water dissolved gases CO_2, O_2, H_2S, N_2, CH_4 etc.

As mentioned, O_2 necessary for bacteria life, presence of CO_2 characterizes water stability (the condition, in which water, as a result of extended contact with iron and concrete, doesn't change its quality).

The content of CO_2 in surface waters doesn't usually more than (20 – 30) mg/L, in underground – to 90 mg/L, in swamping higher.

CO_2 can be found in free state. The free CO_2 is sum of H_2CO_3 i CO_2 (since in natural waters the concentration of H_2CO_3 is only parts % from total quantity of free carbon dioxide, as last without visible error the concentration of CO_2 taken). The related carbon dioxide enters to the composition of hydro carbonates and carbonates. It's content in water causes so called alkalinity reserve (the alkalinity) of water. The excess CO_2 (free) is very effective, called aggressive and impairs working of treatment plants.

2.2.13 Nitrogen content compounds

Nitrogen content compounds normed in natural and WW. The content of nitrates in water, exceeding 50 mg/L, at prolonged consumption can cause blood disease. In drinking water according to the STATE STANDART 2.2.4 – 171 – 10 the norm of nitrates – to 45 mg/L, in Europe countries – to 10 mg/L.

The presence of nitrogen content compounds in water causes overgrowth pipelines and fittings.

2.2.14 Phosphates

The phosphates content norms in drinking and WW, because of they are an element, provides live, and its excess causes to overgrowth blue-green algae and, consequently, ponds eutrophication.

2.3 Bacterial indices of water quality

Water characterized in sanitary respect. Herewith bacterial indices used. Water contains great quantity of microorganisms. As the biological indicator coli-index used

(E. coli). For drinking water by norms coli-index is 3, namely, 3 E. coli can have located in 1 L of water. Sometimes coli-titer used – the volume of water contains 1 E. coli.

Aquatics, inhabiting natural water, in living process affect not only the water environment composition, and also water quality.

They are following:

- plankton – citizens, located in water thicker from the bottom to surface;
- benthos – citizens, located on the bottom of ponds;
- neisthon – citizens, settled the surface layer of water;
- pagon – organisms, located in thicker of ice in winter in suspended animation state (mollusks, crustaceans, rotifers).

Questions for self-control to the section 2

1. What water quality indices related to physical?
2. What water quality indices related to organoleptic?
3. Name the main chemical water quality indices.
4. Wright-down the equation of carbon dioxide equilibrium.
5. What indicator does characterize water oxidation?
6. What total salt content characterize as indicator?
7. Name the kinds of water hardness.
8. What anions cause water alkalinity?
9. What indicator characterized water in sanitary relation?

SECTION 3 NATURAL AND WASTEWATERS – MULTICOMPONENT HETEROGENEOUS SYSTEMS

1. Water as chemical substance.
2. Models of liquid water.
3. Impurities classification and pollutions by its phase and dispersion feature.
4. General characteristic of impurities and pollutions of natural and WW.

3.1 Water as chemical substance

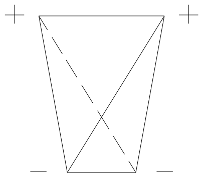
Water is the most common and, at the same time, extraordinary, strange and far from sold substance. Among all substances, studied by physics and physical-chemists, water in many relations is the most difficult [11,12].

Water molecule, consists of two hydrogen atoms and one oxygen atom, described by the simplest formula H_2O. However, this simplicity is indicative, it does not meet composition and structure of water molecule.

Six oxygen isotopes known: ^{14}O, ^{15}O, ^{16}O, ^{17}O, ^{18}O, ^{19}O and three hydrogen isotopes H, D, T, namely the substance, named water by us, isn't simple. It is the mixture of 36 isotope species of water, namely 36 different substances [2, 5].

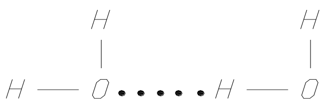
$^{1}H_2{}^{16}O$ (99,73 mol. %) contains the main mass, the residue is ($H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HD^{17}O$ etc.).

Water molecule has 10 electrons (5 couples). There are 4 poles of charges in water molecule, localized in tops of something wrong tetrahedron: two negative (due to electron density excess in non-divided pairs of electrons) and two positive (in place of protons localization).

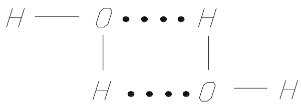


Different poles cause presence dipole moment in water. Because of this the presence of polar bond is possible in liquid water molecule (over molecular associates – $(H_2O)_x$).

The hydrogen bonds formation has the main value for water molecules association.



Each molecule of water can connect to itself 4 water molecules. Double molecules $(H_2O)_2$ have the highest resistant.



Hydrogen bond in general determines unique soluble ability of water. Water bond largely responsible for the availability different structure elements in liquid water. Currently, one meaning doesn’t exist due to the structure of liquid water.

3.1.1 Abnormal properties of water

1. Under normal conditions water can, at the same time, exist in three aggregate states: gas, liquid and solid.
2. Extremely high temperatures of phase transitions (T_{boil}. i $T_{melt.}$). The thermodynamic how natural, so industrial processes determined exactly by these temperatures. The temperature of water boiling at atmospheric pressure is 100 º C, if molecular associates don’t exist in water molecule, the boiling point would be ≈ 63,5 º C.
3. The highest density of water observed at 3,98 º C, thus, even in the coldest season of tear the live saved in ponds (ice protects ponds from deep freezing). At further increasing of the temperature the density decreased, and, eventually, water freezes with lot less density [4, 5].
4. The viscosity of water in edges (0 – 30) º C decreased at pressure increasing (unlike all other liquids). In nature this property determines the hydrodynamics of flows (mixing, sedimentation). In technic these properties used in sedimentation processes.
5. The heat capacity of water – the highest among all of liquid and solid bodies, expected liquid NH_3.

6. The thermal conductivity of water is the highest among all liquids. This property determines it’s wide using in different technic and heat-technic processes.
7. The universal solubility of H_2O. Almost everything soluble in water to varying degrees.
8. From all known liquids, only mercury has the force of surface tension higher, then water. Thanks to the surface tension, water rises by capillary channels in soil to the earth surface, incomes to tissues and cells of plants and living organisms.

3.1.2 H_2O — complex heterogeneous system

One of the possible explanation of water anomalies is the structures feature, formed by water molecules at different aggregate states. It was established, in vapor state water presented, in generally, by one-dimension molecules, less dimers common, but trimers can exist too.

The structure of ice studied quite well. Ice crystals have the form of hexagonal prisms. Six modifications of water structure had been discovered. Everyone molecule of water surrounded by four coming molecules to itself, located at equal distances. For example, in ice structure (tridimite type) the distance between molecules is 0,45 nm, and in the structure of quartz type – 0,42 nm. In the first case this is the water of melting ice with the temperature approx. 0 º C, denser packing of water molecules observed at the temperature approx. 4 º C.

Volume expansion of approx. 10 %, observed at water freezing, explained by rapid changing of denser packing structure to delicate, loose. There is many emptiness in ice structure, which are even larger of self-water molecules. At the temperature, approx. 4 º C this emptiness filled by water molecules and its density becomes maximal.

3.2 The models of liquid water

The liquid state of water studied least of all. This explained, the internal structure of liquid, especially water is much difficult, then solid bodies and gases. To date, there is no unity in views on water structure.

Discussed options reduced to following models:

1) water is one-phase environment, the jump-like change of some properties is impossible in it;
2) heterogeneity of liquid water structure expected and presence of different structure elements in it;

The model of ice structure used in both types of structures.

Different models of water structure [5]

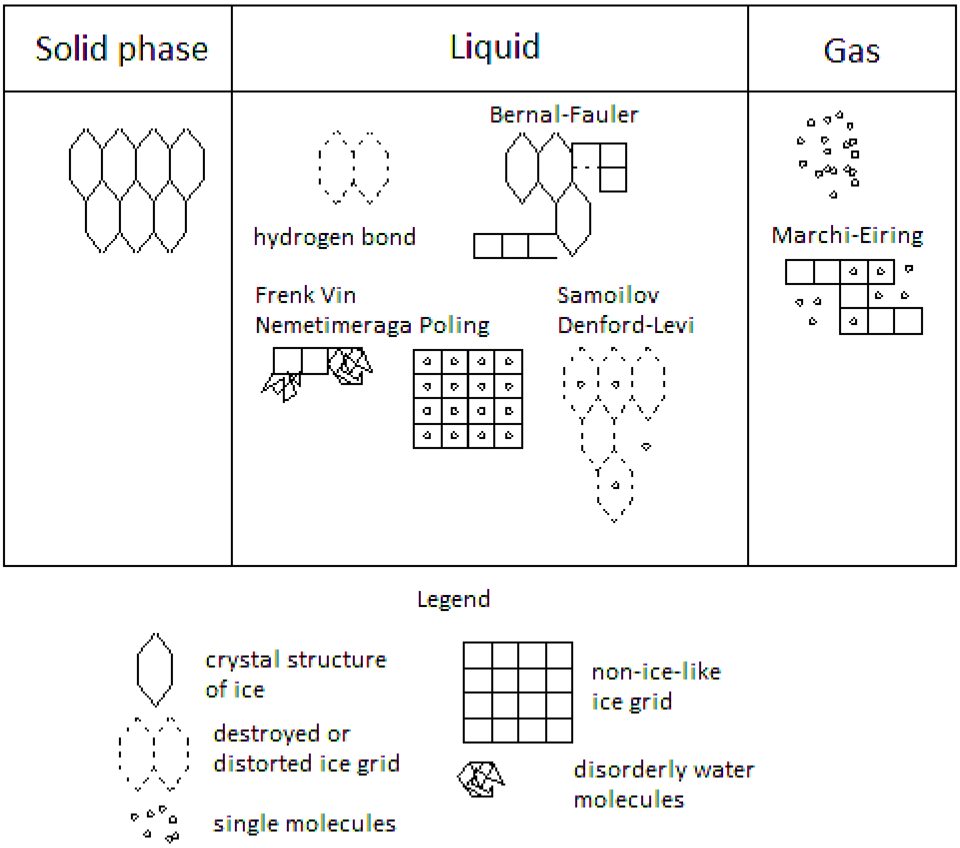


Figure 3.1 – Models of Bernal and Fouler, Polling, Samoilov, Frank-Vine etc.

3.3 Impurities and pollutions classification by its phase-disperse feature

Chemically pure water is absent in nature. Even distilled water after much-time distillation contains dissolved carbon dioxide, nitrogen, oxygen and, slightly, substances of the dishes for water storage. If suggest, the absolutely pure water can be got, then this water is an origin of impurities existing. The reaction of water molecules decomposition to oxygen and hydrogen always happens in it. At room temperature 1 ton of water contains 50 H^+ ions and approx. 25 O^{2-} ions.

Natural and WW present itself complex dispersion systems, contain high quantity of mineral and organic impurities.

Homogeneous system, doesn't contain the surface section inside, separates high quantity of mineral and organic impurities. Systems, contain the surface section inside, called heterogeneous.

Homogeneous systems: a solution of sugar or salt, gas mixture. Heterogeneous – two mutually soluble liquids, ice + water etc.

A dispersion is system, consists of very small substance particles, distributed into other substance (environment). The properties of dispersed systems largely depend on particles size of distributed substance. The measure of fragmentation is transverse particle size or reverse dimension $D = \frac{1}{a}$, called ***dispersion***. The smaller particles, the greater dispersion.

At particles size $a < 10^{-6}$ cm, impurities form ***homogeneous*** systems with water. If particle size $a > 10^{-6}$ cm, impurities form ***heterogeneous*** system with water.

In water, homogeneous systems, called ***true solutions***, impurities can exist in molecular-dissolved or ions shape. In heterogeneous systems impurities form with water or ***colloidal*** solutions ($a = 10^{-6} – 10^{-5}$ cm), or ***suspensions*** ($a > 10^{-5}$ cm).

Suspensions: ***suspensions*** (formed at solid particles dispersion) and ***emulsions*** (formed at liquid or gas-like substances dispersion).

Water impurities – mineral and organic substances, and also microorganisms, the environment of existing is water (these are bacteria, mushrooms, algae, elementary).

Impurities variety causes significant difficulties at water purification and preparation for different consumers.

The quantity of water impurities two orders exceeds the number of impurities, for which the purification methods developed. Considering, the quantity of pollutions kinds will increase in future, no effectivity of the way of purification methods developing for each kind of pollution singly is evidence.

The necessity of studying self-properties of substances had been caused – water impurities and detection of properties determining choosing of water purification method from this particle. The result was in creation of the universal water impurities classification principle.

1) phase-disperse characteristic of substances, determines its behavior in water environment, and, so, its attitude to reagents, incoming in used purification methods;
2) the ability of many substances to change its phase-dispersion state in water environment under the action of physically-chemical factors (pH, salt content, the temperature etc.), opens wide opportunities for improvement methods of natural and WW;
3) conformity of all technological methods of impurities removing by its phase-disperse state.

The essence of Kulskiy's classification is that all water impurities according to its relation to the dispersion environment connected to four groups with general physically-chemical characteristic for everyone among it (table 3.1).

Table 3.1 – Kulskiy's classification of water impurities [9]

Group	**Particle size *a*, cm**	**Phase (physical-chemical) characteristic of impurities**
	Heterogeneous systems	
I	More than 10^{-5}	Hard dispersion impurities: suspensions, emulsions, plankton, pathogeneses microorganisms. Cause water muddy.

II	10^{-5}- 10^{-6}	Impurities of colloidal dispersion level: organic and inorganic substances, viruses, high-molecular compounds. Cause oxidation and color of water.
Homogeneous systems		
III	10^{-6} - 10^{-7}	Impurities of molecular dispersion level: gases, dissolved in water; organic substances. Accord water smells and flavors
IV	$<10^{-7}$	Impurities of ion dispersion level: salts, acids, alkaline (electrolytes). Accord water mineralization, hardness, alkalinity or acidity

3.4 The general characteristic of impurities and pollutants of nature and wastewaters

3.4.1 Impurities of the 1st group

Impurities of the 1st group form with water suspensions, emulsions, foams and also plankton and pathogenic bacteria – kinetically unstable, held in suspended state by dynamically powers of water flow. Following substances income into ponds as a result of rocks erosion, soil washing, with wastewaters. The most often these impurities presented by particles of clay, sand, soil, sludge, and also emulsions of mineral oils, oil products etc. Pathogenic bacteria, viruses, radioactive substances can gather on particles surface. Impurities of the 1st group effectively removed under the action of gravitation forces, forces of adhesion, combined sedimentation.

3.4.2 Impurities of the 2nd group

Impurities of the 2nd group are colloidal (mineral or organic mineral) particles of soil;

- humic fulvic acids washed up from wood, peat and swamp solids and offer water's brown color;
- high-molecular compounds of natural origin, and also incoming into ponds with wastewaters;
- viruses and other microorganisms of colloidal dispersion degree.

Impurities of these group form kinetically and aggregately stable systems with water (impurities practically don't sediment, the time of its sedimentation measured by years). These impurities removed from water, mainly, by coagulation, sorption, oxidant impact.

3.4.3 Impurities of the 3rd group

Impurities of the 3rd group (molecular dispersion level) – gases dissolved in water, organic substances of biological origin, and also submitted with HWW and IWW, organic substances – phenols and its derivatives, aromatic amines, nitrogen compounds etc.

The processes of removing of 3rd group impurities:

- aeration (for gas-like substances removing);
- sorption, extraction (for organic substances removing);
- biochemical purification.

3.4.4 Impurities of the 4th group

Impurities of the 4th group (ion dispersion level) formed in water because of salts, acids and alkaline dissociation. Impurities of this group removed from water by forming of slightly soluble or slightly dissociated compounds. Besides, its removing carried by ion exchange sorption, electrical dialysis, reverse osmosis, and also by the water aggregate state changing.

The dynamic bond between groups enables to change its group accessory in desirable direction and to find rational technological decisions for specific cases of water preparation.

Questions for self-control to the section 3

1. Explain water molecule structure.
2. How many chemical compounds correspond to formula H_2O?
3. What role played by hydrogen bonds?
4. Name the abnormal water properties.
5. What the explanation of liquid water molecule structure complexing?
6. Explain the structure of the most common models of the liquid water structure.
7. Determine differences between homogeneous and heterogeneous systems.
8. What position does the basis of water impurities classification?

SECTION 4 MECHANIC (NON-REAGENT) METHODS OF WATER LIGHTING

1. The sphere of methods using.
2. Primary water purification.
3. Straining on the grids and nets.
4. The theoretical bases of creaming. Stocks equation using for non-aggregating suspensions sedimentation.
5. Hydraulically particle size.
6. Water creaming. The types of sedimentation tanks: horizontal, vertical, radial, thin-layer. Sand-traps, oil-traps.

4.1 The sphere of methods using

Mechanic methods of water treatment intended for removing of the 1st and the 2nd group impurities by Kulskiy's classification. These methods include: straining, creaming, filtration.

The process of suspended substances removing from water, determining transparency or muddy of water (the 1st and the 2nd group), named lighting of water.

Water lighting is the 1st stage of water purification in all schemes and almost for all waters and often named primary purification.

4.2 Primary purification of water

By muddy waters divided:

- low-muddy, M to 50 mg/L;
- secondary-muddy, M = 50 ÷ 250 mg/L;
- muddy, M = 250 ÷ 1500 mg/L;
- high-muddy, M above 1500 mg/L.

Mechanic non-reagents methods used, mainly, for lighting of secondary-muddy and muddy waters.

Sometimes on large rivers on water purification stations artificial buildings suited – scoops – at water in-taking with high muddy [3,9].

Scoop – artificial sedimentation building – suited on river bank or rendered the mainstream by dams (fig. 4.1).

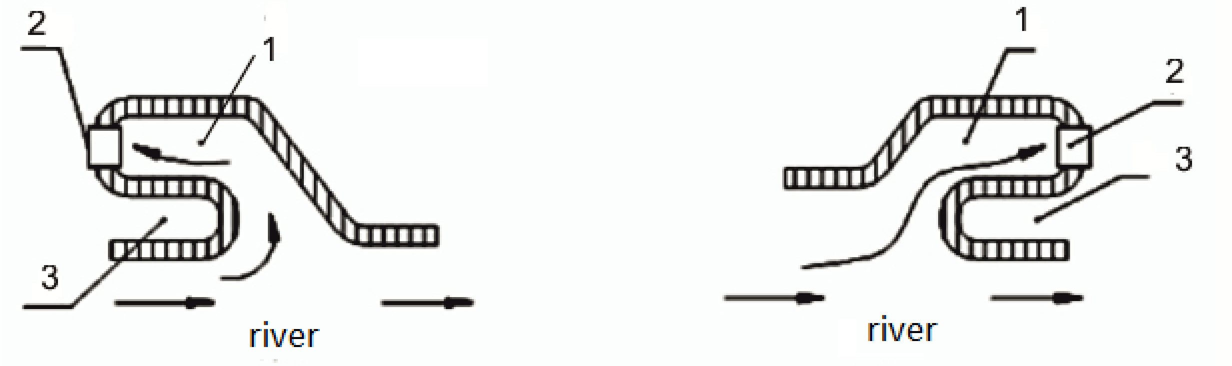


Figure 4.1 – The scheme of water in-taking by scoop

1 – scoop; 2 – water receiving building; 3 − dam

A scoop easier treatment plants work, providing partly suspension sedimentation. Besides, a scoop serves as a buffer, smoothing fluctuations of water muddy. The example of using water pre-lighting method by settling is a scoop (channels – sedimentation tanks) on Odessa and Moscow water-suppliers. The quality of water after scoop improved considerably: the muddy decreases in 2 ÷ 3 times. Especially effectively channels – sedimentation tanks work at extremely deterioration of water quality at floods or rains.

4.3 Straining on the grids and nets

The first and the hardest mechanic method of water lighting is straining through the grids and nets. These treatment plants (devices) established in natural water preparation schemes: grids at water in-taking, and nets – before sedimentation tanks. At the purification of HWW grids established before primary sedimentation tanks. Appointment of these constructions – protecting (protect next constructions from contamination and breakage).

Grids are constructively frame with rods placed on it. Grids size (400 ÷ 1400) – (1000 ÷ 2000) mm. The distance between rods named transparent (16 ÷ 20) mm., (fig. 4.2) [9].

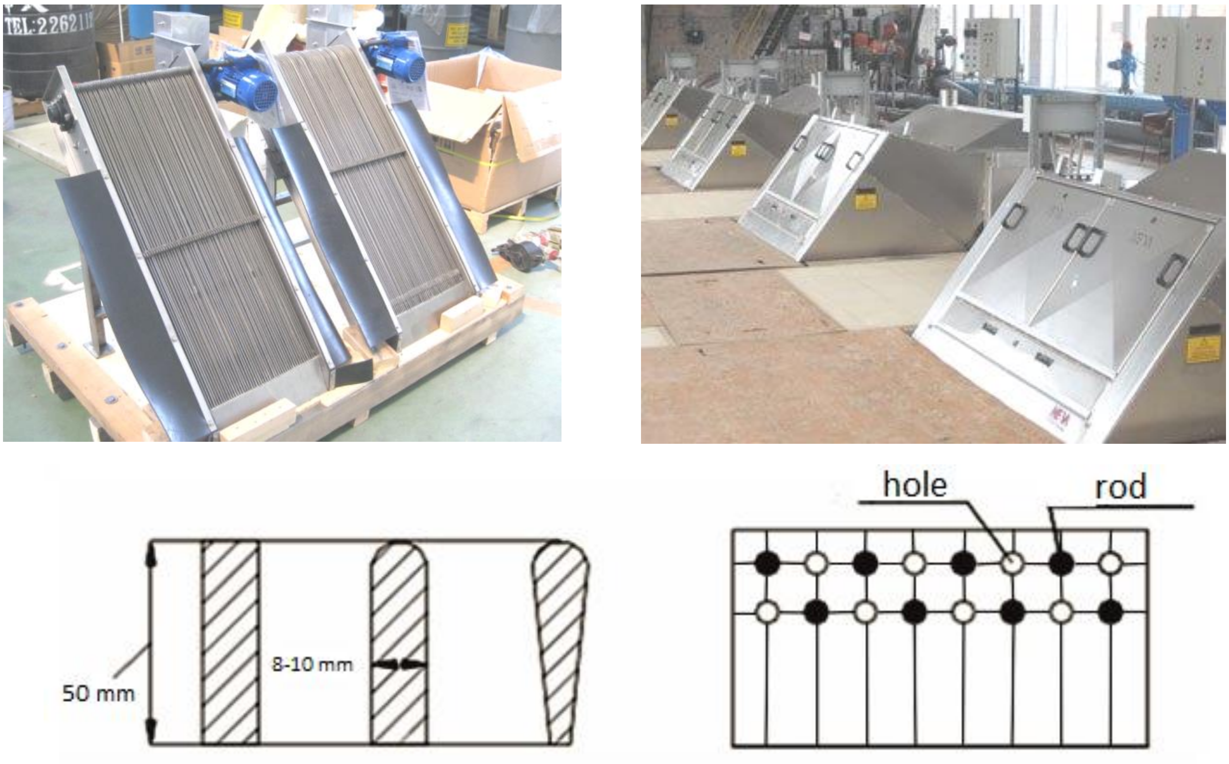


Figure 4.2 – Grids and profiles of grid rods

Grids divided into fixed (the most often used) and grids-crushers (serve for waste milling at the same time). Grids washed up, usually, manually, waste removed with a rake.

Mechanic grids – MGU (unified), with mechanic rakes MR, grids-crushers GC and CGC (combined).

Nets are also metallic frames, blades fixed on it, or net tight on the drum. Net’s cell – 0,5 ÷ 0,8 mm. (fig. 4.3)

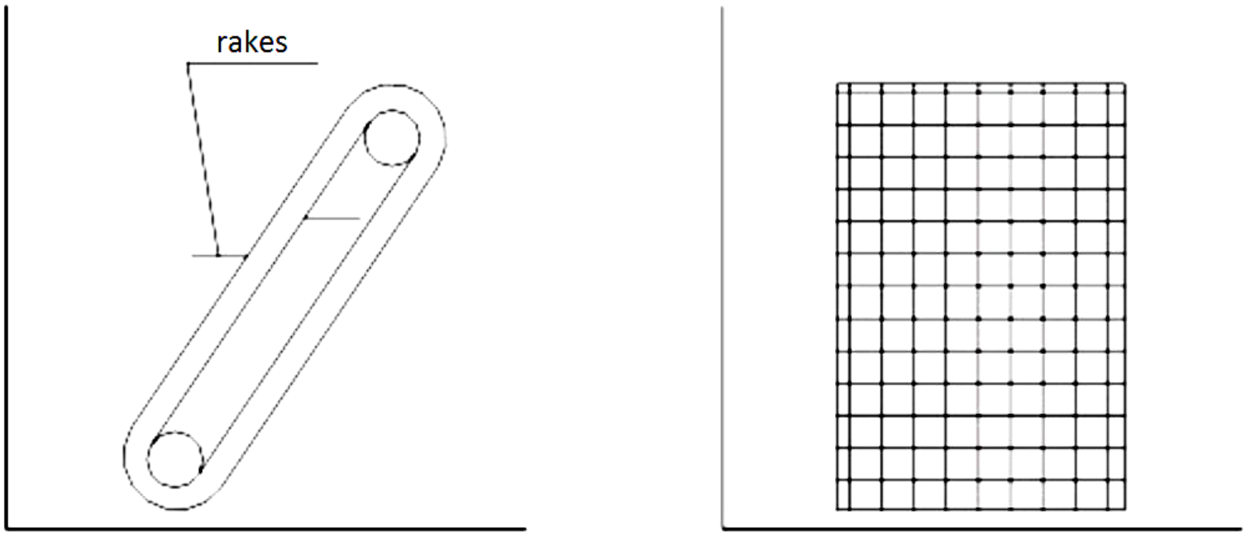


Figure 4.3 – Net’s construction

4.4 The theoretical bases of creaming. Stocks equation using for non-aggregating suspensions sedimentation

The next one stage of water purification after straining is sedimentation.

Stocks equation connects the rate of non-aggregate substances sedimentation with diameter d not above 0,1 mm in laminar liquid flow (20 < Re < 500).

The equation has two following assumptions:

1) the form of particles is spherical;
2) at sedimentation, particles don’t change self-form.

$$u = \frac{d^2}{18\mu} \cdot g \cdot (\rho_S - \rho_L), \tag{4.1}$$

where u – the rate of particles sedimentation m/s;
d – particle diameter, m;
μ – environmental viscosity, Pa · s;
18 – coefficient from Reynolds number for sedimentation rate;
g – acceleration of gravity, 9.81 m/s^2;
ρ – density of solid particle (ρ_S) and liquid (ρ_L), kg/m^3.

Stocks equation can’t have used quantitatively at calculations of constructions for water lighting – because of different character of impurities, its nature changing in time. It gives strong deviation, but it shows qualitatively the impact of different factors (namely u, d, μ, ρ etc.) on sedimentation rate (emersion).

Usually, waters (especially wastewaters), contain solid impurities, has particles of different forms and sizes. Size, density and form of particles, and also physical properties changed at sedimentation process. At sedimentation, pressured sedimentation occurs, accompanied particles collision, friction between itself and changing of rates how large, so small particles. Then the correction coefficient entered to Stocks equation:

$$u = \frac{d^2}{18\mu} \cdot g \cdot (\rho_S - \rho_L) \cdot K, \tag{4.2}$$

where K is coefficient allows for deviation from conditions of Stocks equation (concentration, rheological properties of system, and also particles form).

4.5 Hydraulically particle size

Because of difficulty in the determination of particles diameter and deviation of its form from spherical, the last are easy characterized directly – by the rate of its sedimentation, determined experimentally.

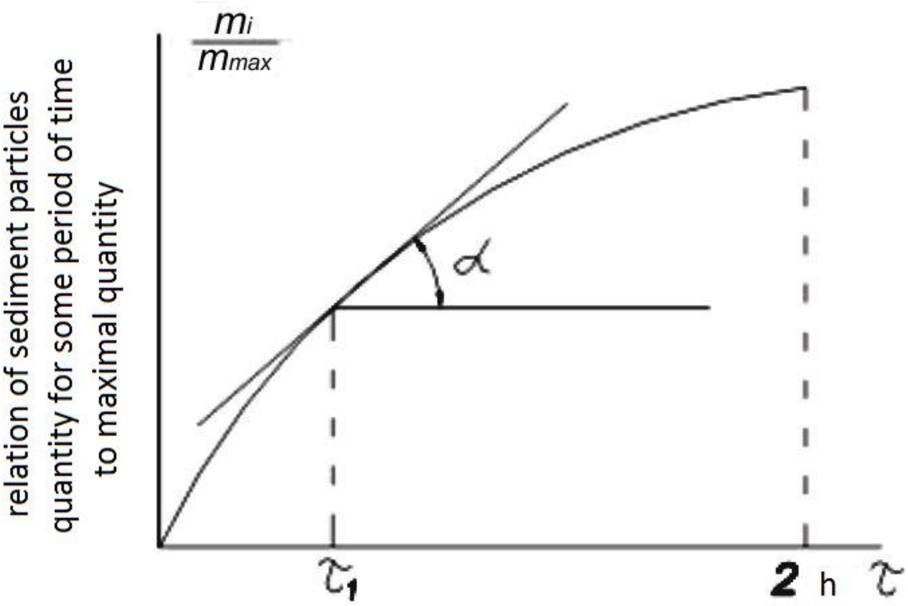


Figure 4.4 – The scheme of particles sedimentation in time

At the temperature 10 ÷ 15 º C, expressed in mm/s, it has the name of hydraulically particle size u_0, mm/s. It determined following: some volume of real water poured into a cylinder of some diameter and height and quantity of sediment particles measured in time.

The value, responding by particles quality, sediment during 2 hours, taken as maximum. Graphic dependence built (fig. 4.4).

A tangent built for everyone τ. Quality value of $tg\alpha$ will be a rate value, namely, u_0 at any period of time.

4.6 Water creaming. The types of sedimentation tanks: horizontal, vertical, radial, thin-layer. Sand-traps, oil-traps.

The simplest and long since used apparatus for severe mineral impurities removing from water (mainly, sand) is sand-trap. Sand traps established in schemes of IWW purification, usually, after neutralization before sedimentation tanks and in schemes of HWW purification between grids and primary sedimentation tanks. In purification systems sand-traps with horizontal straight water moving, horizontal lap-like water moving, lap form with tangency water incoming and aerated are widely used. The construction of facility elected depending on WW quantity and the concentration of solid particles.

For example, horizontal sand-traps are extended in plan facilities with straight moving of water (fig. 4.5).

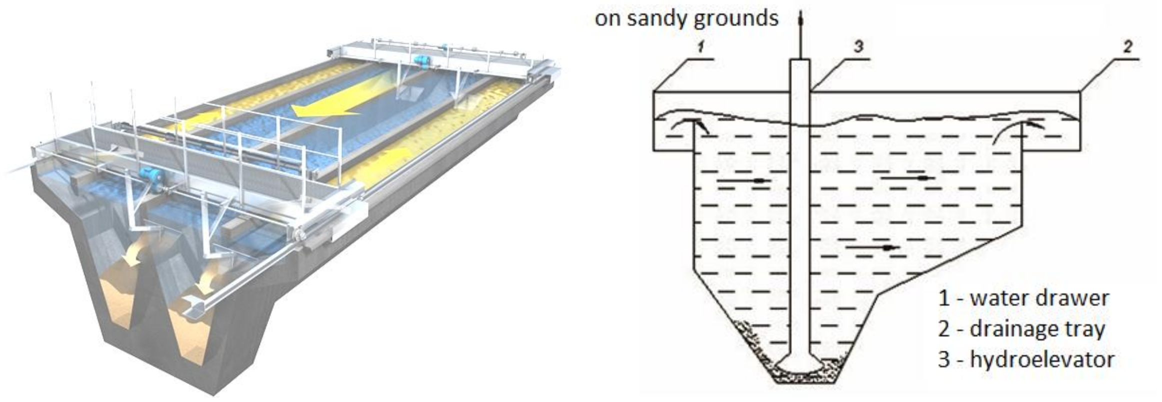


Figure 4.5 – The scheme of horizontal sand-trap

Sand-traps depth – 0,25 ÷ 1,0 m, length to 16 м. The rate of water flow moving isn’t above 0,3 м/с. The precipitate is collected in conic bottom, then it directed to sandy grounds presented by artificial ports, drainage located in bottom part of grounds (tubes system).

Sedimentation tanks. Sedimentation tank is the basic facility of mechanical water purification and used for removing particles, sediment or floated (hard dispersion substances). Depending on flow moving direction, sedimentation tanks classified on: horizontal, vertical, radial. Modern constructions of sedimentation tanks – flowing – a continuous water moving happens in it from enter to exit [4, 7].

Vertical sedimentation tanks are round or square reservoirs in plan with conic bottom. Sedimentation tank located (immersed) in the land.

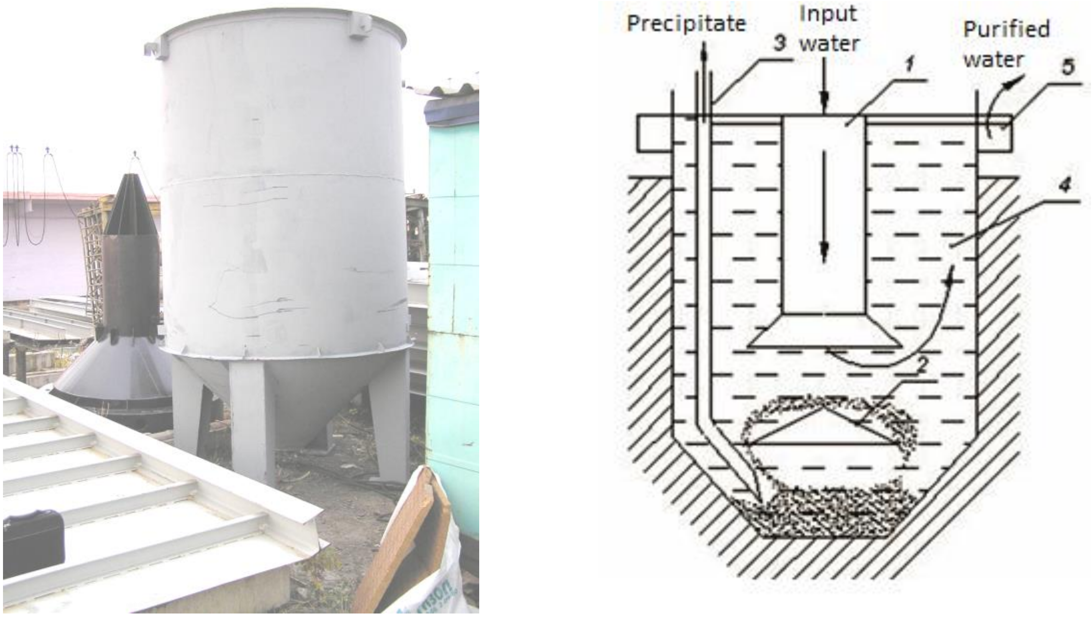


Figure 4.6 – The scheme of vertical sedimentation tank with a central admission tube with a bell

1 – a central input tube with a bell; 2 – a reflector; 3 – hydro elevator (sludge pipeline); 4 – creaming zone; 5 – water output flow

Sedimentation tank depth – not over 7 m (4 ÷ 6 m), diameter – not over 10 m. They used at water outlays to 5000 m^3/day. It recommended at the muddy (M) to

1500 mg/L, and color (C) to 120 deg. Sedimentation tanks with water admission through a central tube with a bell are the most common (fig. 4.6).

A reflector serves to prevent precipitate muddy, collected in conic part of a sedimentation tank.

Vertical sedimentation tanks with descending and rising flow and with peripheral admission of a liquid differed only by a construction of admission and issue devices. They have in 1,3 – 1,5 times more productivity, than sedimentation tanks with a central pipe. Sedimentation tank with descending and rising flow has a device for water incoming in view of ring-like drainage tray of variable section with a toothed spillway. Lightened water issues through a tray, located around a perimeter of sedimentation tank.

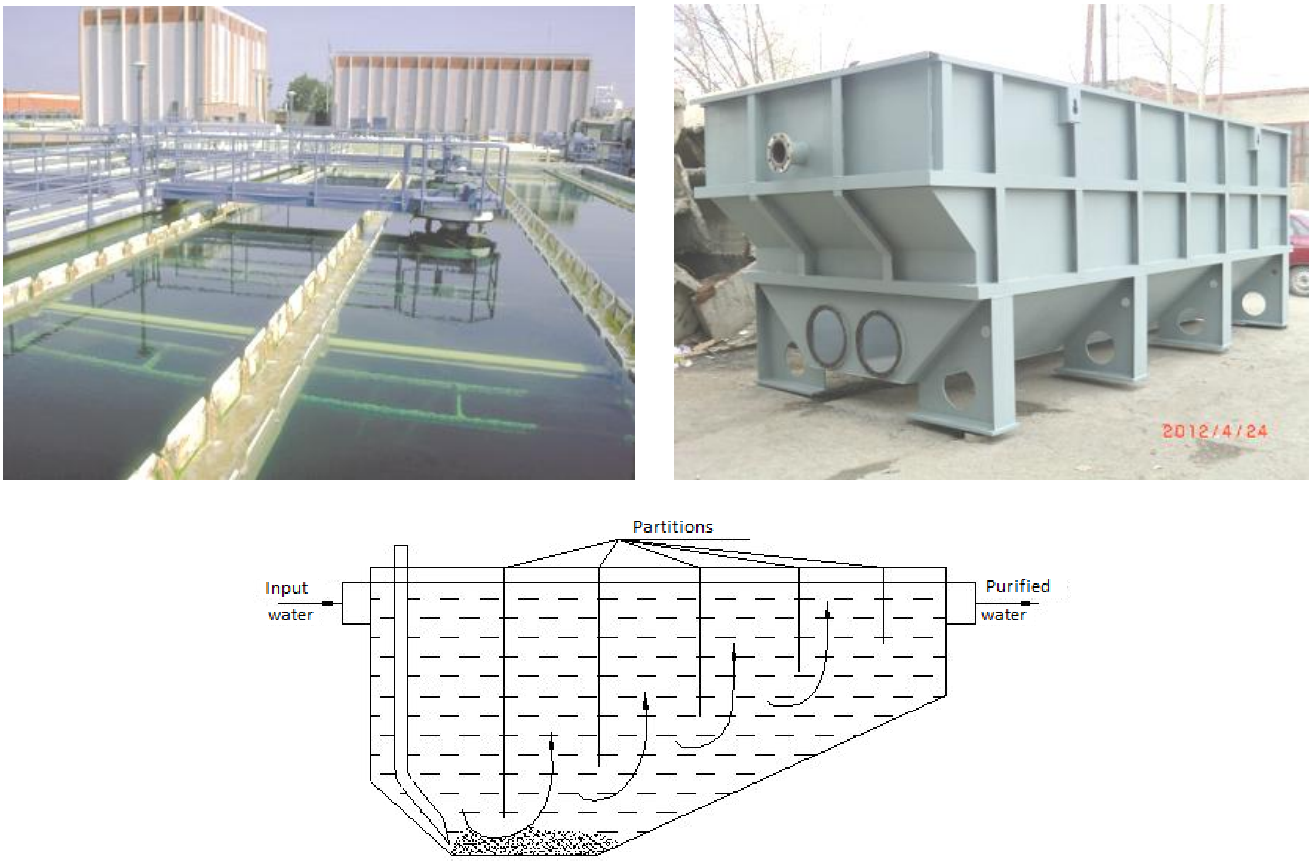


Figure 4.7 – Horizontal sedimentation tank with partitions

Horizontal sedimentation tanks – rectangular (in plan) iron-concrete reservoirs. Designed for high water flows: > 30 000 m^3 / day at M to 1500 mg / L and C to

120 degrees. Depth of sedimentation tanks 1,5 ÷ 4 м, width 6 ÷ 9 м, length — 40 ÷ 120 m (and more) (fig. 4.7 – 4.8).

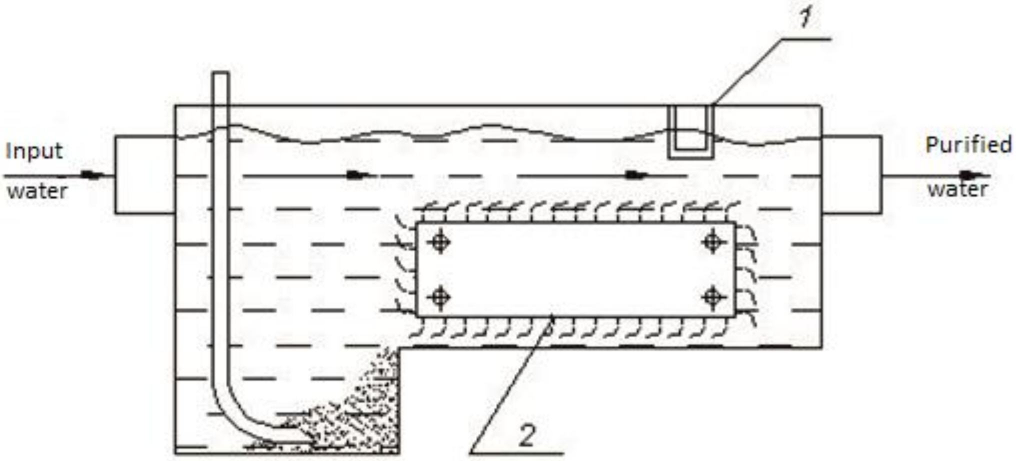


Figure 4.8 − Horizontal sedimentation tank with a mechanic scrapper mechanism

1 – device for removing of floatable particles; 2 – mechanic scrapper mechanism

Scrapper mechanism (tape or cart mechanism) moves (rakes) fallen precipitate to a pit. From a pit precipitates removed by pumps, hydro elevators, grabs or hydrostatic pressure.

Radial sedimentation tanks used for purification of high-muddy waters at flow over 20000 m^3/day. They distinguished by:

1. height and reliability of exploitation, economy, possibility of great performance structures building;
2. presence of moveable farm with scrappers.

Radial sedimentation tanks known in three construction modifications; with central admission (fig. 4.9), with peripheral admission and with collective-drainage rotating devices.

Radial sedimentation tanks are round reservoirs in plan. Water moved in it from a center to periphery. In this case a minimal rate occurred in periphery. Usually, it used for purification of HWW and at very high quantity (the most often light) of precipitate. A depth of sedimentation tank is 1,5 ÷ 5 m, a ratio diameter: depth is from 6 to 30. Sedimentation tanks usually used with a diameter 16 ÷ 60 m.

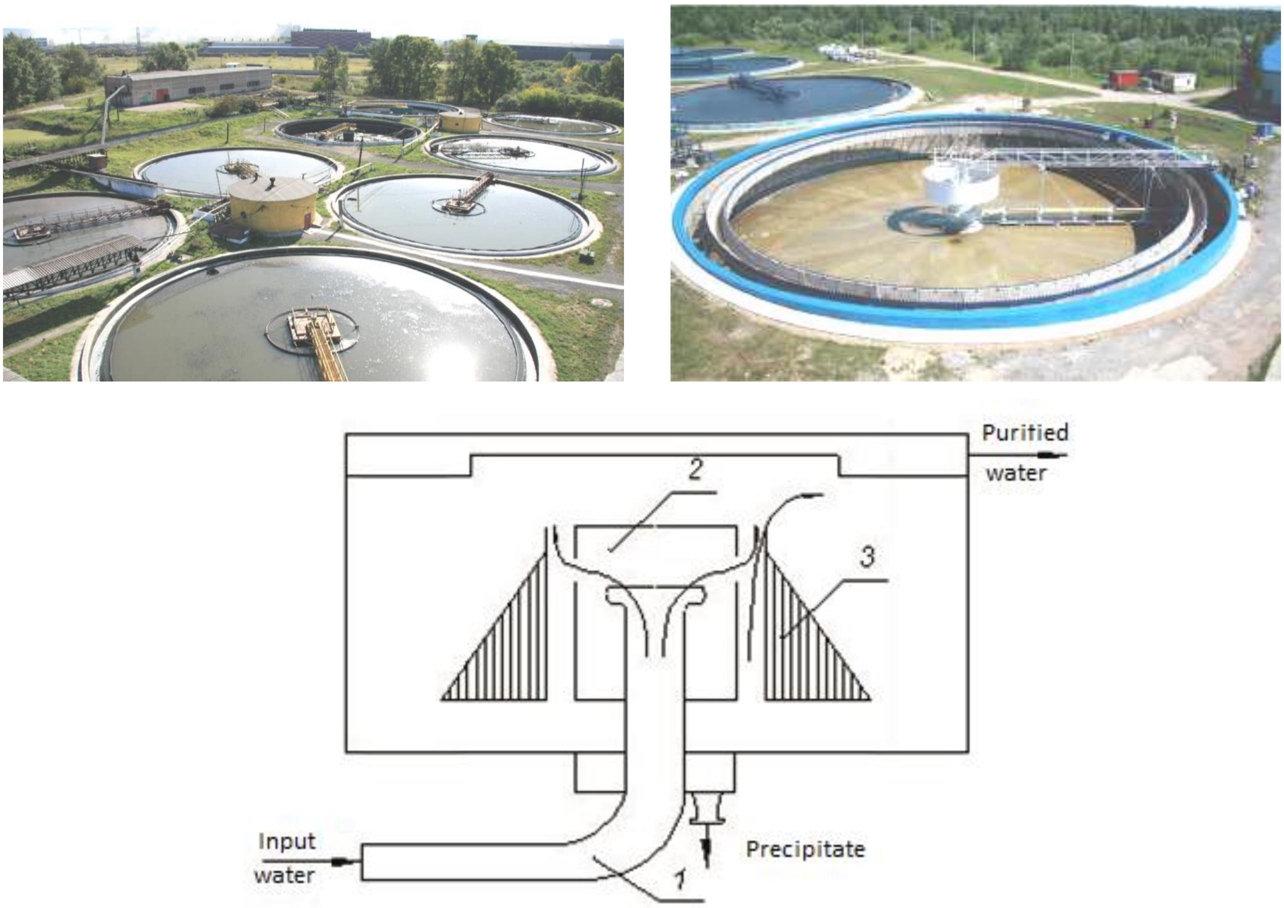


Figure 4.9 – Radial sedimentation tank with central water admission

1 – central water admission tube; 2 – soothing cell; 3 – mechanic scrappers

The effectivity of precipitation in sedimentation tanks of considered designs is 60 - 70 %.

Creaming effectivity can be increased by increasing creaming area and to charge sedimentation process in thin liquid layer, thin-layer tube or plate sedimentation tanks used for this purpose.

Plate sedimentation tanks have a number of parallel plates, set under angle in a case. Water moved between plates and precipitate slips down, into sludge receiver. The effectivity of purification is 80 ÷ 85 %. Purification from a precipitate carried by water flow (fig. 4.10).

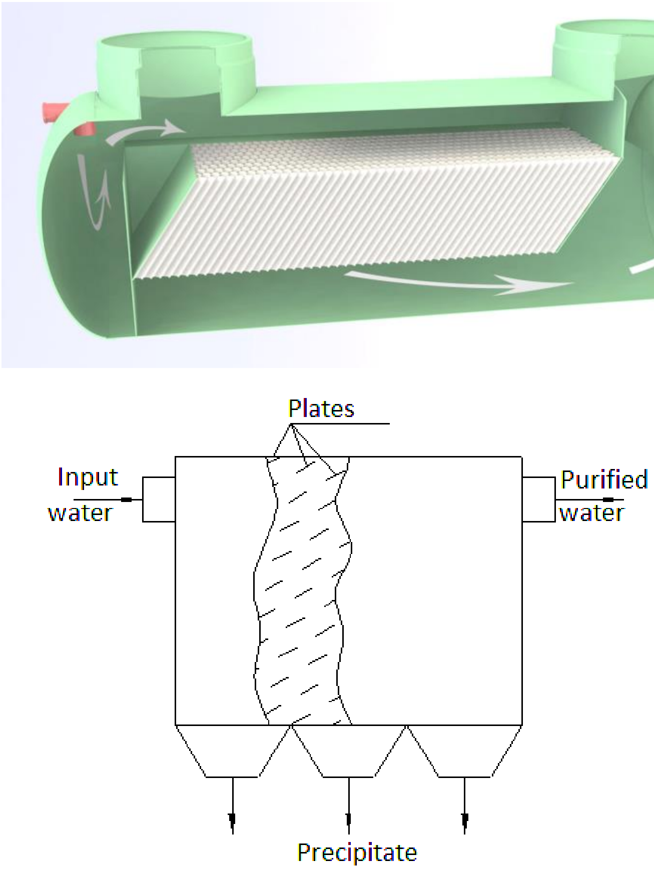


Figure 4.10 – Thin-layer sedimentation tank

Questions for self-control to the section 4

1. What water treatment methods related to mechanical?
2. Name the classification of water of different origin by muddy.
3. What the aim of scoop setting?
4. What the role of grids and nets?
5. Explain assumption for Stocks equation.
6. Characterize the term «hydraulically particle size», explain how does it determined.
7. Explain the construction and work principle of sand-traps.
8. Give schematically a construction of vertical sedimentation tank.
9. For what conditions of water creaming do horizontal sedimentation tanks used?
10. What are radial sedimentation tanks constructively?

SECTION 5 IMPURITIES REMOVING FROM WATER BY FILTRATION

5.1 The process of suspension delaying at slow and rapid filtration.

5.2 Filters with grain backfilling.

  5.2.1 Filters classification by different signs.

  5.2.2 Requirements to grain backfilling.

5.3 Main elements, filters constructions and technological parameters of its working.

5.1 The process of suspension delaying at slow and rapid filtration

Filtration is a final stage of lighting (or only do). Non-creaming filtration used for waters with muddy to 50 mg/L.

Filtration method with pre-creaming keeps to get water of any necessary lighting degree [2, 3].

Filtering material can be nets, cloth, grain backfilling. In water preparation schemes grain backfilling is widely used. The process of suspended and hard dispersive impurities delaying on grain backfilling occurs differently – depending on flows rate.

It can be differed:

- slow filtration – $u = 0{,}1 \div 0{,}3$ m / h;
- rapid filtration — $u = 5 \div 12$ m / h;
- ultra-rapid filtration — $u = 30 \div 100$ m / h.

In the process of water filtering through a layer of grain material, depending on ratio of particles size and grains of filtering backfilling, 3 types of filtering can be differed:

1) delaying of impurities on the surface of filtering material (film filtration);
2) delaying of impurities in pores of filtering layer (volume filtration);
3) Concurrent delaying of impurities in film and its accumulation in pores (mixing filtration).

Film filtration lies in the base of slow filtration.

At the filtration of water through a grain backfilling with slow rate so-called bio-film formed on grains. After several days' water dumped after filtration outdoors.

Suspension delaying happens on self-bio-film. When filtering bio-film increases, suspension delaying happens between grains. Herewith, following forces effect on particle:

1) adhesion forces (sticking) between particle and backfilling grains;
2) oppositely effecting forces of flow, seeking to tear suspension particle from grain backfilling (suffusion - tearing of earlier delayed particle and transferring it by hydrodynamic flow forces into bottom layers of backfilling).

Filtration rates established experimentally for providing of the best removing of suspended particles, staying time of water in apparatus and a type of backfilling.

5.2 Filters with grain backfilling

5.2.1 Filters classification by different features

In water preparation technic filters with grain backfilling used the widest. Filters with grain backfilling classified by following main features:

1) by filtration rate:

- slow (0,1 ÷ 0,3 m/h);
- rapid (to 25 m/h);
- ultra-rapid (to 100 m/h);

2) by working pressure:

- opened gravity (or free-flow) — pressure difference made by difference of water levels on filter and in reservoir of clear water;
- pressure — work under pressure making by pump (to 0,6 MPa);

3) by quantity of filtering flow directions:

- one-flow — filtering conducted up-down;
- two-flows — concurrent moving carried in two directions;

4) by filtering material size:

- fine-grained filters – grains size 0,1 ÷ 1,0 mm;
- medium-grained — grains size 1,0 ÷ 2,2 mm;
- hard-grained — grains size to 40 mm;

5) by quantity of filtering layers:

- one-layer;
- two-layer;
- multi-layer.

The main constructive elements of filters: corps, drainage, incoming and out-coming trays, tubes and fitting.

Some requirements nominated to filters construction:

1) the main – filtering should have implemented in direction from a layer with larger size backfilling to a later with a smaller size backfilling;
2) filters construction should provide even water distribution around all surface, this reached by different types of drainage systems. Drainage system should provide also intensive and effective filter washing.

Filtering cycle consists of following stages: filtration, loosening, washing (takes about 7 hours).

5.2.2 Requirements to grain backfilling

Following requirements nominated to grain backfilling:

1) particle size composition:
  - in slow filters 0,3– 40 mm;
  - in rapid filters 0,5– 2,2 mm;

2) hydrophobic properties of grains surface;

3) porosity of the material;

4) chemical resistance to water;

5) mechanical abrasion strength;

6) availability and, if possible, low cost.

Following substances can be used as backfilling material: sand, quartz sand, dolomite, keramzit (clays, slate, ash calcined and granulated), anthracite, crushed stone, gravel, marble chips, crushed glass, blast furnace slag, polystyrene etc.

5.3 Main elements, filters constructions and technological parameters of its working

Opened gravity are rapid opened filters used at high water flows. Presented by reservoirs of rectangle form in plan.

Drainage system located in bottom part, providing even water out-coming from filter and even washing of filter (fig. 5.1).

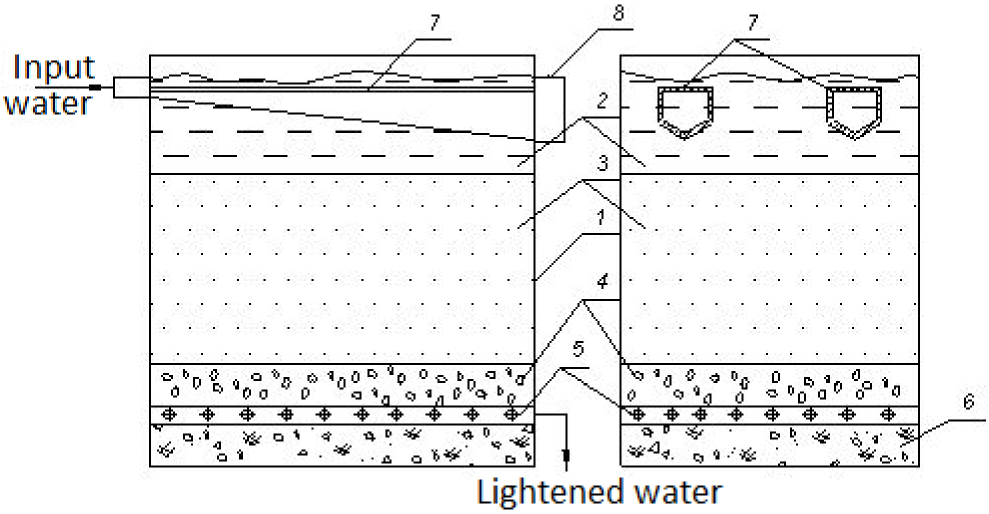


Figure 5.1 – The scheme of opened gravity filter

1 − corps; 2 − water layer above filtering material; 3 − filtering sand layer; 4 – supporting gravel layer; 5 – drainage layer; 6 − anthracite, crushed stone, gravel layer − this layer plays a role of supporting layer; 7 − washing troughs; 8 − overflow pockets

In filtration process water passed through filtering backfilling and supporting layers, and then incomes the distribution system and then into reservoir of clear water. During filter washing water come into distribution system and then up-down into filtering layer, expanding it (rises grains). Sand grains, moving chaotically, self-shocked with each other, herewith pollutions, adhering on it, rubbed away and removed with washing water. Reaching the upper edge of the washing troughs, washing water together with washed pollutants from filtering material, overflow into troughs, and from them into side pocket and out-coming into accumulative facilities of washing water recycling. Troughs located on such altitude for incoming of only pollutions washed from sand, but not sand.

For filters characterization, such indicator used as pollution capacity – the quantity of pollutions, delayed by 1 m^2 of filtering layer surface in one time.

The necessary filters element is drainage system, providing even distribution around all area of filtering surface, even gathering and out-coming of filtered water in one-flow filters. Slotted pipes, caps, porous ceramic plates, porous concrete used as drainage.

Cap drainage is the most often used (fig. 5.2).

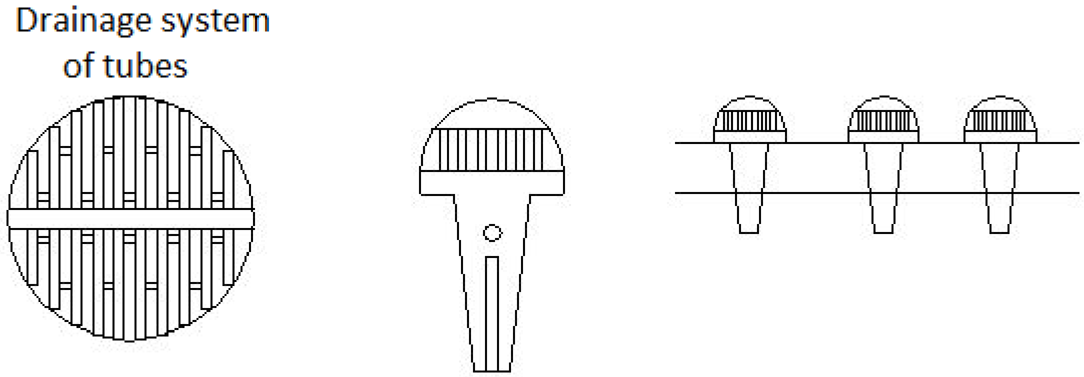


Figure 5.2 – Drainage cap system

One square meter contains 35 ÷ 50 caps. Caps produced of plastic, porcelain, stainless steel.

Pressure filters widely used in industrial water preparation for water lightening after treatment by coagulants, and also at non-reagent water lightening with a content of suspended substances to 20 mg/L. They presented by closed steel cylindrical reservoirs with spherical bottoms. Work pressure 0,4 ÷ 0,6 MPa. Vertical and horizontal pressure filters used in practice (fig. 5.3).

The main overall dimensions:

- filter’s diameter — 1000 – 3400 mm;
- building height — to 4 m;
- thickness (height) of filtering layer — 1,2– 2 m.

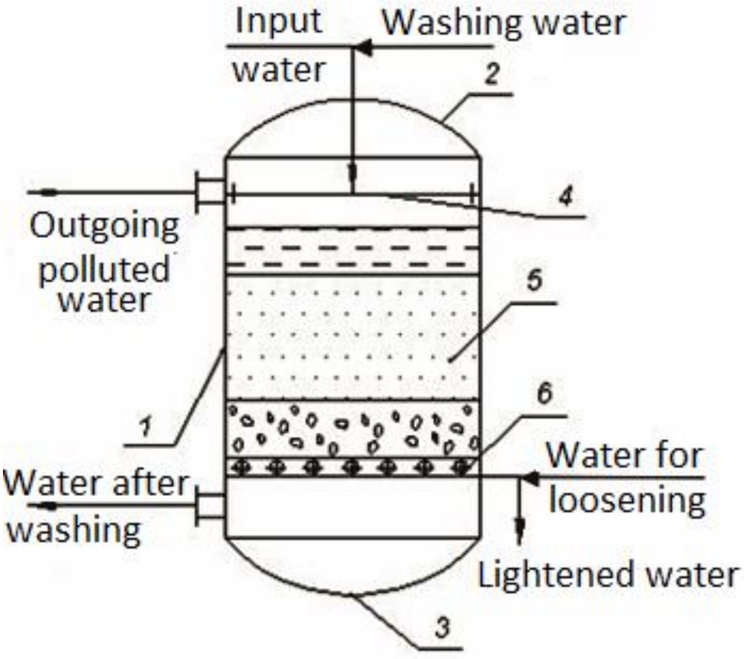


Figure 5.3 – The scheme of vertical pressure filter

1 – corps; 2 – overhead bottom; 3 – underneath bottom; 4 – overhead distribution device; 5 – filtering working later; 6 – drainage-distribution device

Approx. 3 % of water spent for filter washing – for self-need.

Horizontal filters used for high productivity (fig. 5.4).

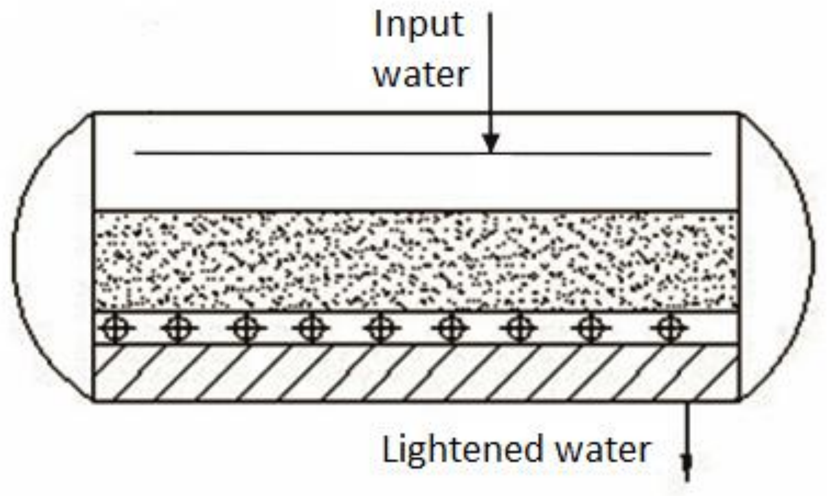


Figure 5.4 – The scheme of horizontal pressure filter

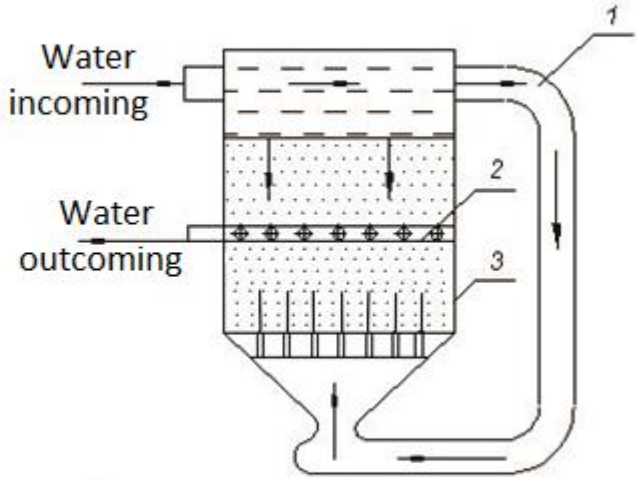


Figure 5.5 – Two-flows filter

1 – tube-line of water serving; 2 – overhead drainage-distribution system; 3 – underneath distribution device

A part of water incoming through a vertical sand layer, another part – around a pipe-line (pos. 1) incoming through an underneath pallet up-down, filtered water outcome through a drainage.

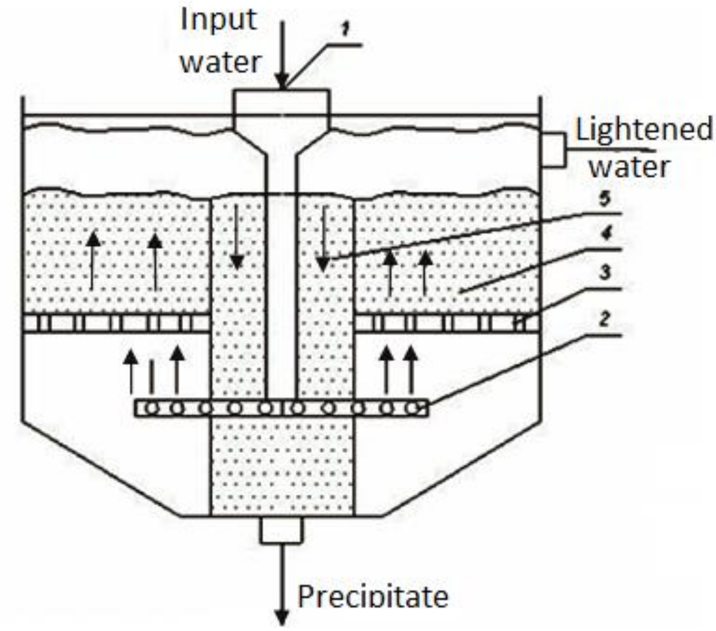


Figure 5.6 – The scheme of lightening with suspended layer of sludge

1 – air separator; 2 – feeding distribution device (drainage for input water); 3 - failure grill; 4 – layer of formed precipitate; 5 – tube for sludge out-coming

Filters (lighters) with suspended layer of precipitate – precipitators and accelerators – filtering material is precipitate layer formed earlier – these apparatuses of cylindrical form with conic bottom (fig. 5.6).

Water incomes to supply tube (pos. 2) through an air separator (pos. 1) and through a drainage system passes up-down through a layer of precipitate formed earlier, consisted of flakes mass suspended in up-flow. They moved, but all layer is unmovable in general. A volume of precipitate layer isn't increased, because continuous removing of precipitate occurs into a seal.

Questions for self-control to the section 5

1. What kinds of filtration can be differed for filtration rate?
2. Name 3 kinds of water filtration through a layer of grain material.
3. What forces effect on particle at slow filtration?
4. What main features are filters with grain backfilling classified by?
5. What stages are filtering cycles consisted of from?
6. Name requirements nominated to grain backfilling of filters.
7. What materials used as grain backfilling?
8. Explain the principle of opened gravity filters forking?
9. What types of drainage systems used in filtration apparatuses?

SECTION 6 REMOVING FORM WATER SUSPENDED AND FLOATED PARTICLES BY FLOTATION

6.1 The essence of method and the field of its using.
6.2 Physically-chemical bases of flotation process. Factors affect an effectivity of process.
6.3 Principal schemes of pressure flotation.
6.4 Hardware design of the process: impeller floater, floater of «Aeroflotor» system, electrical floater, floaters with porous caps.

6.1 The essence of method and the field of its using

The method exists in two modifications – non-reagent and reagent. It used for removing of hydrophobic impurities of the 1st and the 2nd group from water and used in following schemes:

1) for purification of waters, containing different oil products, fats, oils. These are productions of organic, cellulose, skin plants, textile and food enterprises, perfumer and pharmaceutical industries;
2) for removing of effective sludge after secondary sedimentation tanks in schemes of biochemical purification;
3) currently for natural waters preparation;
4) there are examples of using for removing of some radioactive substances;
5) for removing of heavy metals from wastewaters.

Usually, all of 3 phases take part in flotation process: solid, liquid and gas-like [1-2]. Interaction exists between these particles:

1) adhesion of hydrophobic particle and gas bubble (air);
2) adhesion forces between gas and liquid, namely forces of surface tension.

The essence of flotation is in following: forming of complex hydrophobic particle – gas bubble happens by adhesive forces. Adhesive work is a function of liquid surface tension and wettability of hydrophobic particle by liquid. A complex hydrophobic particle – gas bubble formed and risen on liquid surface, namely floats.

Hydrophobicity (or hydrophilicity) of particles characterized quantitatively by the value θ — wetting contact angle (fig. 6.1).

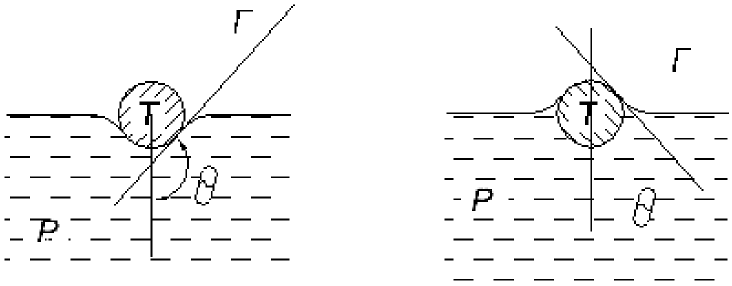


Figure 6.1 – The graph image of particles hydrophobicity and hydrophilicity

$\theta > 90^0$ – hydrophobic (non-wetting) particle;

$\theta < 90^0$ – hydrophilic wetting particle

6.2 Physically-chemical bases of flotation process. Factors affect an effectivity of process

The effectivity of flotation depends on:

1) size and wettability (hydrophobicity) of particles removed from water;
2) nature of self-liquid (a value of surface tension);
3) quantity and sizes of gas-phase bubbles.

Naturally, particles nature can be regulated changing its hydrophobicity or hydrophilicity, bringing special substances – flotation reagents, but trying to do this at WW purification – not bring secondary pollution. In water preparation processes gas bubbles quantity and size regulated.

Necessary concentration of air bubbles in water can be provided by more methods:

1) a process of water saturation by air and flotation charged at different pressures. Pressure changing causes uniform allocation of air bubbles in whole volume of water;

2) air desperation carried by mechanic method in floaters with impeller or mixers;

3) necessary size and quantity of air bubbles provided by using membranes and porous materials;

4) chemically – gas phase formed by chemical reaction or biochemical processes.

6.3 Principal schemes of pressure flotation

By the method of water saturation by air pressure and vacuum flotation can be classified. At pressure flotation water saturation by air under the pressure 0,3 ÷ 0,5 MPa, but the process happens at atmospheric pressure. At vacuum flotation water saturated by air under atmospheric pressure, but the process charged at dilution 200 ÷ 300 mm Hg.

In industry, the most common is ***pressure flotation***, it has many advantages – equipment is simpler and reliable in exploitation. This method keeps to carry water purification with high content of suspended substances 4 ÷ 5 g / L (the concentration of oil products > 2 g / L). Herewith residual concentration of oil reaches 10 ÷ 15 mg / L, sometimes for increasing purification degree coagulants can be added to water.

The advantages of ***vacuum flotation*** are: gas bubbles formed with particles happens in a quiet environment (probability of destroying aggregates bubble – particle is minimal).

The disadvantages – minor degree of water saturation by gas bubbles, that’s why this method can’t have used at high concentration of suspended substances (not more 250 ÷ 300 mg / L); necessity to build hermetically closed floaters and to put scrapper mechanisms in it.

Three kinds of pressure flotation schemes can be differed:

- direct-flow (fig. 6.2);
- partly direct-flow (fig. 6.3);
- recycling (fig. 6.4).

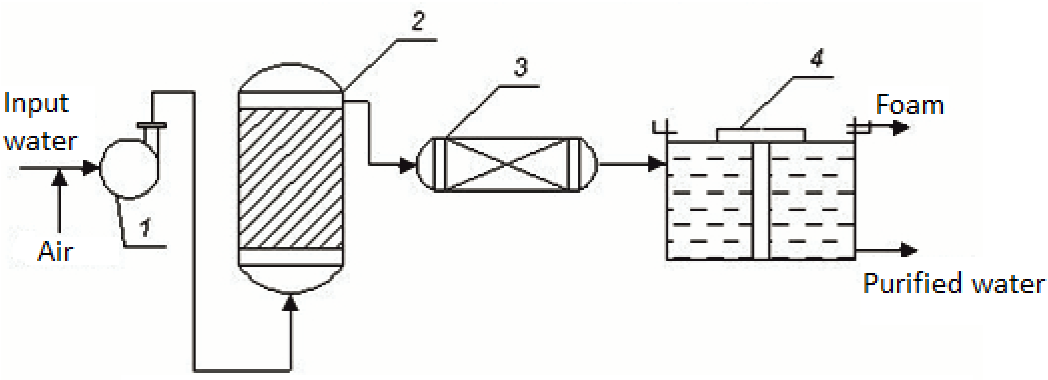


Figure 6.2 – The scheme of pressure direct-flow flotation

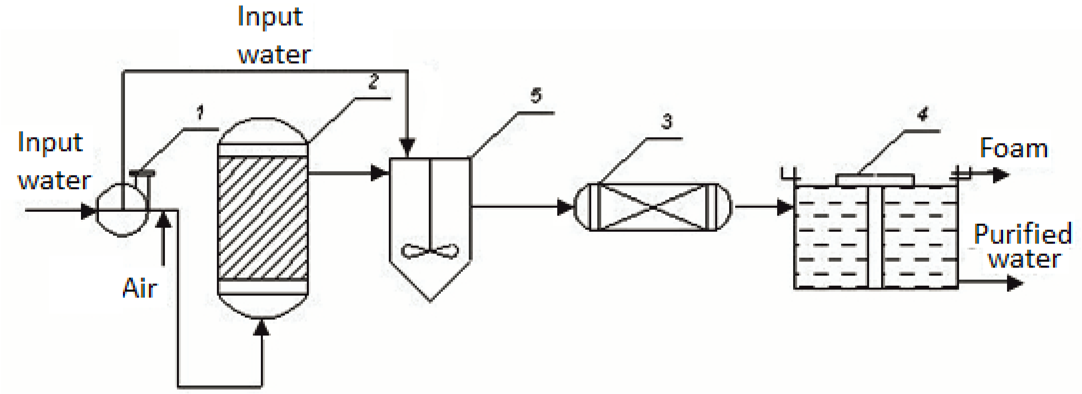


Figure 6.3 – The scheme of pressure partly direct-flow flotation

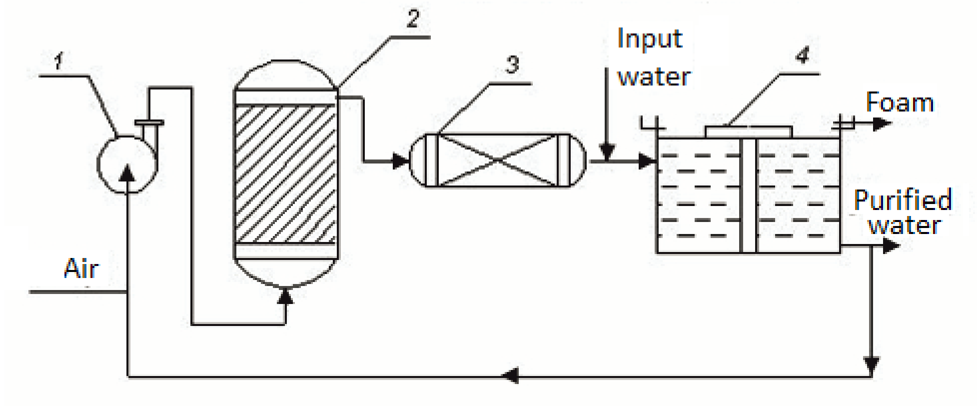


Figure 6.4 – The scheme of pressure recycling flotation

1 — pump; 2 — pressure tank (saturator); 3 — reducing valve;
4 — floater; 5 — mixer

Among presented schemes the first (fig. 6.2) is the simplest. Input water saturated by air and passed into pressure reservoir (saturator) (pos. 2), where air dissolved under pressure, and insoluble bubbles outcome from water. In the case of using reagents for WW purification (coagulants, flocculants) flakes forming happens in saturator. Then water passes through a reducing valve (pos. 3), a pressure decreased to atmospheric and directs to flotation device (pos. 4).

The disadvantages of this scheme: increased emulsification of oil products and resins, present in input water at pumping by centrifugal pumps, and also necessity to pump overall water volume. However, this scheme used at many homeland and foreign enterprises. The productivity of pressure flotation installations is different – from 5 ÷ 10 to 1000 ÷ 2000 m^3/h.

Staying time of water in a pressure reservoir 1 ÷ 4 min., in floater 10 ÷ 20 min.

The scheme, presented by fig. 6.3, is less common, than 1st, although it is more economy. From 30 to 70 % of input water volume incoming to saturator. The most often used, when coagulation stage take place in water preparation scheme.

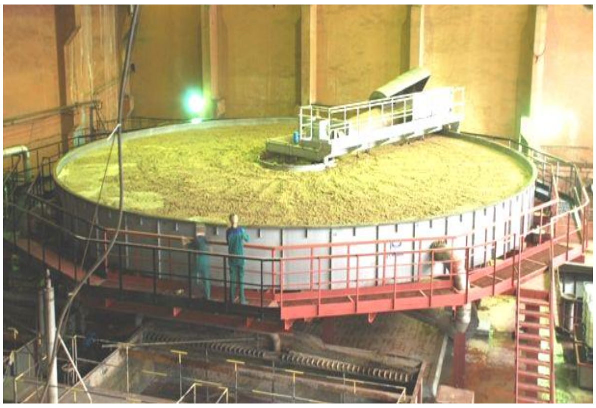
By the 3rd scheme (fig. 6.4) a part of water from floater submitted by pump into a pressure tank. The advantages of scheme: precipitate flakes destroying or increased emulsification of oil products and resins in centrifuged pumps doesn’t happen in reducing valve. For effective water purification from 20 % to 50 % of purified water volume submitted to recycling.

The disadvantages of this scheme: pumping water volume decreasing happens by purified water recycling and, consequently, increasing volume and quantity of flotation installations.

Foam layer formed in the flotation purification process, its quantity depends on character of WW impurities.

6.4 Hardware design of the process: impeller floater, floater of «Aeroflotor» system, electrical floater, floaters with porous caps

Floaters of several types used in practice: impeller (fig. 6.5), with porous caps (fig. 6.6), «Aeroflotor» (fig. 6.7).



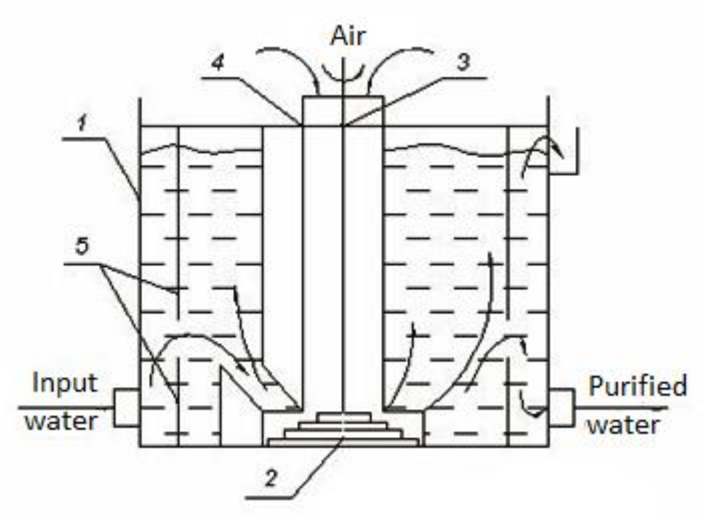


Figure 6.5 – The scheme of impeller floater

1 – floater's corps; 2 – impeller; 3 – axle; 4 – tube; 5 – inside partitions

Mechanic desperation of air in floater provided by turbines of pump type – impellers, presented by disks with radial up-returning blades. At rotation of impeller numerous small vortex flows formed in liquid, dividing on bubbles of some size. Grinding degree and flotation effectivity depend on impeller's rotation speed, namely, higher speed – smaller bubbles and higher flotation efficiency.

Input water incomes to reception pocket of floater and gets to impeller, rotating in bottom end of axel, around pipeline. An axel concluded into pipe (air sucked through it). Decreased pressure zone formed at impeller rotating. High degree of water saturation by air is necessary for flotation (0,1 ÷ 0,5 air volumes per 1 volume of water).

Floater usually consists of several successively connected cells.

Floater with porous caps presented in fig. 6.6.

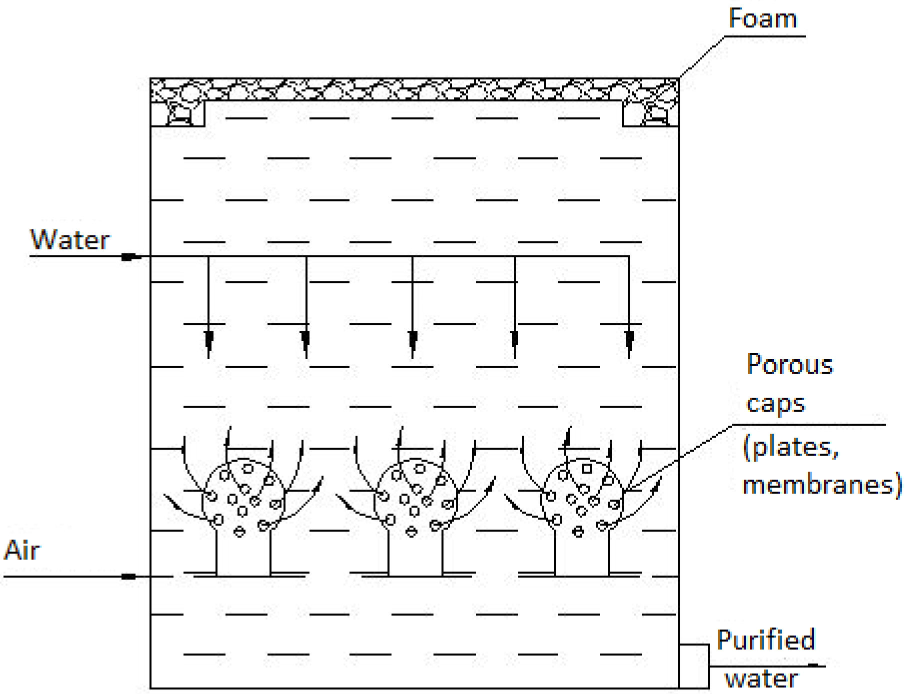


Figure 6.6 – The scheme of floater with porous caps

At air transmission through porous ceramic plates or caps small bubbles formed. WW inputting from above, and air – underneath through porous caps. Foam overflowed into ring gutter and separated from it.

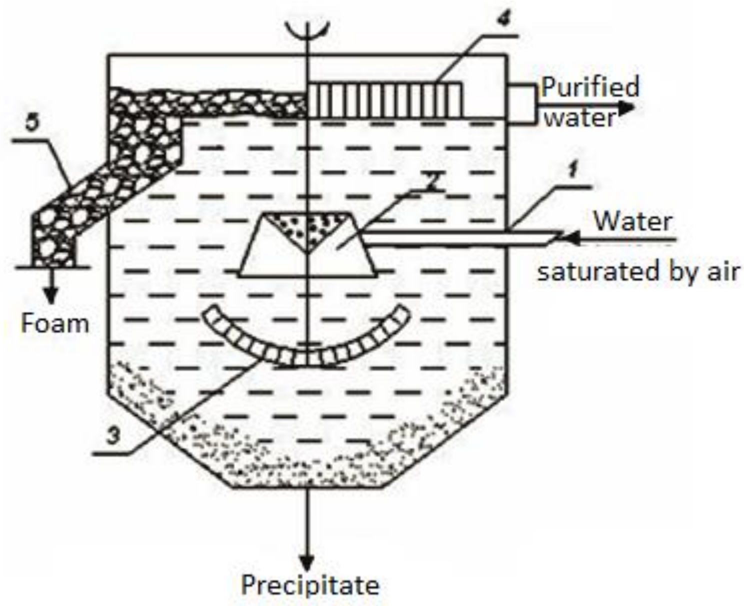


Figure 6.7 – The floater of «Aeroflotor» system

1 – pipeline, incoming water saturated by air; 2 – distribution cell; 3 – bottom scrapper mechanism; 4 – upper scrapper mechanism; 5 – pocket for foam outgoing

The advantages: construction simplicity, high degree of water saturation by air, low energy consumptions.

The disadvantages: often clogging and overgrowing of porous material holes.

The floater of «Aeroflotor» system presented in fig. 6.7.

The advantages: has high effectivity of floated and sediment particles removing from water. More even distribution of air around the intersection of device.

The disadvantages: high energy consumption and often breakages.

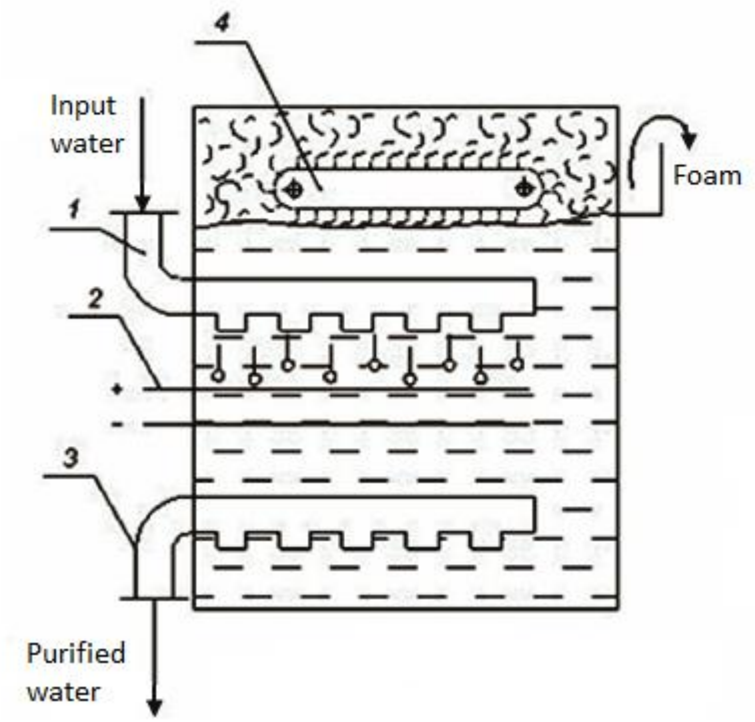


Figure 6.8 – Electric floater

1 – pipeline of input water entering; 2 – electrodes; 3 – pipeline of purified water outcoming; 4 – upper scrapper mechanism

Electric floater construction presented in fig. 6.8.

Water saturation by gas bubbles happens by electric chemical processes.

The disadvantages:

- increased energy consumptions;
- explosive dangerous ($H_2 + O_2$);
- low degree of using electrode metal (30 ÷ 60 %).

The advantages:

- full automation of the process;
- compact equipment.

Electrodes produced from sheet stainless steel. If electrodes would manufacture from metals: Fe, Al, Cr, Zn, Ni, Mo etc., electrochemical removing of these metals, dissolved in water, will occur and the method will have name electric coagulation.

The flotation method has following advantages:

1) higher water purification degree (85 ÷ 95 %), than at mechanic purification;
2) foam – sludge formed with lower sludge;
3) installations are more compact, than at mechanic purification

Questions for self-control to the section 6

1. Name the essence of flotation.
2. In what schemes of water preparation is flotation used?
3. What kinds of interaction exist between particles in flotation?
4. What indicator is particles hydrophobicity or hydrophilicity determined by?
5. Name factors of flotation effectivity.
6. What methods can necessary concentration of air bubbles in water have provided by?
7. Explain the difference between pressure and vacuum flotation.
8. Analyze schemes of pressure flotation.
9. Explain work principles of impeller floater.
10. What advantages and disadvantages inherent by floaters with porous caps?
11. Characterize the principle of floater «Aeroflotor».
12. What advantages and disadvantages inherent by electric flotation installations?

SECTION 7 COAGULATION METHODS OF WATER PURIFICATION FROM SUSPENDED SUBSTANCES

1. The essence and scope of the method.
2. Physically-chemical bases of water impurities coagulation.
    - 2.1 Colloidal systems and its properties.
    - 2.2 Kinetic and aggregative stability of colloidal systems.
    - 2.3 Hydrolysis stages and micelle's structure.
    - 2.4 The theory of ion stabilized lyophobic soles stability – DLVO theory.
3. Coagulants using for water purification.
4. Requirements to coagulants.
5. Coagulant dose choosing.
6. Flocculants are used for water purification.
7. The schemes of water lightening by coagulation and its apparatus design.

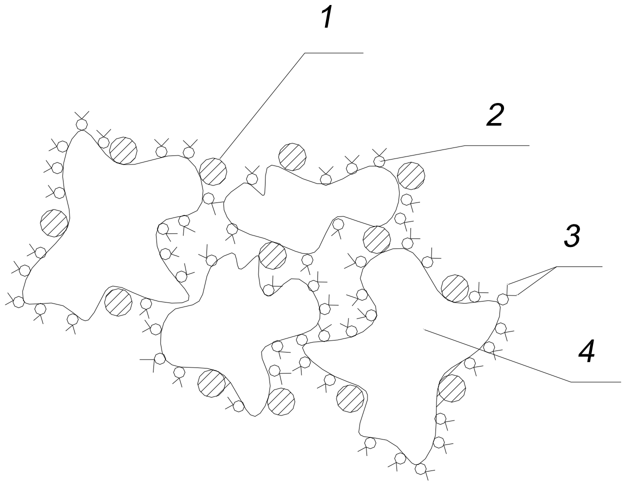
7.1 The essence and scope of the method

In English *coagulation* «adhesion». The method used for impurities of the 2nd group removing from water (colloidal dispersion degree).

A colloid – Greece word, kola – glue, eidos – kind.

A dispersion – lat. – diffused, scattered.

The essence of coagulation is in making special reagents into water, named coagulants, these substances capable to form colloidal systems in water. They form solid phase with very developed surface. On this surface by adhesion forces, sorption, and mutual co-precipitation, colloidal impurities of water fixed, form aggregates. Aggregates sediment under gravity forces and then removed from water. The method used for suspended substances of the 2nd group of Kulskiy removing from water ($10^{-5} \div 10^{-6}$ cm) as from natural, as from WW at any concentration (content) in water (fig. 7.1).



1 – clay particles;
2 – coagulant particles (flakes);
3 – humic and fulvic acids;
4 – captured water.

Figure 7.1 – The schematic image of colloidal particles coagulation from water

Colloidal particles are small aggregates of crystal or amorphous structure. By large specific surface area of colloidal particles, they have very significant surface energy, and, so, high sorption capacity.

7.2 Physically-chemical bases of water impurities coagulation

The colloidal systems are emulsions, foams and also fog. Colloidal systems classified by aggregate state. If dispersion phase is a gas, they are aerosols, if dispersion phase is a liquid – lio-sols, if dispersion phase is water - hydrosols [1-2, 4, 13-14].

7.2.1 Colloidal systems and its properties

Colloidal systems properties:

1) colloidal solutions with small size particles, prone, as molecules, to thermal Brownian motion;
2) colloidal particles capable to dissipate light – opalescence effect – herewith solution changes its color;
3) colloidal particles have complex micellar structure and charge.

7.2.2 Kinetic and aggregative stability of colloidal systems

Dispersed colloidal and suspended particles of natural waters impurities, in most cases, have same charges, causing appearance of intermolecular repulsion forces and aggregative stability.

Particles of rather high mass ***sediment*** by gravity forces.

Small particles serve even distribution of particles around whole volume during long-term – ***kinetic stability of system***.

Herewith, if particle (aggregates) size isn't increased – ***aggregative stability*** of colloidal system (namely particles resist sticking).

Colloidal systems have stability, namely are in this state for a long time.

Following stability kinds can be differed:

1) resistance to sedimentation – kinetic stability;
2) resistance to aggregate state changing (constant of sizes and dispersion degree) – aggregative stability.

The 1st stability caused by small particle size. The 2nd caused by charge presence in colloidal particles.

Colloidal particle charge connected directly with properties of dispersion phase surface, can adsorb ions of different charge. Ion adsorption on particles surface leads to bond polarization and, by high range order, the nearest particles to these ions polarized in water.

This leads to forming of hydrate (solvate) shells. Hydrate shells form steric factor, preventing particles approach.

7.2.3 Hydrolysis stages and micelle's structure

1) Coagulant hydrolysis leads to forming of solid phase flakes with developed surface. Electric double layer is formed (EDL):

$$FeCl_3 + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ + 3Cl^-.$$

2) Adsorption of potential-determining ions on solid phase surface and enlarged particle core forming:

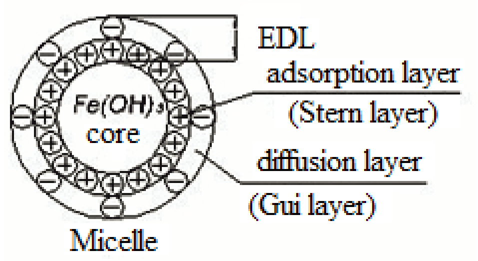
$$\underbrace{\{[Fe(OH)_3]nH^+\}}_{\text{core}}$$

3) Micelle formation:

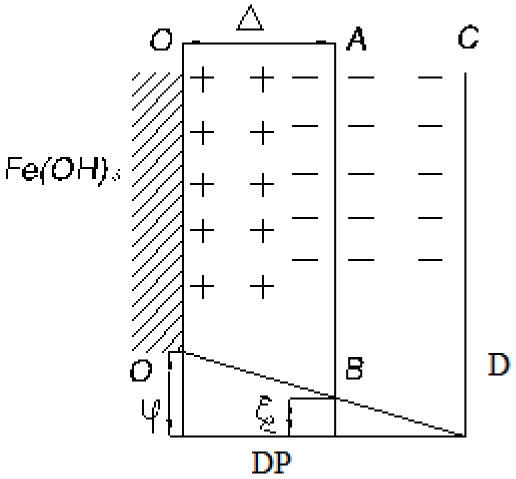
$$\underbrace{\{[Fe(OH)_3]nH^+\}}_{\text{core}}\underbrace{Cl^-}_{\text{EDL}}$$

EDL — electric double layer.

Micelle = core + EDL



Particle’s core has charge, meeting a mark (charge) of potential forming ion, and micelle (aggregate in general) – electric neutral.



Colloidal particles, as noted, are in constant motion, herewith, a part of solution, surrounding particle, captured by it and moves as thin layer with it.

Line O – O presents surface of solid particle with positive ions, adsorbed on it.

Stern layer located directly near core, then counterions of diffusion layer, limited by C – D line.

Width of Δ layer – sliding surface.

Adsorption and diffusion layer form EDL (electric double layer).

Heterogeneous systems with large general phase surface has high free energy excess and arbitrarily seeks to its decreasing. In waters (natural and waste) in colloidal-dispersion state substances of different nature can be at the same time. Different surface tension inherent it. Colloidal-dispersion particles take charge by ion adsorption, a mark of charge responds a mark of adsorbed (potential forming) ions. An environment, surrounding particle, gets charge of opposite ion, namely EDL forms, caused potential difference between particle and environmental charge. Ion lining of EDL gets diffuse structure by diffusion and mutual repulse of excess ions. Colloidal particle together with adsorption and diffusion layer named ***micelle***.

The effectual potential difference between moveable colloidal particle (micelle) and environment, establishing, named electrical-kinetic (dzeta-) potential, moreover, ξ less than φ.

The more counterions fall together with particle into liquid layer, the ξ- potential is less.

Micelle state, in which ξ- potential is 0, named isoelectric, herewith moveable particle includes such quantity of counterions, sum of charges of which is sum of adsorption layer charges.

ξ - potential (DP) — the main characteristic of colloidal systems. Higher ξ- potential responds to more stable colloidal system.

7.2.4 The theory of ion stabilized lyophobic soles stability – DLVO theory

For breaking system's stability, it's necessary to decrease its charge. Colloidal systems can be hydrophilic and hydrophobic. In natural waters colloidal systems presented, in generally, by hydrophilic particles. In WW with equal probability hydrophilic and hydrophobic particles can be presented.

The clear single theory of ***hydrophilic*** colloidal systems calculating is absent currently.

For hydrophobic the theory DLVO exists – by scientists first names: Deriagin, Landau, Vervey, Overbeck – the theory explains the mechanism of lyophobic soles coagulation for two edge cases – high- and low-powered systems. By quantitatively theoretical calculations ξ- potential, responding coagulation, can be determined.

The base of theory is following: intermolecular attraction and repulsion (ionic electrostatic or electrostatic nature) forces effect between particles surfaces. The last caused by presence solvate or adsorptive-solvate layer on particles surface. Depending on balance of these forces in thin liquid layer between bodies coming near, there is or positive disjoining pressure, preventing its connection, or negative, causing to layer thinning and contact forming between particles.

The main postulates of the theory DLVO

1) Lyophobic sols coagulation can be caused by any electrolyte.

2) Coagulating will be, naturally, ion opposite to a mark of colloidal particle.

3) In low-charged systems (small values of ξ - potential) coagulation will by the neutralization mechanism.

4) In high-charged colloidal systems (high values of ξ - potential) coagulation will by the concentration mechanism – by pressuring of diffusion layer, namely increasing of coagulating ion concentration in diffuse layer causes to decreasing its thinning and, so, - a potential by ion spheres pressuring.

7.3 Coagulants using for water purification

The main industrial coagulants are alumina and iron compounds — $FeCl_3$, $Fe_2(SO_4)_3$, $FeCl_2$, $AlCl_3$, $Al_2(SO_4)_3$ (recently the last was the most often used coagulant).

$Al_2(SO_4)_3$ producing from bauxites (alumina Al_2O_3) or from Al-containing wastes.

The following reaction exists at hydrolysis:

$$Al_2(SO_4)_3 + 6H_2O \leftrightarrow 2Al(OH)_3 \downarrow + 6H^+ + 3SO_4^{2-}.$$

A solubility product (SP) ($Al(OH)_3$) = $1{,}9 \cdot 10^{-33}$, the difference – works good at presence of natural color, pH limit is 7.5 ÷ 7.7, self $Al(OH)_3$ precipitated at pH interval 4,5 ÷ 12. Presented mechanism is not entirely accurate, because different hydrolysis products forming is possible, for example, $Al_2 (OH)_2^{4+}$, $Al_4 (OH)_8^{4+}$, $Al_2 (OH)^{5+}$, $Al_{13} (OH)_{34}^{5+}$ etc.

Until recently $Al_2(SO_4)_4$ was the single coagulant at water preparation.

According to THE STATE STANDARD for drinking water the residual content of Fe – 0,3 mg/L, of Al – 0,1 mg/L.

The disadvantages: coagulant based on Al works bad at low temperatures. This is due to a high hydration. A precipitate isn't very dense (density is 1,5 time lower, than in precipitate on Fe-coagulant).

The producer – PU «Chemprom».

Coagulants based on Fe salts

$FeCl_3 \cdot 6H_2O$ got by iron shave chlorination (industrial wastes).

— synthesized by chlorination of iron filings (industrial wastes). $SP(Fe(OH)_3) = 3{,}8 \cdot 10^{-38}$, precipitation pH 4÷9.

The advantages: forming rapidly sediment precipitate.

Environmental pH has little effect on $Fe(OH)_3$ precipitation.

The Iodic-bromine plant (Armyansk) and «Coagulant» plant produce it in Ukraine.

Following substances

are rarely used: $Fe_2(SO_4)_3 \cdot 9H_2O$ и $FeSO_4 \cdot 7H_2O$.

$$FeCl_3 + 3H_2O \leftrightarrow Fe(OH)_3 + 3HCl;$$

$$FeSO_4 + 2H_2O \leftrightarrow Fe(OH)_2\downarrow + H_2SO_4.$$

Effectually, the mechanism is more difficult.

$$4Fe(OH)_2 + O_2 + 2H_2O \leftrightarrow 4Fe(OH)_3\downarrow.$$

The substantive disadvantage of coagulation based on Fe salts – non-uniform precipitation of $Fe(OH)_3$ in volume, namely more accurate dosing should have carried out.

One's more important moment of coagulation is forming acids (H_2SO_4 i HCl) by hydrolysis. Even if natural waters have little alkaline reserve, a coagulation process is charged at the same time with adding alkaline into water for preventing precipitates

($Al(OH)_3$ or $Fe(OH)_3$) destroying, namely equilibrium moving to reverse side ($Ca(OH)_2$, Na_2CO_3, NaOH are added).

Alumina and iron hydroxides have been formed, together with substances, removing from water, is sludge, polluting environment.

The substantive disadvantage of coagulation is some deficit and cost of coagulants and also losing Fe and Al compounds with sludge.

Here two decisions can take place:

1) finding and producing new kinds of coagulants;
2) possible regeneration of Fe and Al compounds from sludge has been formed.

Recently hydroxyl-chlorides and sulfates of Fe and Al – $[Al(OH)_{3-x}Cl_x]_n$ and $[Fe(OH)_{3-x}Cl_x]_n$ are also used.

These coagulants have series of advantages:

- wider interval of the temperature and precipitating pH;
- they are got from wastes (low cost).

These coagulants had been used in Chernobyl, by co-workers of CTF NTUU «KPI».

Mixed coagulants are also used, consisting salts and Fe, and Al in its content.

At adding coagulants into water, a decreasing of system aggregative stability by electrolyte action (incoming salt), ionic sorption on particles surface and forming new insoluble compound with concentration, much higher, than its solubility, happens, as noted.

Solid phase excretion (coagulator) from supersaturated solution (crystallization) proceeds in three main stages (fig. 7.2) [1, 15]:

1) incubation period;
2) increasing solid phase particles (a main crystallization stage);
3) solid phase aging.

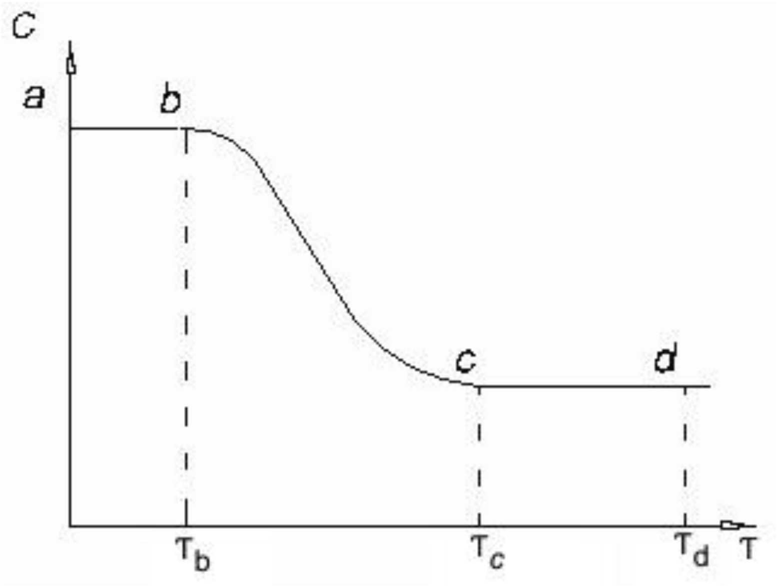


Figure 7.2 – The changing of coagulating (crystallized) substance concentration in time

C – the concentration of substance, crystallized from solution; τ – time

An area *a – b* responds incubation period of crystallization. A concentration of coagulating substance in this area isn't changed practically, because of hidden processes.

An area *b – c* responds a period of mass crystallization (coagulation). A period of time $\tau_b - \tau_c$, depending on conditions, provides a main growth and forming micelles.

An area c – d responds slow crystallization. The processes of aging or re-crystallization of solid phase mainly respond this area.

A kinetic of coagulation (crystallization) process depends on many factors:

- quantity and size of crystal forming centers;
- oversaturation degree of solution;
- temperature;
- reagents mixing effectivity;
- content of input water and other factors.

A sludge, has been formed (($Me(OH)_3$, $CaCO_3$, $Mg(OH)_2$)), has significant moisture – 96 ÷ 99,9 %.

Friable space structure of precipitate flasks contributes significant water quantity.

7.4 Requirements to coagulants

1) At adding to water these substances should form hydrophobic colloidal systems.

2) A solid phase forming should have minimal solubility, namely has as low as possible value SP.

3) Self coagulants and all intermediate and finish products shouldn’t be toxic.

4) New-formed solid phase should have as much as possible density for rapid precipitate forming, should delay minimal quantity of water.

5) Preferably, coagulants effect at wider temperature intervals, environmental pH, water content, color etc.

6) Coagulants should have got from available materials and to have low cost.

F*act*ors effect on coagulation effectivity:

1) Environmental pH (alkaline reserve of water). For rapid and full coagulant hydrolysis process flowing, the determined alkaline reserve of water is necessary, namely, presence some quantity of OH^- - ions in it, binding hydrogen ions, outing at salts hydrolysis:

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O.$$

By buffer system of HCO_3^- - ions and CO_2 (carbon dioxide equilibrium) presence in water with the pH value approx. 7, water pH at coagulants hydrolysis is changed very little in most cases.

2) The process temperature during all three stages of micelle forming .

3) Input water content [13-14, 16].

4) Intensively mixing should be only at the stage of reagents mixing, but self-process of coagulation should have carried out at relaxed atmosphere.

7.5 Coagulant dose choosing

Coagulant dose (D_C) is the function of following water parameters (fig. 7.3):

- temperature;
- color;
- alkalinity;
- muddy.

D_C is determined experimentally.

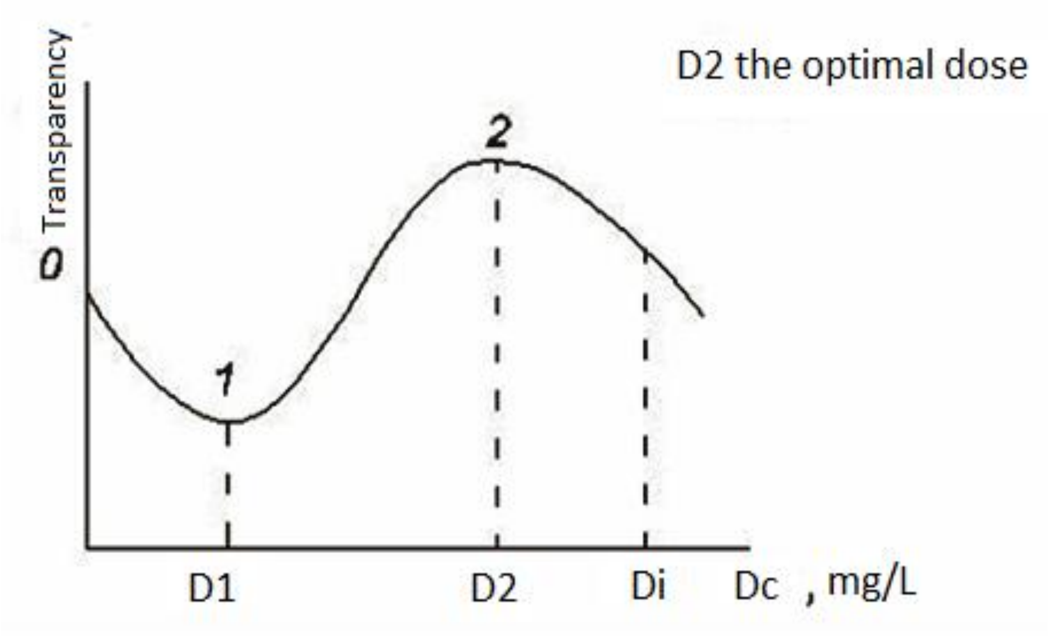


Figure 7.3 – The Graph dependence of water transparency on coagulant dose

An area 0 – 1 responds stealth or incubation period of micelle forming. At this stage to dose D1 even decreasing of water transparency occurs.

In the interval 1 – 2 water transparency is increased, because an explicit coagulation flows, a height of liquid transparency column passes through the maximum. D2 point responds the maximum – the optimal dose of coagulant.

In the point 2 ζ – potential is 0, after the point 2 transparency decreasing is occurred, associated with precipitate re-stabilization (aging, re-crystallization). Sometimes, at coagulant dose increasing one or several maximums of water transparency can occur. In this case the version with minimal coagulant dose is selected as optimal. There are special tables of depending D_C from input water muddy and coagulant kind (table 7.1).

Table 7.1 – Depending of coagulant dose on suspended particles content in water

Suspended substances content, mg/L	**Anhydrous $Al_2(SO_4)_3$ coagulant dose in terms of Al, mg/L**
to 100	25 ÷ 35
100 ÷ 200	30 ÷ 45
200 ÷ 400	40 ÷ 60
400 ÷ 600	45 ÷ 70
600 ÷ 800	55 ÷ 80
800 ÷ 1000	60 ÷ 90
1000 ÷ 1500	65 ÷ 105
2200 ÷ 2500	90 ÷ 130

7.6 Flocculants are used for water purification

Different methods and techniques are used for intensification of coagulation (besides the mixing):

1) muddy agents, adding in water, play a role of crystallization centers (clays, kaolin, alumina silicate);
2) flocculants entering into water, improving processes of flakes forming and precipitation;
3) adding alkaline agents into water $Ca(OH)_2$, Na_2CO_3 etc. for forming and supporting optimal pH values;
4) water chlorination for destroying hydrophilic inorganic colloids.

All processes are carried at purification facilities.

HMC (high molecular compounds) are used as flocculants:

- polyacrylamide (PAA);
- effective silicic acid (SA);
- starch;

- dextrin;
- polyethylene oxide.

They belong to linear polymer class. Chain form of macromolecules is characteristic for it.

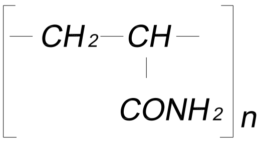
The most common is the following flocculation theory: high-molecular polymers construct network (web) and adsorb flakes on surface, charging several colloidal particles to themselves.

The flocculants using contributes increasing of flakes forming rate to 15 – 20 %.

Flocculants are «catalysts» of coagulation.

Flocculants are usually used with coagulants, flocculants dose is usually from 0,25 to 1 mg/L. For WW purification, the dose of flocculants can be ≈25 mg / L.

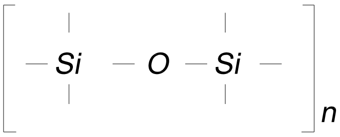
PAA ($M = 1 \cdot 10^1 \div 1 \cdot 10^6$) is got by synthetic way.



$$\left[-CH_2-\underset{\displaystyle CONH_2}{\underset{|}{CH}}- \right]_n$$

PAA dose is 0,1— 1,0 % from solid phase mass. SA — effective silicic acid — colloidal solutions of silicic acid or its difficulty soluble salts are used. For getting SA Na_2SiO_3 (liquid glass) and activating agent (sulfuric acid, chlorine, alumina sulfate, sodium hex fluoric silicate) are used.

$H_2SiO_3 \rightarrow Si(OH)_4$ (amphoteric properties).



$$\left[-\underset{|}{\overset{|}{Si}}-O-\underset{|}{\overset{|}{Si}}- \right]_n$$

HMC with siloxane bonds is formed.

Effects by PAA principle.

SA has the series of advantages:

1) higher efficiency;

2) full harmlessness;

3) significantly expands a field of coagulants effective doses and pH interval, at which coagulation flows successfully;

4) effectively works at low temperatures

5) improves flakes structure, accelerates flakes forming;

6) low-cost, is got from non-deficit raw materials.

Dextrin $(C_6H_{10}O_5)_n$ is starch with decreased content of amylose - крохмаль зі зменшеним вмістом амілози — contributes water purification. It is used for WW purification.

Flocculants contribute color decreasing of natural and WW. If using cation type flocculent, in some cases conventional coagulant can't have used.

7.7 The schemes of water lightening by coagulation and its apparatus design

Coagulation processes are carried at purification facilities include reagents storage and water lightening department.

The reagent storage includes flocculants, coagulants, lime storages, solvation tanks for its preparation, different measures, tanks and dosage pumps.

Coagulant dosage in Ukraine is carried as solution, this is worse, than inputting as salt (more number of equipment is necessary, than at dry dosage), but it takes place by reasons, that properties of homeland coagulants aren't very high quality.

Coagulation process is carried at department, containing:

- different mixers;
- flakes formation cells;
- sedimentation or lightening tanks.

The following mixers are used in water preparation practice:

- horizontal;
- vertical;
- vortex;
- washers;
- holes etc.

The delaying time of water in mixer 1 – 3 min. Washers and holes mixers are the most common at low muddy and costs.

Cells for flakes forming designed to water mixing and providing more complete agglomeration of small coagulant flakes into large. There are vertical and horizontal cells of flakes forming.

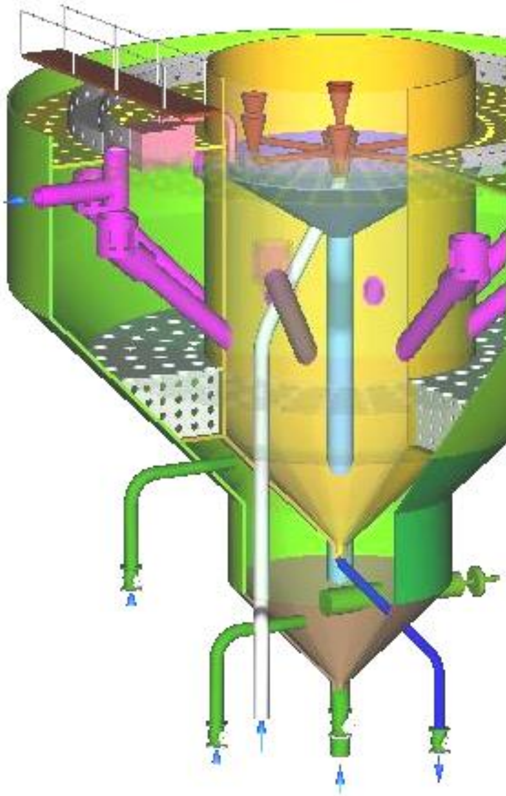


Figure 7.4 – The scheme of vertical clarifier (VTI construction)

There is autonomy or embedded into sedimentation tanks by places of location. The advantages of cells, embedded into sedimentation tanks are in prevention of flakes sedimentation on communications, and also a rate of flakes forming is increased to 20 – 30 %.

Cells of flakes forming can be vortex, blade, whirlpool, with a layer of suspended precipitate.

The staying time in cell of flakes forming, depending on water spending, is 20 – 40 min.

Cells of flakes forming:

a) vertical sedimentation tank with opened cell of flakes forming;
b) partition cell of flakes forming with horizontal and vertical water moving, combined with horizontal sedimentation tank;
c) vertical (vortex) cell of flakes forming combined with horizontal sedimentation tank;

d) vertical cell of flakes forming embedded into horizontal sedimentation tank;

e) blade cell of flakes forming – mechanic with 2 – 5 pairs of mixers;

f) bubbling cells – mixing is carried by pressure air.

There are following options of technological schemes combination depending on input water composition:

1) M < 1500 mg / L, Q to 5000 m^3 / day — vertical sedimentation tank with a cell of flakes forming and rapid filter; 2) M < 1500 mg/ L, Q > 30 000 m^3 / day — horizontal sedimentation tank with embedded cell and rapid filter;

3) lightening tanks with suspended precipitate layer and rapid filters are established at high muddy to 2500 mg / L and any color at Q > 5000 m^3 / day.

At high water muddy two-step creaming can have organized: sedimentation tank – cell of flakes forming – sedimentation tank – rapid filter. This scheme keeps reaching the drinking standards of water.

The occurrence of contact coagulation is often used – coagulation process flows more intensively:

1) flakes formation happens in layer of formed precipitate;
2) reagents are added before filter with grain backfilling. Multi-layer filters are used in this case.

Questions for self-control to the section 7

1. Explain the essence of coagulation.
2. What are colloidal systems? Name colloidal systems properties.
3. Explain the stages of forming and the structure of micelle.
4. Name the main postulates of DLVO theory.
5. Compare properties of coagulants based on alumina and iron compounds.
6. Write-down hydrolysis reactions of coagulants $FeSO_4$, $AlCl_3$.
7. Explain the stages of coagulator solid phase allocation from supersaturated solution.
8. What factors effect on coagulation process?

SECTION 8 OXIDATION METHODS OF WATER DISPOSAL

1. The methods of water disinfection and field of its using.
2. The chlorination of water.
   - 2.1 The essence of chlorination.
   - 2.2 Reagents using at water chlorination.
   - 2.3 Water chlorination methods.
3. Water ozonation.
4. Water disinfection by precious metals ions.

8.1 The methods of water disinfection and field of its using

Water disinfection is carried for destruction pathogenic microorganisms, viruses, bacteria.

At water treatment by coagulation with followed by settling and filtration, approx. 90 – 95 % pathogenic microorganisms is removing from water. However, pathogenic bacteria and viruses can have proved among other, that's why filtered water, especially usable for household-drinking aims, is disinfected. A disinfection can be effectively only if water doesn't contain suspended substances.

All disinfection methods can have divided into 4 groups [2, 4]:

1) thermal;
2) by strong oxidants or reagent methods;
3) olihodynamiya (the influence of precious metals ions);
4) physical methods of water disinfection (by ultrasonic, radioactive rays, UV-rays etc.).

Thermal water disinfection. It is usually used for low quantities of water disinfection, - in health centers, hospitals, ships, trains. Complete water disinfection, namely dying of all pathogenic bacteria, is reached by 5 – 10 min boiling. Boilers of type «Volcano», «Titan» are used.

The method isn't widely used even at small water-lines, because of its expensively and low productivity of apparatuses.

Water disinfection by bactericide rays has a number of advantages: natural taste and chemical properties of water aren’t changed; a bactericide action of UV-rays flows many times quicker, then using chemical reagents, after exposure water can have supplied consumers at once.

The installations are simple in exploitation, economy. Following origins of bactericide exposure are the most common: mercury-quartz and argon-mercury lamps.

The disadvantages: relatively low productivity, strict compliance of the temperature (not lower +5 º C), absence, for the present, operative control method of disinfection effect, limiting of input water quality (coli-index – not more 1000), the method is unsuitable for muddy waters disinfection.

Using roentgen, radioactive rays and also high frequency currents are possible for using. However, these methods aren’t good studied. The ultrasonic disinfection, for the present, is on the stage of laboratory experiments.

Reagent methods are the most common. Unlike the coagulation processes, leading to microorganisms removing with precipitate, the disposal methods suppress vital functions or lead to microorganisms dying.

The oxidation of humic substances in water, molecular organic substances, metal ions with variable valence etc. happen at using oxidation methods. It follows, that oxidation methods can have used for some substances removing from water, which are related to all four impurities groups.

As oxidation reagents are used for water disposal, following reagents can have used: chlorine, chlorine (IV) oxide, chloric lime, ozone, iodine, potassium permanganate, hydrogen peroxide, sodium or calcium hypochlorite.

8.2 The chlorination of water

The chlorination of water is the most common method of water disinfection at water-lines in all over the world. It is charged in all cases of water selection from surface origins (after compulsory pre-purification), and also at water selection from underground origins in case, if bacterial indicators of this water are responded by

STATE SANITARY NORMS AND RULES 2.2.4 – 171 – 10 «Hygienic requirements for drinking water appointed for human consumption».

Water chlorination is charged by gas-like chlorine Cl_2 or substances, containing effective chlorine: chloric lime, hypochlorite, chlorine amine, chlorine (IV) oxide etc.

The term ***«Effective chlorine»*** mines chlorine, capable at pH 4 to give off equivalent quantity of iodine from water solutions of potassium iodide.

8.2.1 The essence of chlorination

The essence of chlorine disinfection is in oxidation and chlorination of substances, entering into content of bacteria cells cytoplasm, causing bacteria dying. The causative agents of typhoid, parotyphoid, dysentery, cholera is very sensitive to chlorine.

Even highly infected water by epidemic causatives is disinfected relatively easy by very small chlorine doses, but total sterilization of water at its chlorination isn’t occurred, the single chlorine resistance organisms are remained in water, they serve viability, microorganisms, bacteria.

The bactericide effect (this is the property of some substances to destroy bacteria) of chlorine largely effects on its initial dose and its contact time with water. Only the minor part of chlorine is usually spent at water chlorination for bacteria destroying, the major part of it is spent for reactions with different organic and mineral substances present in water.

These are following:

- humus;
- products of degradation fiber and proteins;
- salts Fe^{2+};
- ammonia;
- hydrogen sulfide;
- ammonia salts;
- nitrites NO_2^-;
- organic compounds of artificial origin etc.

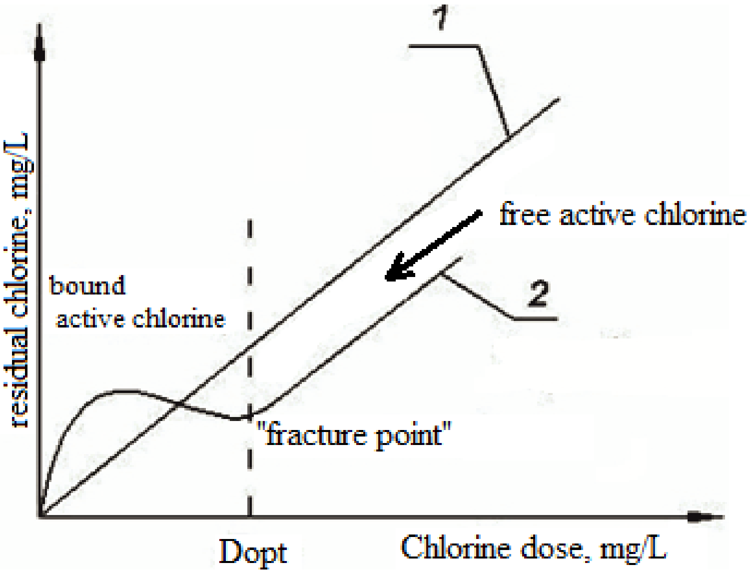
The reactions of chlorine with these compounds flow with different rate and, depending on quantity of introduced chlorine, pH, temperature, suspended substances content, composition of input water they can have stopped at some stage.

The chlorine quantity, absorbed by water by its treatment for interaction with these substances, is called chlorine absorbability of water.

The chlorine absorbability of water is determined by chlorine quantity (mg/L), adsorbing at 30 min. contact with investigated water. The chlorine absorbability of water depends on introduced chlorine dose, content of substances, reacting with it.

The chlorine absorbability of river and lake waters is 2 ÷ 2,5 mg Cl_2 / L, of ponds and swamps – is increased to 5 mg Cl_2 / L. The extreme increasing of absorbed chlorine quantity can testify about water pollution by organic substances and its sanitary distress.

The water chlorine indicator can have used for comparison of the chlorine absorbability of different waters. It is presented by conditioned fraction, the numerator is 1, and the denominator – the dose of chlorine, providing residual chlorine content in water 0,5 mg/L after 30 min. contact.



1 – at absence of ammonia; 2 – at presence of ammonia

Figure 8.1 – The curve of the absorbability of water (τ = 30 min)

In practice some excess of chlorine is brought for prevention secondary bactericide pollution at passing through the line. The content of residual effective chlorine in water-line water, as the indicator of chlorination effectivity, normed by STATE SANITARY NORMS AND RULES 2.2.4 – 171 – 10 and should be not less 0,3 and not more 0,5 mg/L after 30 min. chlorine contact with water. The optimal chlorine dose, necessary for getting given value of residual chlorine, is established experimentally, by construction of the chlorine absorbability of water during 30 min. (fig. 8.1).

Some decreasing of the residual chlorine content is due to its interaction with ammonia compounds:

$$NH_3 + Cl_2 \rightarrow NH_2Cl + HCI;$$

$$NH_3 + 2Cl_2 \rightarrow NHCl_2 + 2HCI;$$

$$NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCI.$$

Consider, chlorine presents in mono- and dichloride amines at the 1st area of the curve.

The maximum at the curve responds the time, when all NH_3 presents in water spent for chloride amines forming.

The minimum at the curve responds the moment of total chloride amines destruction:

$$4NH_2Cl+3Cl_2+H_2O \rightarrow N_2+N_2O+10HCl.$$

The curve has the fracture point, responding the optimal chlorine dose. An ammonia and its compounds, presenting in water, do main effect on the chlorination curve view (fractions etc.). The pH and temperature of water and etc. effect on the course of curve.

The chlorine, as noted, oxidases and destroys the organic impurities of water along with disinfection. It leads to decreasing of water color, its flavors, smells (sometimes water’s ability to foam).

However, there are known cases, when chlorination causes to forming products with strong smell. Chloride phenol flavors and smells are especially persistent and unpleasant. They are at the chlorination of water, polluted by wastes, containing phenol and other aromatic compounds, related to the 3rd group of impurities.

The edge of human taste: chloride phenol is turned out to taste at the concentration $4 \cdot 10^{-6}$ mg / L.

Figure 8.2 – The scheme of typical industrial chlorinator

8.2.2 Reagents using at water chlorination

The chlorine is the gas of yellow-green color with sharp suffocating smell. At water saturation by chlorine the chlorine water is formed. It has strong oxidation properties:

$$Cl_2 + H_2O \leftrightarrow HCl + HClO.$$

Further, hypochlorous acid is dissociated:

$$HClO \leftrightarrow H^+ + ClO^-.$$

The dissociation degree of HClO depends on water pH, pressure, temperature, mixing intensity and other factors. Hypochlorous acid is strong oxidant.

Chloric lime - $CaOCl_2$

$$2CaOCl_2 + 2H_2O \leftrightarrow CaCl_2 + Ca(OH)_2 + 2HClO.$$

The hypochlorous acid, forming in this scheme, is formed slower, than at using Cl_2, but its further behavior in water is the same.

$$2ClO_2 + H_2O \rightarrow HClO + HClO_4.$$

ClO_2 — chlorine (IV) oxide is green-yellow poisonous gas with more intensive smell, than chlorine. The chlorine oxide has the advantage in comparison with chlorine: chloride phenol's smells are absent at phenolic water treatment, because the phenol is oxidized almost completely to quinone and maleic acid. These substances don't provide smell and flavor of water.

In industrial spaces MPC (Cl_2) = 1 mg/m^3, MPC (ClO_2) = 0,1 mg/m^3.

Recently hypochlorite and chloride amines are used, they are especially comfortable in field conditions.

8.2.3 Water chlorination methods

All methods of water treatment by substances, containing «effective» chlorine, can have combined into 2 main groups:

- post-chlorination;
- pre-chlorination.

The post-chlorination is the process of water disinfection, charging after all other stages of its treatment and is, thereby, the final stage of water purification. If water isn't amenable to other treatment, except disinfection, it will be post-chlorination.

The post-chlorination can have charged by as small (normal chlorination), as increased doses (super chlorination). It is used together with other disinfection substances (combined chlorination).

The combined chlorination methods, namely water treatment by chlorine together with other bactericide drugs can have used for strengthening chlorine or its fixation in water for longer time. The combined methods are following: chlorination with manganese, chlorine-silver or chlorine-copper methods, and also chlorination with ammonization.

The chlorination with manganese ($KMnO_4$) is carried at water treatment with unpleasant smells and flavors, caused by organic substances, algae presence etc.

The chlorine-silver or chlorine-copper methods are carried by introduction into water chlorine and silver and copper ions.

The chlorine-silver or chlorine-copper methods are used not only for natural drinking waters disinfection, and also for prevention its re-contamination by bacteria, namely for water conservation (for example, in pools).

The ammonization with chlorination fix effective chlorine in water very good (it is introduced as ammonia and ammonia salts).

The pre-chlorination of water is used as means, improving some processes of water purification (for example, coagulation and iron removing), and also as effective method of some toxic substances disposal.

In water preparation practice for input water treatment with high color and increased content of organic substances the double chlorination – pre- and post-chlorination are used.

For water treatment by chlorine special installations are used – chlorination stations. They include: storage, chlorine dispensers, pump installations and auxiliary facilities. The chlorine is served in balloons or containers.

For example, the vacuum chlorinator of Kulskiy system includes following elements: balloon – filter – manometers – reducing valve – rotameter – regulating valve – mixer.

8.3 Water ozonation

The perspective method of water disinfection is its ozone treatment.

The disinfect action of ozone is based on its high oxidation ability, explaining by ease of returning effective oxygen atom by it:

$$O_3 \rightarrow O_2 + O.$$

By high oxidation potential ozone vigorously reacts with numerous organic and mineral substances, including with cytoplasm of bacterial cells, destroying it.

Ozone, as disinfection agent, effects 15 – 20 times rather, than chlorine. Herewith, its consumption is much lower. So, at introduction 0,45 mg/L of ozone, the poliomyelitis virus dies after 2 min., at adding 2 mg/L of chlorine – only after 3 hours.

Effects of ozone on bacteria spores 300 ÷ 600 times stronger, than chlorine.

The dose of ozone, necessary for water disinfection, usually is 0,5 – 5 mg/L depending on oxidation substances content in water.

Herewith, the content of ozone after ozonation installation should be 0,1 – 0,3 mg/L.

The temperature of water, muddy, pH and other properties exercise less influence on water ozonation effect, than chlorination. It facilitates reagent dosage and control of water disinfection effectivity.

The important advantage of ozonation is: water at treatment isn't contaminated additional impurities. Residual ozone hasn't been used after short period of time is decomposed and transformed to oxygen. Ozone dosage doesn't require such accuracy, as chlorine dosage.

Water ozonation is caused not only its rapid disinfection, and also helps eliminate of smells and flavors as natural, as industrial origin, and also decoloration of natural water by oxidation and decomposition of organic water impurities.

Ozone is a blue gas with characteristic smell, filling at dilution air 1:500 000 (at this dilution it already causes headache). Ozone is produced by passing of purified air through a high voltage electric charge (5000 – 25000 V) in ozone producing machine.

Ozone is very toxic gas, MPC in air of industrial zone is 0,001 mg/m^3.

The disadvantage of ozonation is short time of its effect.

8.4 Water disinfection by precious metals ions

Olihodynamiya (Greece word: oligos – traces, dynamic – effect, namely traces effect).

Silver even at low concentration has ability to destroy microorganisms.

The upper edge of silver ions bactericide effect is $2 \cdot 10^{-11}$ mole/L. Even in ancient times people knew about healing properties of water, contacting with metallic silver. In Vth century B.C., for extended serving of water silver dish had been used.

There is no one point of view on silver ions influence directly on bacteria. It is known, that bacteria with negative charge of protoplasm draw to themselves charged silver ions.

At collision of silver ions with bacteria, the last, by physical effect of metal ions of it, dies.

Water enrichment by silver ions is reached by several methods – water contacting with developed metal surface (Rashig rings, beads and sand of G. Krauze, S.V. Moiseev, and also oxidation – silvered preparations of V.A. Uglov), by the method of directly dissolution silver preparations in water (amargen of P.E. Yermolayev, olygozinum etc.) and electrolytic (Kulskiy's method).

The electrolytical method presents the greatest practice value. It is based on anodic silver dissolution. This method, providing possibility of rapid getting desirable concentrations of silver ions in solution, makes it possible to carry out accurate silver dosage and process regulation by electric measured devices.

Transparent waters, don't contain high quantity of chlorides (to 25 mg/L), are advisable to disinfect by silver ions (optimal doses of silver – 0,5 – 0,2 mg/L).

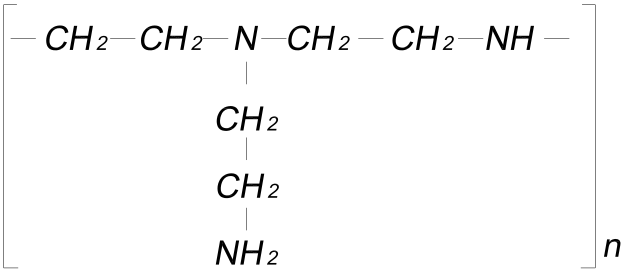
The electrolytic method presents the greatest practice value.

The different modifications of ionators by Kulskiy system are the widest used.

Iodine and bromine are used, expecting chlorine, for water disinfection. In practice of water supply these methods haven't entered the large volume yet. Although, iodination has a number of advantages:

- higher bactericide effect;
- lower contact time with water;
- iodine isn't alien element for human organism.

The alternative of disinfection can be PHMG – poly hex methylene guanidine designed by co-workers of Igor Sikorsky Kyiv Polytechnic Institute and «Ukrvodbezpeka», the reagent of complex effect, that has coagulation and flocculation properties expect disinfection effect.



$$\left[-CH_2-CH_2-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\NH_2}}{N}-CH_2-CH_2-NH-\right]_n$$

Questions for self-control to the section 8

1. What is the aim of water disinfection?
2. Name the methods of water disinfection.
3. In what cases, can thermal methods of water disinfection have used?
4. What processes occur in water at using reagent (oxidation) methods?
5. What the essence of water chlorination?
6. What conditions determine the bactericide effect of chlorine?
7. Explain the term «chlorine absorbability» of water.
8. How can chlorine optimal dose have determined?
9. Wright-down the reaction of chlorine water forming.
10. Compare the disinfection effect of gas-like chlorine and chlorine (IV) oxide.
11. Explain the difference between chlorination methods; pre- and post-chlorination.
12. What methods are related to combined?
13. Name the advantages of water ozonation.
14. Characterize the method of water disinfection, naming “olihodynamiya”.

SECTION 9 WATER PURIFICATION BY ADSORPTION

1. The essence of the method and fields of its using.
2. The nature of physical adsorption.
3. The main kinds of sorbents, using at water preparation, its characteristics; requirements to sorbents.
4. The theoretical models of process: Langmuir and BET theories.
5. Stages of adsorption.
   5.1 Stages of adsorption
   5.2 The initial curve of sorption dynamic
   5.3 Shilov's equation

6. The methods of sorbents regeneration.
7. The typical schemes of water purification by adsorption: consistent, reverse-flow introduction of sorbent; continuous installations.
7. Constructions of sorption purification devices: devices of filtering type, tiered adsorber.

9.1 The essence of the method and fields of its using

Data about solid bodies with developed surface using had come us from ancient times. Known, that in Ancient Egypt coal had been used medicinally. In times of the creator of antic medicine Hippocrate (400 years B. C.) coal was a common recipe for removing bad smell, coming from ulcers and wounds.

Besides, the development of industrial adsorption method had been begun from brilliant discovering of Petersburg's pharmacist Lovitz. In 1785 he had found, that tree coal, introduced into solution of vine acid, discoloring it, absorbing organic impurities. The scientist had payed attention on universality of coal, as absorber: solutions had been purified from different impurities by it. These conclusions had been realized after 9 years. Coal had been begun used for purification of sugar alcohols, alcohol from oils, at Russian marine – for drinking water purification.

Later the ability of coal to absorb gases (Cl_2, H_2S, SO_2, NH_3, HBr, HCN та ін.) had been established. The chromatographic methods of analysis are based on selective properties of adsorbents. Later, a gas mask (protection from toxic substances) had been created, basing on sorption properties of adsorbents (M.D. Zelinskiy, during the First World War).

Adsorption is the concentrating of substances on surface phase distribution or in volume of solid body pores.

Minimally 2 agents take part at adsorption: a body, on surface or pores volume of which the concentration of absorbing substance occurs (adsorbent), and removable substance. The last, if it is in gas or liquid volume phase, namely in non-adsorbed state, is called adsorptive, and after transferring into adsorbed state – adsorbate. Anyone solid substance has surface and, so, it is potentially adsorbent. However, solid adsorbents with highly developed surface (pores volume) are used in technic.

The essence of the method – at liquid contacts with solid body, the liquid molecules can transfer on solid body surface and maintained on the surface.

There are different sorbents used in water preparation practice – hydrophobic and hydrophilic [2,17].

Hydrophobic include: coal, activated carbon (granulated or powdered).

Hydrophilic sorbents are natural materials: montmorillonite, alumina gels, silica gels, zeolites.

The method of adsorption is used, the most often, for removing from water impurities of the 3rd group (organic compounds).

The concentration edges – not more $2 \div 3$ g/L of organics.

There are two main processes, where this method is used:

1) coaling of natural waters for removing colored substances (humic acids), cause such indicators: color, smell, flavor. (the coal dose is $\approx 20 \div 80$ g/m^3 of water);

2) deodorization and de-chlorination of water in drinking water preparation processes for decreasing chlorine content to the necessary value – not more 0,5 mg/L. (the dose of coal $\approx 30 \div 60$ g/m^3 of water);

3) since 1985 the method of adsorption is recommended as method of refining biological WW from organic substances, so-called tertiary purification;

4) also for removing single organic components or components groups of the same class at local purification installations.

9.2 The nature of physical adsorption

Adsorption is unauthorized process. By the type of forces, caused adsorption, all adsorption effects can have divided into 2 main groups: ***physical adsorption*** and sorption, caused by forces on chemical interaction – ***chemical sorption***.

The physical sorption is caused by forces of molecular interaction.

Adsorption is always exothermic process.

The physical sorption can be comparing with condensation, the process of chemical sorption should be considered as chemical reaction, flowing on surface phase distribution.

Physical and chemical sorption can be differed by a heat of adsorption. The heat of physical adsorption isn't over 80-120 kJ/mole. The heat of chemical adsorption can reach several hundred kJ per 1 mole. The chemical adsorption usually flows with slow rate. The chemical sorption is characterized by abrupt change in absorbability by a component, removing from water.

The adsorption process from solutions has extrusion character (as opposed to gas phase). For providing the organic substance ability to absorb from solution, it should squeeze water from adsorbent surface.

The lower energy of water molecules interaction with adsorbent surface responds the simplicity of water squeeze by adsorbate.

As noted, there are hydrophilic and hydrophobic sorbents. The energy of water interaction with hydrophilic adsorbents will be higher, than with hydrophobic.

Hydrophilic adsorbents are used for removing from water very large organic molecules ($C > 10$). For organic compounds removing from water, that has not very large molecules, the hydrophobic adsorbents are the most effective for using.

9.3 The main kinds of sorbents, using at water preparation, its characteristics; requirements to sorbents

The activated carbon is the most often used as sorbent among carbon sorbents. It is got from natural by following treatment: firstly, material is subjected thermal treatment without air, then coal-adobe is activated by oxidation with gas, vapor or treatment by chemical reagents.

There are two sorbent groups:

1) base on activated carbon;

2) silica- and alumina- gels.

The activated carbon of following grades is the most often used in water preparation with different way of producing and feedstock:

AG – gas;

BAC – birch activated carbon;

AGr – granulated carbon;

SKT – granulated carbon;

MT – milled tree;

LC – lightening coal.

All this information is available in the references.

Solid sorbents, usually, differ by «tracery» inside structure, including pores of different size. Depending on sizes, pores can be divided into 3 types: micro-, meso-, and macro pores.

Micro pores – the smallest pores – commensurate with adsorbed molecules. Its effective radiuses are mainly in interval 0,5 ÷ 1,0 nm, the top edge – 1,5 nm.

Sometimes the largest micro pores 0,75 ÷ 1,5 nm are isolated into super-micro pores.

Meso pores – the effective radiuses of larger pores – meso pores is much more molecules sizes: in interval from 1,5 to 100 ÷ 200 nm. Walls of such, relatively large pores, formed by very large number of atoms or molecules of adsorbent substance; for this case, there is a meaning of surface phase distribution, namely about surface of adsorbent pores.

Macro pores – the largest pores of adsorbents – macro pores have effective radius over 00 nm. Macro pores play role of large transport arteria in adsorbent grains.

The equivalent (effective) pore radius is a ratio of section area to the value $2r\pi$.

$$R_{еф.} = \frac{F_{пори}}{2r\pi}, \tag{9.1}$$

where *r* – pores radius.

The adsorption in pores and on surface has different values of bond energy. Strength of this bond depends on molecules localization in pores (surface layer etc.). Sometimes adsorbents can be unfit, namely molecule can’t get into a pore.

For porous adsorbents, the meaning «pores volume» is applied, in this case the primary is pores volume, but not its surface. In coal marks the volume of micro pores is 0,35 ÷ 0,4 cm^3/g, responding ≈ 1000 m^2/g. A volume of meso pores in activated carbon can be the same or less.

Non-porous carbon materials, for example, graphite, have surface ≈ $1m^2/g$.

Requirements to adsorbents:

- should have as large as possible adsorption volume;
- should be hydrophobic;
- porous structure of sorbent should be available for adsorbed substances;
- adsorbent should be inert to water;
- sorbents should be able to regeneration;
- sorbents should have mechanic abrasion resistance.

9.4 The theoretical models of process: Langmuir and BET theories

The adsorption from solutions is the result of very complex interactions:

1) interaction adsorbate (organic substance) – adsorbent;

2) interaction solvent (water) – adsorbent;

3) interaction adsorbate – solvent as in volume, as in sorbent phase;

4) interaction adsorbate – adsorbate as in solution, as in adsorbent.

The resulting value of all these interactions is adsorption. The measure of resulting interaction, namely adsorption from solution, is decreasing of standard free adsorption energy:

$$-\Delta F^0_{ads} = RT \ln K_a = RT \ln \frac{a}{C_p} \quad , \qquad (9.2)$$

where K_a – the constant of adsorption equilibrium; a − the value of adsorption, related to single mass or volume of sorbent, is called the specific adsorption, mole/kg; C_p – the concentration of adsorbate in solution, mole/kg, corresponding to it at equilibrium.

The values ΔF^0_{ads} had been determined for numerous organic substances and are in references.

Adsorbents are characterized by absorbing or adsorbing ability (capacity) – sorbent activity, is determined by the concentration of adsorptive in single mass of volume of adsorbent. The maximal possible under these conditions absorbing ability is called equilibrium activity.

At equilibrium, some distribution of substance in sorbent phase and volume is established. It is determined by the value of constant of sorption equilibrium and portrayed graphically by adsorption isotherm (fig. 9.1).

At adsorption from water a curve – mainly 1st.

Constructing the adsorption isotherm, the following information can have got:

1) adsorption isotherm keeps to calculate the constant of adsorption equilibrium;

2) adsorption isotherm keeps to determine adsorbent capacity, adsorption volume of micro-, meso- and macro pores.

There are many analytic models exist for explaining the adsorption process, but opposite concepts are in its base:

1) monolayer adsorption;

2) poly-molecular adsorption.

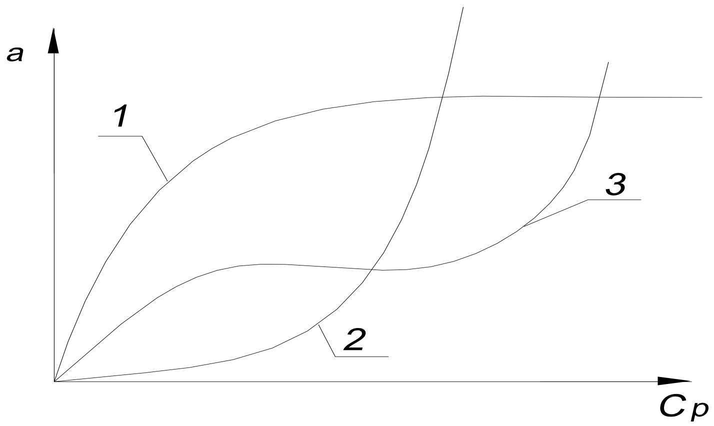
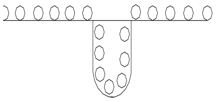


Figure 9.1 – The main types of adsorption isotherm curves (T = const)
1 – convex adsorption isotherm; 2 – concaved adsorption isotherm; 3 – «S» - shaped adsorption isotherm

The monolayer

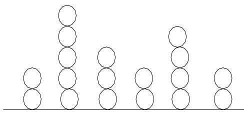


The monolayer theory had been adopted by Langmuir at outputting the equation of adsorption isotherm:

$$a = a_m \frac{b \cdot C_P}{1 + bC_P} \quad , \qquad (9.3)$$

where a_m – the specific adsorption of monolayer; b – the constant of Langmuir equation, its physical meaning is determined by live period of molecules, namely monolayer capacity. The capacity of monolayer -is the constant characteristic of sorbent.

The second one model is the model of poly molecular layer.



The theory BET (Bruner - Emmet - Teller had got the equation of poly molecular adsorption).

The equation BET is following:

$$a = \frac{a_m \cdot K' \cdot {C_p}/{C_S}}{(1 - {C_p}/{C_3}) \cdot \left[1 + (K' - 1) \cdot {C_p}/{C_S} \right]}, \qquad (9.4)$$

where K' – the constant of BET equation, directly connected with molar heat of adsorption; the value K' determines isotherm kind; if $K' < 2$ isotherm is concaved; if $K' > 2$ is convex or sigmoidal; C_S – the solubility of adsorbate at a given temperature.

Despite the changing of general process model, a behavior of everyone adsorbed layer singly responds Langmuir's concept.

9.5 Stages of adsorption

9.5.1 Stages of adsorption

The whole adsorption process can have presented consisting of 3 stages:

1) diffusion of organic substance from solution volume to surface of adsorbent grain (outside diffusion);

2) diffusion of adsorbed substance inside of porous structure of adsorbent grain (inside diffusion);

3) actual adsorption.

The rate of the 1st stage depends on the rapid of substance supply to grain surface and the concentration of components.

The rate of the 2nd stage depends on trajectory of molecule to the center of adsorption (liquid properties) and sizes of sorbent solid particles (pores etc.).

The kinetic, namely the adsorption rate, is determining experimentally in devices with mixing (the parameters change: mixing rate, different grain size, temperature etc.) and is establishing, which stage will control the rate of whole process.

On the basis of kinetic studying, namely the rate of equilibrium reaching, the following parameters are determined:

1) area of process – outside or inside diffusion (the limit stage is established);

2) the theoretical equation is upped and the experimental kinetic equation is specified for process time determining $\tau = f(C)$. On the basis of this the volume of apparatuses ($V_{ap} = R\tau$) and other parameters can have calculated;

3) the calculations of kinetic dependences for adsorption processes can have calculated with PC.

9.5.2 The initial curve of sorption dynamic

The model: sorption filter (length L), into which the solution with initial concentration C_0 supplies continuous and moves by flow by one way through the unmovable layer of sorbent. In periodic process in everyone elementary layer the equilibrium isn't reached and the value τ is impossible for calculating.

For τ calculation (so-called the time of protective action) the model of layered front or working sorbent is used – ***Shilov's model***.

The dynamic of sorption processes considers the space-time distribution of components between phases of system (one of them is solid), taking place at moving of these phases against each other.

The model of Shilov has simplifications: the isotherm has convex view relatively abscissa (curve 1) for saturation area.

The running time of adsorption filter working is measured by the time until appearance of breakthrough, namely until appearance the minimal available for determining concentration of removing substance in filtrate. The breakthrough concentration is usually adopted in all calculations $C_{break} = 0{,}05C_0$, and the time of filter work until the beginning of breakthrough is called ***the time of sorbent protection***.

The main task of sorption dynamic is determining optimal conditions for maximal using of whole sorbent capacity, downloading to the filter, namely providing conditions, at which sorbent is saturated to the equilibrium with the initial concentration of substance, namely the dynamic capacity of sorbent would be as greater as possible in dynamic conditions.

The task of dynamic is to establish the dependence of sorbent layer protection time on its length (height), filtration rate, the initial concentration of substance in solution and to get calculation equations for determining this time, considering the static and the kinetic of adsorption.

The 1st layer of sorbent is called frontal. At filtration, the whole adsorbed substance from the 1st portion of the flow isn't absorbed, and, consequently, at the same time, in the process of mass transfer, the next elementary layers, following by frontal, take part.

The dependence of adsorbate concentration changing in the flow around the length of sorbent layer has the form (figure 9.2):

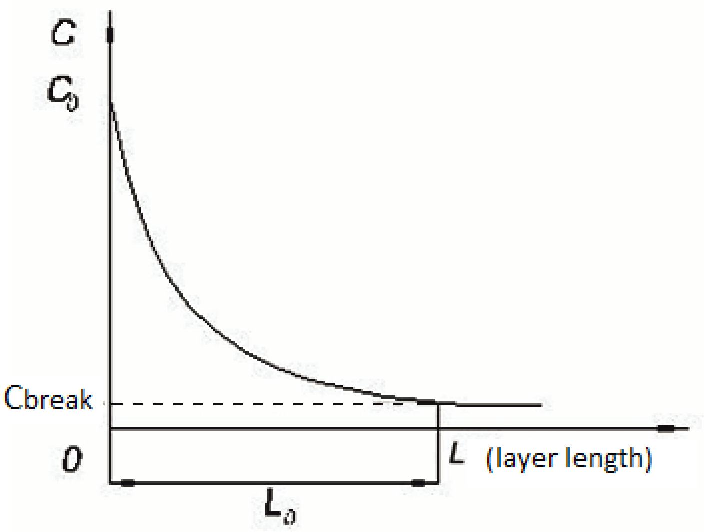


Figure 9.2 – The dependence of adsorbate concentration changing in the flow around the length of sorbent layer

The area of layer, where the decreasing of the concentration from C_0 to «0» (C_{break}) occurs, is called the ***working layer*** or mass transfer zone. The curve is called the ***gradient area***.

The substance distribution curve in anyone phase (more often in adsorbent) is called ***the sorption front***.

The whole process of sorption dynamic can have conditionally divided by 2 stages:

1) firstly, the front of sorption is formed. For example, on the 1st layer (frontal). When the point L_0 moves around length – the breakthrough takes place (and it becomes L_1), namely the absorption begins to be further on the next layer with length > L_0. The 2nd stage begins from this moment;

2) moving of sorption layer along backfilling parallel itself. The mass transfer zone, doesn’t changing profile, is moved down to the bottom edge of layer.

The dynamic of sorption is studying experimentally by filtration of solution through the layer of unmovable sorbent and is measured the dependence of substance concentration in filtrate on time of filter's work or volume, passed through the layer. This dependence is called the initial curve of ***sorption dynamic***.

The initial curve displays the distribution of substance along the layer length (fig. 9.3).

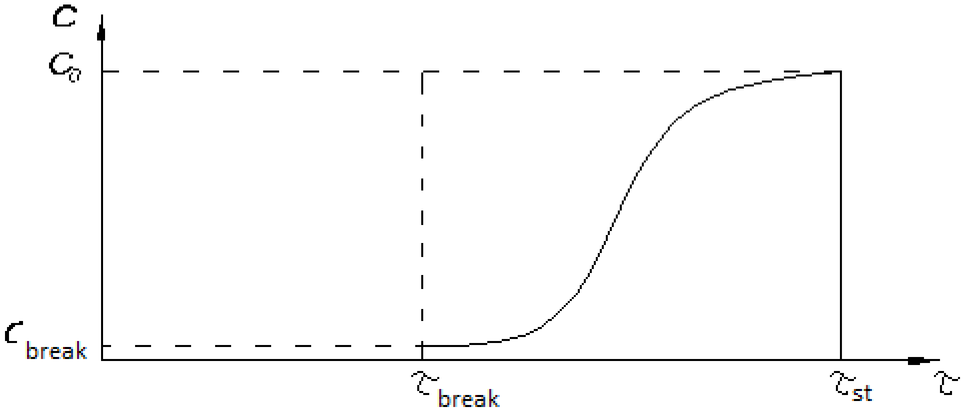


Figure 9.3 – The distribution of substance along the layer length

The time of filter protection is determined from the initial curve (τ_{break}).

9.5.3 Shilov's equation

If a rate is very high, everyone layer is completely wasted. The time of filter's work in this case is determining from the equation of material balance.

Let:

V - flow rate, $m^3/m^2 \cdot h$;

C_0 - the initial adsorbate concentration, kg/m^3;

a_0 - the specific adsorption, kg/m^3;

L - length of the layer, m;

S - sectional area of the filter, m^2;

τ - breakthrough time, h.

Coming:

The quantity of adsorbate, incoming with solution, at the moment of total sorbent wasting:

$$m_{insol} = V \cdot C_0 \cdot S \cdot \tau \, . \tag{9.5}$$

Expenses:

The quantity of adsorbate, delayed on adsorbent:

$$m_a = L \cdot S \cdot a_0 \, . \tag{9.6}$$

At the moment of equilibrium:

$$V \cdot C_0 \cdot S \cdot \tau = L \cdot S \cdot a_0 \tag{9.7}$$

$$\tau = \frac{a_0}{V \cdot C_0} \cdot L \tag{9.8}$$

Really, because of not whole layer of sorbent is wasted, the actual or real time will be less:

$$\tau_{break} = \frac{a_0 \cdot L}{V \cdot C_0} - \tau_0 \tag{9.9}$$

If $\frac{a_0}{V \cdot C_0} = k$,

then $\tau_{\text{пр}}^{\text{ф}} = k \cdot L - \tau_0$ – Shilov's formula,

where k – the protection coefficient, showing, what time responds delaying substance by 1 cm thickness of adsorbent in stationery mode; τ_0 – protection time loss connects with the initial period of formation of adsorbate distribution curve.

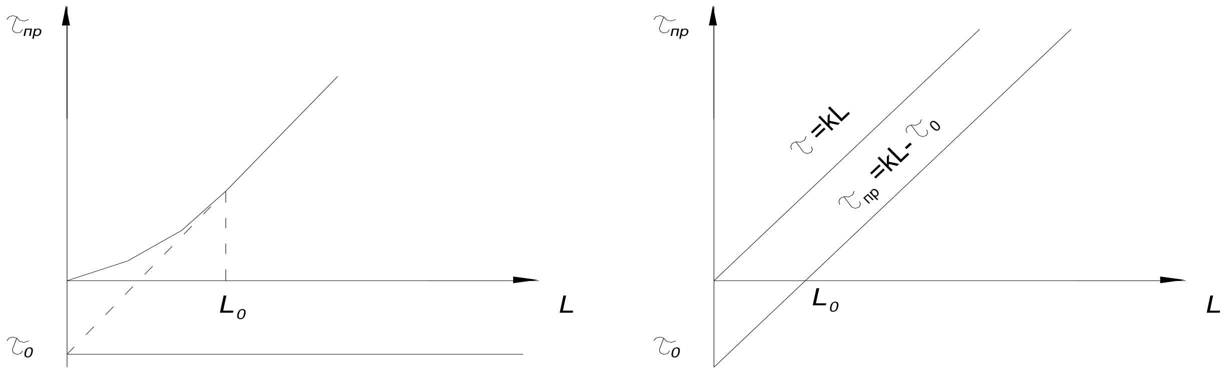


Figure 9.4 – The dependence of protection time of the layer on its length L

The dependence of protection time of the layer (the time until breakthrough τ_{break} on its length L) (fig. 9.4).

On the basis of Shilov's equation the height of the layer L_0 can have determined for some specific conditions.

9.6 . The methods of sorbents regeneration

There are following aims at sorbents regeneration:

1) to extract the adsorbed substance and to use it henceforth;

2) to regenerate sorption capacity of the adsorbent.

Exactly the regeneration stage determines the economy of water purification by adsorption in general (the part of costs for regeneration in total cost is from 40 to 85 %). Among the regeneration methods the most widely used methods are: chemical (treatment by acids, alkaline or oxidants, pollutions removing by extraction, stripping with water vapor, blowing by neutral gas-carrier), and also thermal regeneration (at 650-900 º C with water vapor or products of gas flaming). At the thermal regeneration, the adsorbent losses take place.

The regeneration method is selected from the economic and technology needs [2, 11].

9.7 The typical schemes of water purification by adsorption: consistent, reverse-flow introduction of sorbent; continuous installations

The process of adsorption purification is carried at following modes: at intensive mixing, at water filtration through the layer of adsorbent or in fluidized (boiling) layer in installations of periodic and continuous action.

The schemes of adsorption installations (fig. 9.5 – 9.7).

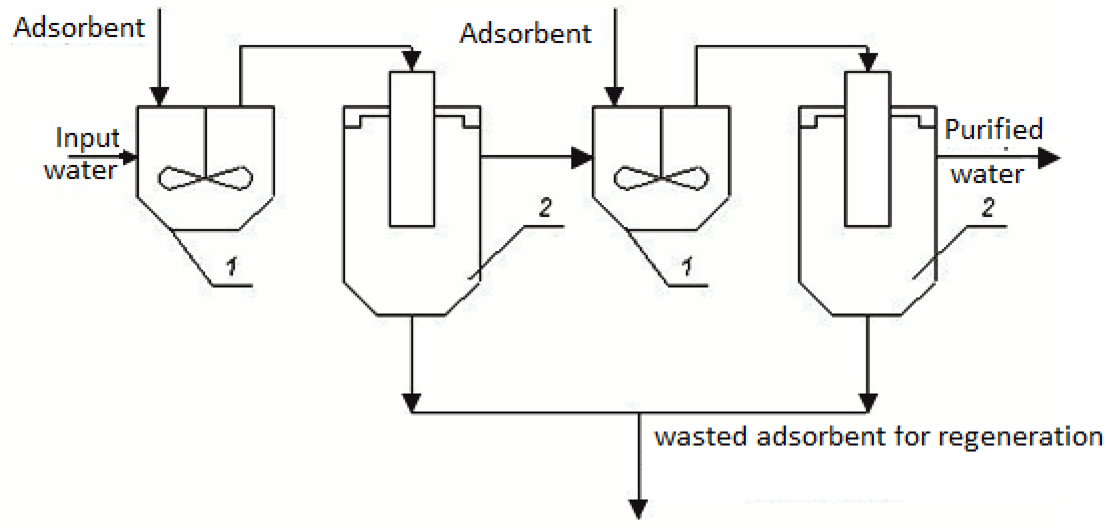


Figure 9.5 – The scheme of adsorption installation with serial input of adsorbent

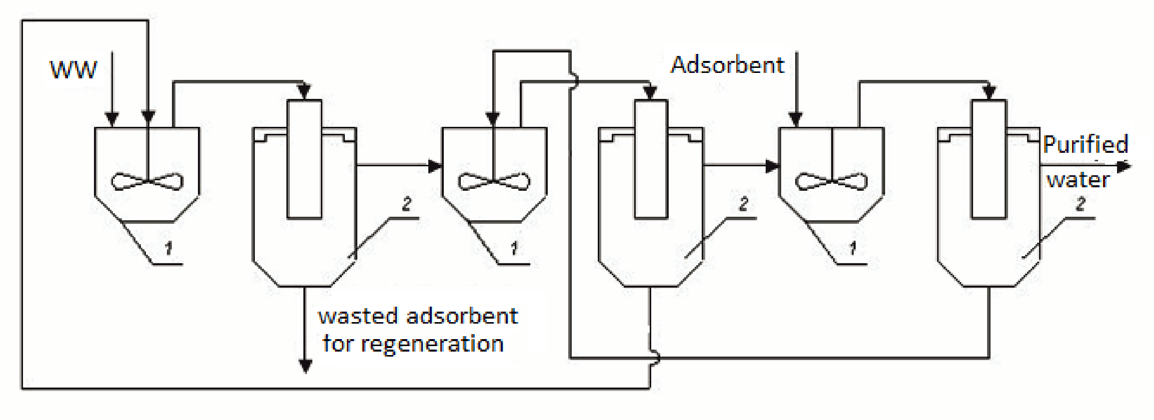


Figure 9.6 – The scheme of adsorption installation with against-flow input of adsorbent

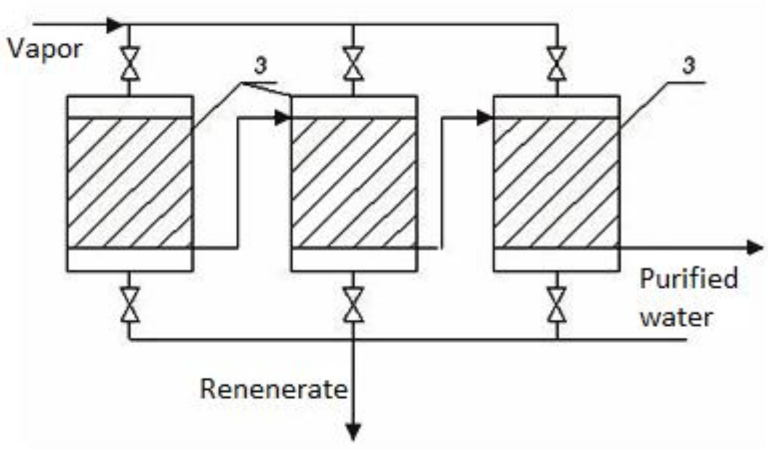


Figure 9.7 – The scheme of adsorption installation of continuous action

1 – mixer, 2 – sedimentation tank, 3 – filter (adsorption column)

9.8 Constructions of sorption purification devices: devices of filtering type, tiered adsorber

The main construction of the apparatuses: filtering type; the system mixer – sedimentation tank; the fluidized layer.

The apparatuses of filtering type have the same construction with mechanic pressure filters (section 5).

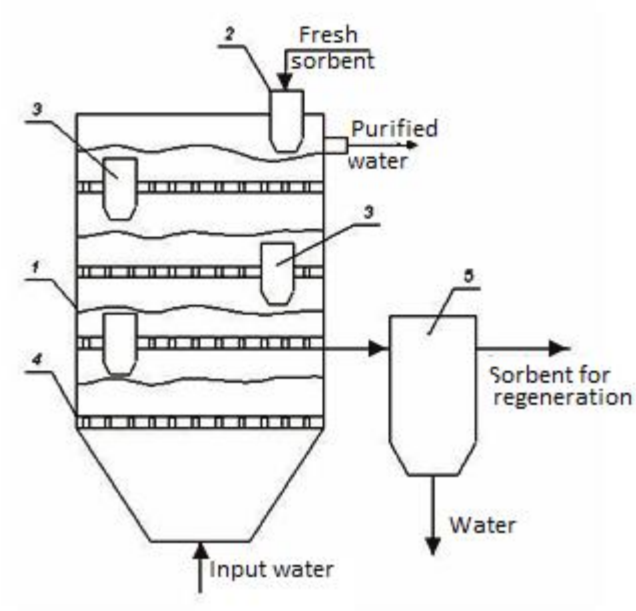


Figure 9.8 – The scheme of tiered adsorber

1 – corps; 2 – dosage; 3 – overflow devices; 4 – distribution devices;

5 – seal-tank

Figure 9.9 – Industrial sorption facilities

Questions for self-control to the section 9

1. Give the definition of adsorption.
2. Name the essence of adsorption.
3. Specify applications of adsorption in water purification.
4. Give the characterization of physical adsorption.
5. How to divide chemical and physical adsorption?
6. Give the characterization of sorbents, that are used in water purification.
7. Name the classification of inside sorbents pores.
8. What requirements are nominated to sorbents?
9. Compare the theoretical models of sorption.
10. What information can be got from adsorption isotherm?
11. What the main stages does adsorption consist of?
12. Name the main postulates of Shilov’s model, what the meaning of “the protection time of sorbent”?
13. What values can be determined from Shilov’s equation?
14. Characterize the methods of sorbents regeneration. What the aim of regeneration?
15. Explain the difference, pointing advantages and disadvantages of adsorption schemes with mechanic mixing of sorbent and water.
16. What types of adsorption apparatuses are used in water purification?

SECTION 10 PURIFICATION OF WASTEWATERS FROM IMPURITIES BY EXTRACTION

1. The essence and spheres of method using.
2. The requirements to extractants.
3. The factors, effecting the extraction effectivity.
4. The schemes of extraction purification.
5. The main hardware design of extraction.

10.1 The essence and spheres of method using

Extraction — extraction — removing. The essence of extraction – water, containing pollutants, is mixed with other liquid (extractant), in which the substance is mixed much better, than in water. The most often the extractants – organic substances – solvents. The degree of extraction is characterized by extraction (distribution) coefficient.

$$Kd = \frac{Ce}{C_W} \approx const, \tag{10.1}$$

where Кd – the distribution (extraction) coefficient; C_e and C_W – the concentration of dissolved substance in extractant and in water, respectively; The distribution coefficient depends on the number of factors: temperature, impurities in water and in extractant, pH of the environment etc. However, really *Kd* is often deviated from the value, calculated by the formula (10.1), because of interaction of dissolved substance with each other with formation of dimers or with molecules of solvent (for example, molecular complexes formation), some mutual solubility of extractant and water etc. Then the amendment is introduced and the equation takes a form (10.2):

$$Kd = \frac{(Ce)^n}{C_W}\ , \tag{10.2}$$

where n − the exponent characterizes the deviation of system from ideal. The value n is determined experimentally. For example, for the system «water – phenol –

butyl acetate» n = 0,98, Kd = 38,0; «water – phenol – isopropyl ether» — n = 0.89, Kd = 13.3. In some cases, n can be over 1.

The extraction method can have used for removing from water impurities of the 3rd group (organic substances – phenols, oils, organic acids, dyes, (aniline)), and also metal ions (impurities of the 4th group). The concentration edges by removable substance – not less than 2 ÷ 4 g/L.

The refining by adsorption methods is usually carried after extraction. Schematically the extraction method can have presented in view (fig.10.1):

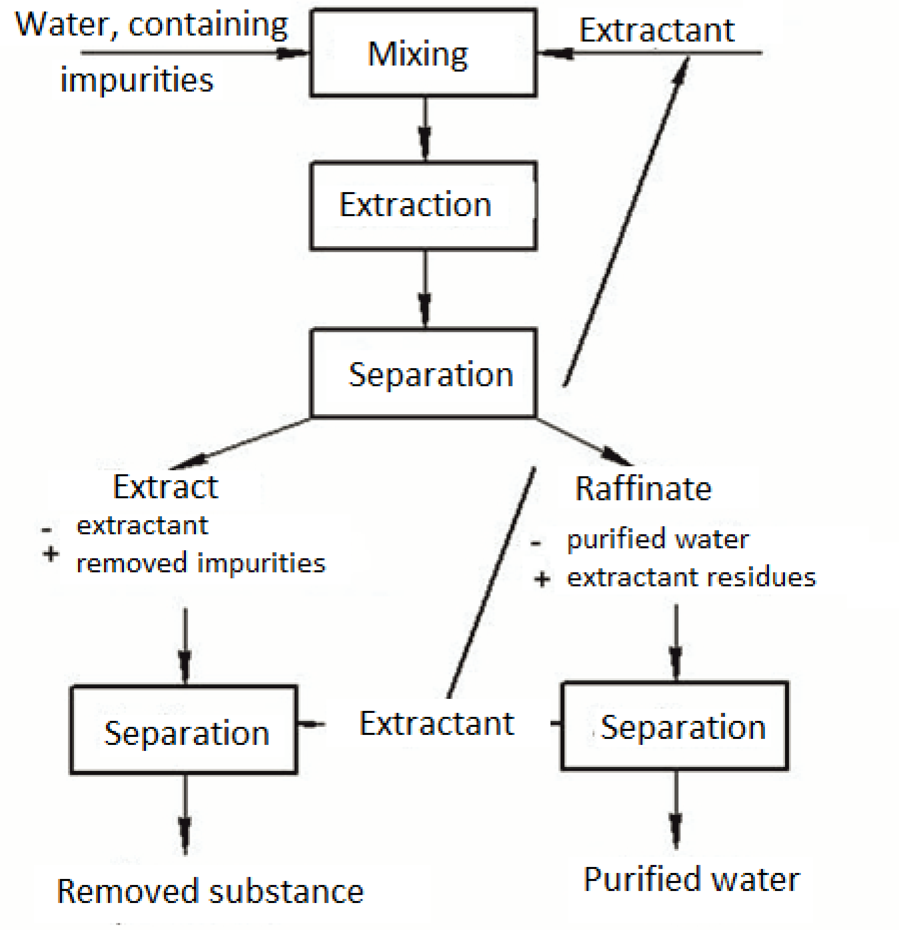


Figure 10.1 – The scheme of extraction

The extraction includes following operations:

1) mixing of water and extractant;

2) actual extraction;

3) mixture distribution into extract and raffinate;

4) removing extractant residues from raffinate;

5) removing extractant from extract.

For decreasing the content of organic impurities to concentrations, less than maximum permissible, it is necessary to choose truth extractant and the rate of its introducing into water. At extractant choosing (the most often organic solvents) its physical-chemical properties, possible regeneration methods etc. should be considered [2, 18].

10.2 The requirements to extractants

The extractant should request following requirements:

to extract removable substance much better, than water, namely has high distribution coefficient. To have, if possible, the highest solubility in relation to the removable component. What it is higher, the costs of extractant are less, namely lower cost of purification;

to have high solubility selectivity. What it will dissolve components less, necessary to stay in water, the removable substances will remove more fully;

to have low solubility in water and not to form stable emulsions, because in opposite case, the productivity of installation is decreased, the separation of extract and raffinate is complicated, the time of process is increased, and also the costs of solvent are increased;

the density of extractant should be much differ from the density of WW (it is usually less), because of only enough difference of densities provides rapid and full phase separation;

to have high diffusion coefficient. What it is higher, the rate of mass exchange is higher, namely the rate of extraction;

to have ability to be regenerated by simple and cheap way;

to have boiling temperature, much different from the boiling temperature of extraction substance (for providing the simplicity of separation), to have low evaporation heat and low heat capacity;

if possible, not to interact with removed substance, - this can difficult the extractant regeneration and to increase its costs;

if possible, not to be toxic, explosive- and flammable and not to cause the corrosion of equipment;

if possible, to have low cost.

10.3 The factors, effecting the extraction effectivity

1) Hydrodynamic mode – the rate of extractant introducing into water should be minimal. The extractant should distribute evenly in water volume. The forward flow isn't used in extraction.

2) The temperature of extraction – such temperature is selected, the solubility of removable substance should be minimal and the highest in solvent. For example, at phenol removing from water the value of Kd at 10 ˚ C is 55; at 40 ˚ C – 40, if the process is carried at 20 ˚, Kd = 50.

3) At some salts content – the effect of salting takes place. Naturally, that at extraction no one salts are added to WW.

4) The structure of removable substance, and its chemical nature.

At the content in water of several impurities, one of the components is advisable for removing by extraction – the most valuable or toxic, and then, if necessary, the 2nd etc.< herewith, the different extractant should be for everyone component. At necessity of extraction several components from WW at the same time, the extractant shouldn't have the removable selectivity, but to have close and very high distribution coefficients for whole removable substances. Charging of this purification process difficult the selection of extractant and its regeneration.

The necessity of extractant removing from the extract and raffinate connects with its necessity to be return into extraction. The regeneration should be charged using secondary extraction – with other solvent, and also by evaporation, distillation, chemical interaction and sedimentation.

The extraction can't have charged, if necessity of its returning into the cycle is absent. For example, after removing of some substance the extract can have used for technology aims or as fuel. In the last case, the extracted substances are destroyed at burning. It's advisable to do, if they aren't highly valuable.

Since there are no absolutely insoluble substances in water, at the extraction the part of reactant is dissolved in WW (purified), becomes the new its pollutant, that's why the extractant should be removed from the raffinate. It's also necessary to carry out for reducing losses of solvent. The losses of solvent with raffinate are permissible only at its solubility in water not over MPC, but only at its very low cost. The widest method of solvent removing from raffinate is adsorption or vapor (gas) stripping. For this aim it is advisable to use wasted vapor or out-coming smoke gases.

10.4 The schemes of extraction purification

For the extraction purification of water, the processes of opposite flow extraction and continuous opposite flow extraction are often used.

There are: cross-flow (fig.10.2), stepwise-opposite-flow (fig. 10.3) and continuous-opposite-flow (fig.10.4) extraction schemes.

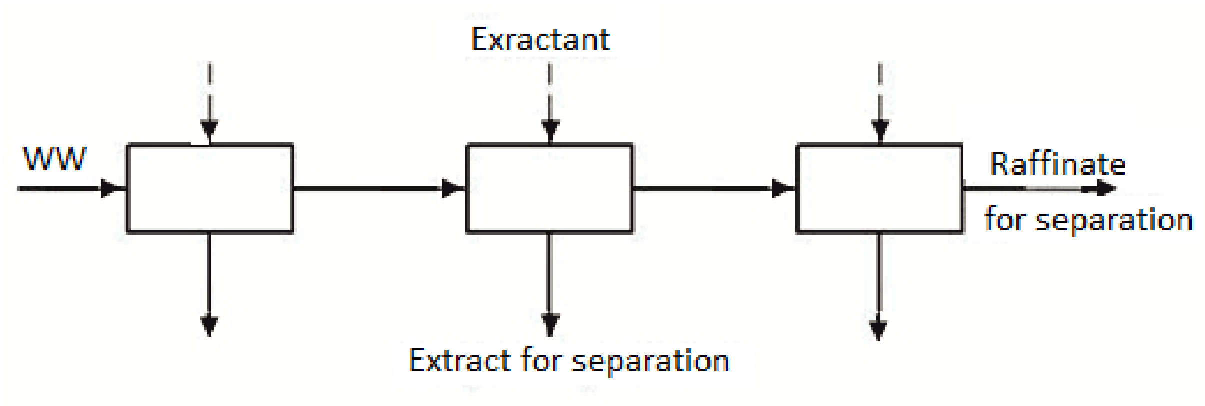


Figure 10.2 – The scheme of multi-step cross-flow extraction

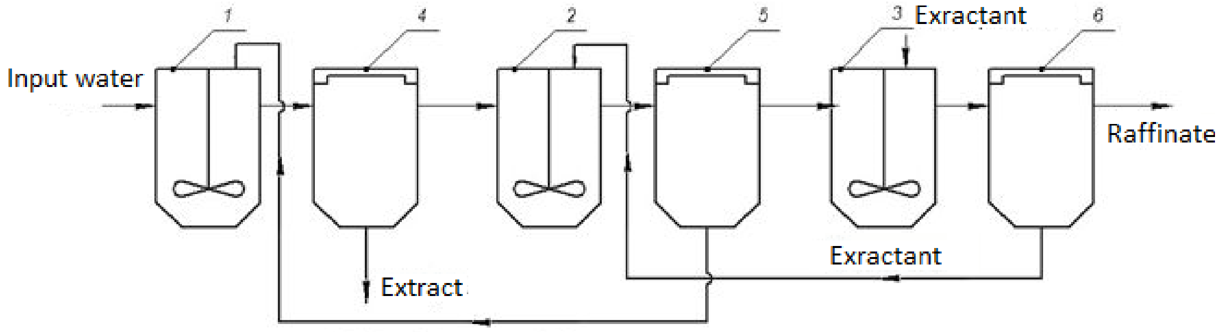


Figure 10.3 – The scheme of multi-step opposite-flow extraction

1,2,3 – extraction devices; 4,5,6 – sedimentation tanks or separators

Fresh extractant and WW income from opposite sides. At the 3rd step WW with low content of impurities is moved with fresh extractant, at the 1st stage the input water is mixed with extractant, containing high quantity of the extracted substance. Such moving of flows improves the formation of greater driving force of the extraction process and effective purification of WW.

The forward-flow isn't used at extraction.

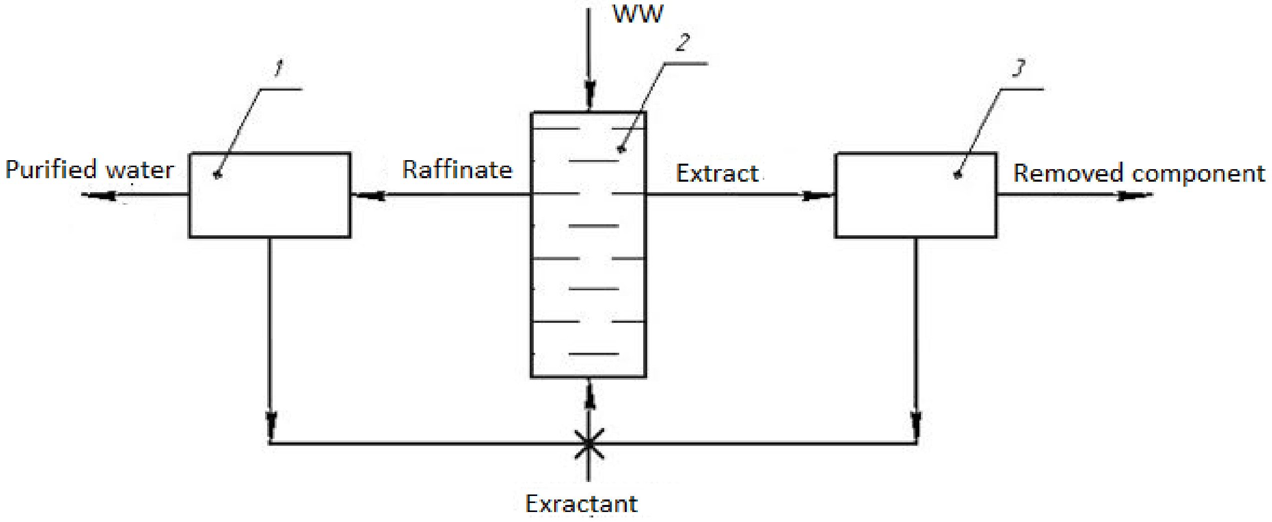


Figure 10.4 – The scheme of continuous opposite-flow extraction with regeneration of extractant from extract and raffinate

1 – the system for extractant removing from the raffinate; 2 – extraction column; 3 – the system of extractant removing from the extract

10.5 The main hardware design of extraction

The extraction is charged in apparatuses of different construction: loosening extractors, nozzle, plate columns, and also in centrifugal extractors. The construction of extractor with mechanic mixing – rotor-disk extractor – is presented in fig. 10.5.

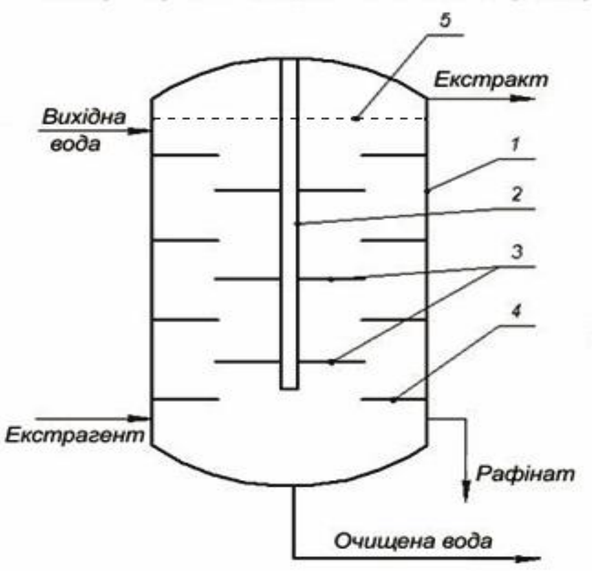


Figure 10.5 – The rotor-disk extractor

1 – corps; 2 – axel; 3 – rotatable disks; 4 – unmovable ring partitions; 5 – calming perforated grille

The advantage of extraction is high purification level 95- 97%.

There are following methods of the extractant introduction and input water, depending on the value of extractant density (fig. 10.6).

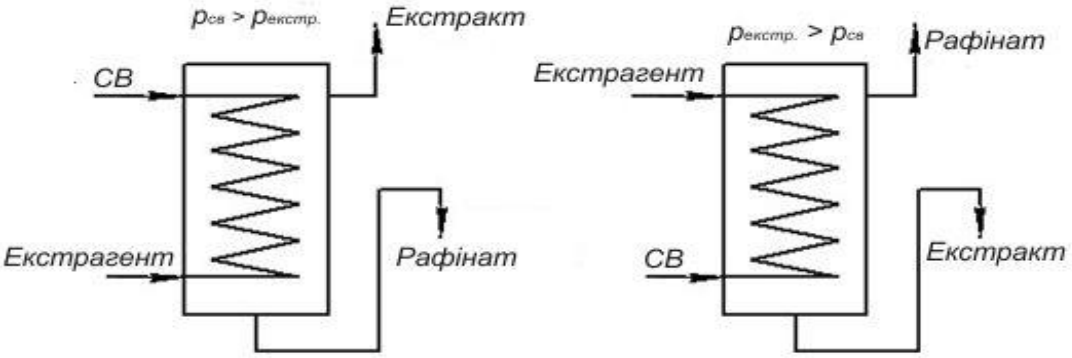


Figure 10.6 – The methods of the extragent introducing into the apparatus depending on liquid density

The disadvantages – the expensive method, economically advantageous only at extractants regeneration.

Questions for self-control to the section 10

1. Explain the essence of extraction removing of impurities from water.
2. What does the extraction coefficient characterize?
3. Give the scheme of extraction.
4. Name the requirements to extractants.
5. Explain the factors affect the efficiency of extraction.
6. What the aim of extractant regeneration?
7. Compare the technological schemes using at the extraction.
8. What apparatuses are usually used for extraction?
9. Explain the principle of the rotor-disk extractor.

SECTION 11 BIOCHEMICAL WATER PURIFICATION

1. The essence and sphere of using biochemical water purification.
2. The biological bases of the method.
    - 2.1 The active sludge and bio-film.
    - 2.2 The increasing of biomass and biological oxygen consumption (BOC).
3. The requirements to WW, incoming to bio-purification.
4. The characteristic of main facilities for water purification in natural and artificial conditions.
    - 4.1 The aerobic purification.
    - 4.2 The types of aero tanks.
    - 4.3 The anaerobic purification.

11.1 The essence and sphere of using biochemical water purification

The biochemical method of water purification is based on biological oxidation. This process is inherently natural. The biological oxidation is carried by microorganism's community (biocenose), including numerous different bacteria, the simplest and a number of higher-organized organisms – algae, mushrooms etc., connected with each other into the one complex by complex relationships (metabioz, symbiosis, antagonism). The symbiosis is cohabitation of two organisms of different kinds, bringing them mutual benefits. The great role in this community owns bacteria, the number of which is variated from 10^6 to 10^{14} cells per 1 g of dry biological mass (biomass). The number of bacteria families can reach 5 – 10, the number of kinds – several tens and even hundreds [2, 4].

Such variety of micro-organisms kinds is caused by presence organic substances of different classes in purified water. If only one or several closed homologs of organic compound present in WW, the development of bacteria monoculture is possible.

There are heterotrophs and autotrophs among bacteria at purification facilities, moreover, the predominant development one or another one group gets depending on conditions of the system's work. These two bacteria groups are differed by its relation to the origin of carbon consumption. The heterotrophs use prepared organic matter and recycle it for obtaining energy and cell biosynthesis. The autotrophs consume inorganic carbon for cell synthesis, and they get energy by photosynthesis, using light energy or chemosynthesis energy by oxidation some inorganic compounds (for example, ammonia, nitrites, Fe^{2+} salts, H_2, elementary sulfur etc.).

The microorganisms have versatile and active fermentative equipment, whereby in natural conditions they provide the circulation of biogenic elements – nitrogen, carbon, sulfur, phosphor etc. the microorganisms are capable to rend complex organic substances even to the simplest derivatives, which can have assimilated again by plants and animals.

There is high number of groups (the predominant race) of microorganisms:

- oxidize the compounds of C_1 – Methanomonas;
- oxidize the compounds of C_2-C_4 – Beffecterium, Pseudo-monas;
- oxidize the aromatic compounds – Bacillum (бацили);
- nitrogen decomposable – Nitrosomonas;
- sulfur-bacteria – Desulfovibrio.

11.2 The biological bases of the method

The biological purification method is used for removing from WW dissolved organic and inorganic substances – impurities of the 3rd and the 4th group (NH_3, H_2S, nitrites etc.).

The aerobic and anaerobic methods of WW biochemical purification are known. The aerobic method is based on using organism’s groups, for living of which the continuous oxygen origin is necessary. At the aerobic purification, the microorganisms are cultivated in active sludge or bio-film. The anaerobic purification methods flow without oxygen, they are used, mainly, for purification of high-concentrated WW and for disposal of WW’s precipitates (fermentation).

11.2.1 The active sludge and bio-film

The active sludge consists of living microorganisms and solid substrate. The living organisms are presented by communities and single bacteria, the simplest worms, fungi, yeast, actinomycetes and less insect larvae, crustaceans, and also algae etc. The community of whole living organisms, settling sludge, is called biocenose.

The clusters of bacteria in active sludge surrounded mucous layer (capsules0. Such clusters are called zoo-glayes. They improve the structure of sludge, its sedimentation and compaction. The mucous substances contain antibiotics, capable to thread inhibit bacteria.

The active sludge is amphoteric colloidal system, at pH 4-9 it has negative charge. Despite significant differences of WW, the elementary composition of active sludge is enough close (for example $C_{97}H_{199}O_{53}N_{28}S_2$). The dry substance of active sludge contains 70 ÷ 90 % of organic and 30 ÷ 10 % of inorganic substances. The substrate (to 40 % in active sludge) is solid part of dead algae residues and different solid residues. The organisms of active sludge are attached to it.

The representatives of four kinds of the simplest are met in active sludges: sarkodovi, flagellates, ciliates and sucked ciliary. The simplest organisms don’t take part directly in destroying of organic pollutions, but it absorbs the high quantity of bacteria (one ciliary passes through its organism from 20 to 40 thousand of bacteria), supporting its optimal content in sludge. They improve sludge sedimentation and lightening of WW. At formation of active sludge, the bacteria appear firstly, then the simplest. They have cementing ability, that’s why the active sludge is brownish-yellow lumps and flakes with size 3 ÷ 150 μm. The flakes have the surface approx. 1200 m^2 per 1 m^3 of sludge (100 m^2 per 1 g of dried substance). One cubic meter of the active sludge contains approx. $2 \cdot 10^{14}$ bacteria.

The bio-film is the thin layer of active sludge on the nozzle-filler of bio filter.

It looks like the mucous fouling with thickness 1 ÷ 3 mm or more. Its color is changed with changing of WW composition from grayish-yellow to dark brown. The bio-film consists of bacteria, yeast and other organisms. The more different representatives are met in it: the simplest, rotifers, worms, than in active sludge. The larvae of mosquitoes and flies, worms and mites eat the active sludge and bio-film, causing its loosening. It improves the purification process. The number of microorganisms in bio-film is less, that in active sludge. One cubic meter of the bio-layer contains $1 \cdot 10^{12}$ bacteria.

The biochemical activity of microorganisms is characterized by biochemical indicator – the ration of BOC_{total} / COC (chemical oxygen consumption). This indicator has a very wide interval of the values – from $\approx 0,001$ to $> 0,5$. The IWW have a low indicator – $0,05 \div 0,3$; HWW – over 0,5. The scheme of water purification, the ability for recycling water supply etc. are determined by the value of this indicator.

By the biochemical indicator, the concentration of pollutions and toxicity the IWW are divided into 4 groups:

the 1st: The biochemical indicator $> 0,2$: the WW of food industry (yeast, starch, sugar, brewery), direct petroleum distillation, the synthesis of fat acids, the protein-vitamin drugs etc.

the 2nd: The biochemical indicator $0,1 \div 0,02$: the WW of coking, nitrogen fertilizing, coke, soda plants. These waters after mechanic purification can have directed to the biochemical oxidation.

the 3rd: The biochemical indicator $0,01 \div 0,001$: the WW of sulfurization, chlorination, oil and SAS (surface active substances) producing, H_2SO_4 plants, steel, heavy machinery. These waters can have directed to the biochemical oxidation after local purification facilities (mechanic, physically-chemical purification).

the 4th: The biochemical indicator lower than 0,001: the WW contain, mainly, suspended particles. The WW of coal- and ore-dressing factories.

11.2.2 The increasing of biomass and biological oxygen demand (BOD)

The increasing of biomass occurs during water purification. The increasing of biomass depends on many factors and parameters: the chemical nature of pollutions, class and recycling of microorganisms, *BOD / COD*, the concentration of P and N in WW, the temperature, the rate of microorganism's reproduction etc.

For approx. calculations, the increasing of biomass is determined by the formula:

$$I = K(COD - BOD_{total}),$$

where *K* – the coefficient, characterizing the quantity of sludge in mg, forming from 1 mg of the difference $COD–BOD_{20}$, and it is determining experimentally and changes in the interval 0,1 ÷ 0,9 (for IWW). The value of I isn't exposed exact calculation, it is determined experimentally.

11.3 The requirements to WW, incoming to bio-purification

There are enough hard requirements are nominated for waters, directing to the biochemical purification:

- the active reaction of the environment – pH – the best is neutral or closes to it 6,5 ÷ 8,5; (pH is allowed 5 ÷ 9, but there are bacteria, developing good in acid environment pH 4 ÷ 6 (mushrooms, yeast);
- the temperature of WW: the optimal is 2 ÷ 35 ˚ C (20 ÷ 30 ˚ C), although there are microorganisms can exist at 3 – 45 ˚ C – mesophillous, and at 5 – 80 ˚ C – thermophiles. It's necessary to exclude sudden changes in temperature;
- the BOC – depending on aero tanks construction the BOC_{total} is allowed 500 mg O_2 / L, for displacers and BOC_{total} = 1000 mg O_2 / L for aero tanks – mixers;
- the quantity of suspended substances in WW shouldn't be over 100 ÷ 150 mg/L;
- the total salt content in water – not over 10 g/L;
- the content of petroleum products and oils shouldn't be over 25 mg/L;
- the sufficiency of nutrition for bacteria is determined by the ratio: BOC: N: P = 100:5:1 (for IWW is different);
- the quantity of dissolved O_2 shouldn't be less than 2 mg/L;

- the absence of biologically hard drugs (aromatic, SAS, quaternary ammonia compounds);
- the limitation according to MPC of toxic and poison substances;
- if possible, the constant content of wastes, since the biocenose is adaptable to the water composition.

11.4 The characteristic of main facilities for water purification in natural and artificial conditions

11.4.1 The aerobic purification

The aerobic purification can have implemented in natural and artificial conditions. In natural conditions the purification is in the fields of irrigation, fields of filtration and biological ponds. The artificial facilities are aero tanks and bio filters.

The fields of irrigation, biological ponds are specially prepared ground areas. In Russia, the first fields of irrigation were arranged in Odessa (1987), and then in Kyiv (1894), in Moscow (1898).

The fields of irrigation are used at the same time for WW purification and agricultural aims. The purification of WW happens at ground microflora, sun, air and plants. If these fields aren't used for growing crops – these are the fields of filtration.

The biological ponds are the cascade of ponds (3 – 5 degrees). The purified water flows through it with slow speed. The ponds are intended for final biological purification and WW refining in complex with other purification facilities. There are ponds with natural and artificial aeration. The temperature in ponds in less than 6 ° C, during the winter period the ponds don't work.

11.4.2 The types of aero tanks

The aero tanks are iron-concrete reservoirs (opened pools), equipped by devices for forced aeration.

The aero tanks are differed by following features:

1) by the hydrodynamic mode – mixers, propellants and aero tanks of intermediate type (with introduction of dispersed WW);

2) by the method of the active sludge regeneration – with single and inside regeneration;

3) by the loading on active sludge – high-loadable (for incomplete purification); common and low-loadable (with extended aeration);

4) by the quantity of degrees – one-, two- and multi-degree;

5) by the construction features (2-, 3- and 4-corridor) (fig. 11.1).

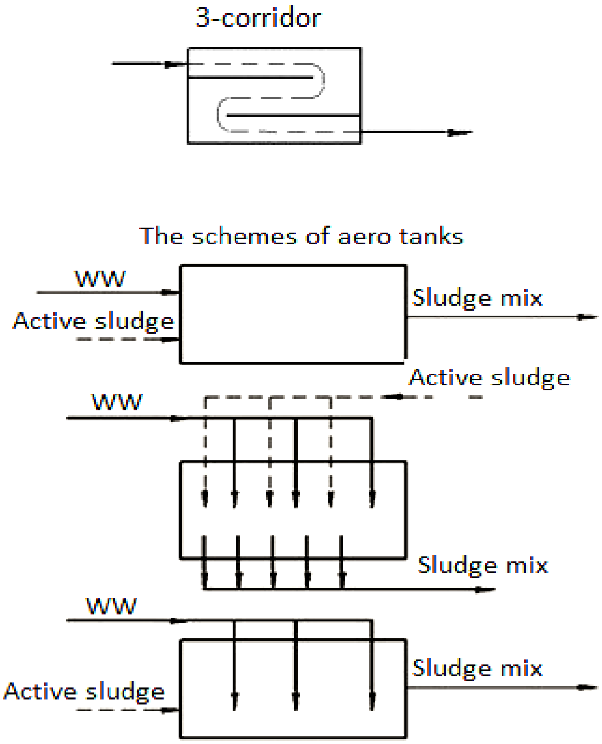


Figure 11.1 – The schemes of aero tanks

1 – aero tank – displacer; 2 – aero tank – mixer; 3 – the aero tanks with distributed water supply

The aero tanks are usually rectangle (or round) in plane, with length to 120 m (depth 2 ÷ 5 m). The ratio of length and width 30:1.

The dose of active sludge in aero tanks 2 ÷ 4 g/L by dried substance.

The pneumatic, mechanic and pneumatically-mechanic methods are used for the aeration (the air is passed through porous plates, crushed jets etc.).

The most typical scheme of the biochemical purification with a remote regeneration (fig. 11.2).

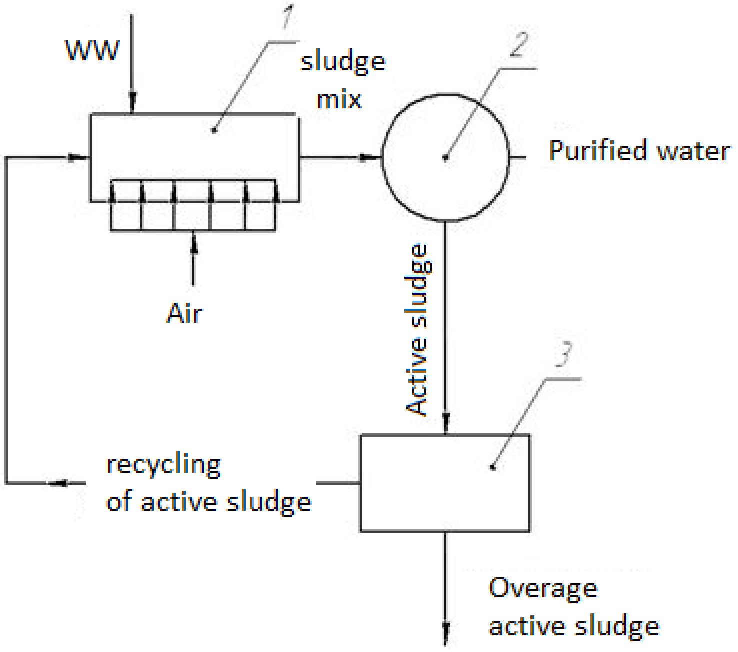


Figure 11.2 – The typical principle scheme of the biochemical purification
1 – aero tank; 2 – sedimentation tank (secondary); 3 – regenerator

The regenerator is often one of the corridors of aero tank.

The biofilters are facilities with backfilling inside, the microorganism’s biofilm is formed om it. They are presented by opener round or rectangle in plane, opened towers, working at atmospheric pressure.

The wasted (died) biofilm is washed by flowing WW and outcomes away from filter. The following substances are used as backfilling: crushed stones, grave, slag, keramzit, ceramic and plastic tips of different configuration, steel and plastic nets, twisted in rolls etc.

The filtration is carried up-down with a very slow speed for escaping the biofilm separation. Firstly, a water is rejected during some time (until the biofilm increasing).

The advantages over the aero tanks – higher degree of purification, the disadvantage – lower productivity.

If oxygen is used for blowing instead of air – the apparatuses are called oxy tanks [2].

The refining for waters, discharging into ponds and its recycle using, is usually necessary after the biochemical purification, in such cases the filtering through a sand filters, flotation, adsorption, disinfection etc. are used.

4.3 The anaerobic purification

The anaerobic methods are used for purification high-concentrated WW and precipitates fermentation after primary and secondary sedimentation tanks. The methane tanks are cylindrical apparatuses, working at > 0,5 MPa. The temperature is $30 \div 55$ ˚C (depends on bacteria kind). The fermentation period $20 \div 24$ days. Water, CO_2, CH_4 (methane, alcohol, acetone etc. fermentation) are outed into gas phase. The WW have BOC $4000 \div 5000$ mg/L. The process is very difficult, multi-stage, its mechanism isn't finally established.

The particular attention should be paid precipitates, forming after the biochemical purification. Possible utilization ways: producing of vitamin additions, activated carbon, but in everyone particular case the qualitative composition of active sludge should be included, - this is the content of necessary metals, toxic substances of the different origin.

Questions for self-control to the section 11

1. Explain the essence of the biochemical method of water purification.
2. What the difference between heterotrophs and autotrophs?
3. What is the active sludge, biofilm?
4. Characterize the biochemical indicator.

5. How to determine the increasing of the biomass?
6. What requirements are nominated to WW, directing to the bio-purification?
7. Name the facilities, exercising the aerobic purification.
8. What features are the aero tanks differed by?
9. Give the typical scheme of the biochemical purification with remote regeneration of the active sludge.

SECTION 12 THE METHODS OF REMOVING FROM WATER IMPURITIES OF THE FOURTH GROUP (METHODS OF WATER DEMINERALIZATION)

1. The characteristic of the methods of removing impurities of the 4th group and spheres of its using.
2. The essence of water demineralization by ion exchange.
    2.1 The structure and properties of resins.
    2.2 The static of the ion exchange.
    2.3 The kinetic and dynamic of ion exchange.
3. The regeneration of resins.
4. The main types of technological schemes of water purification by the ion exchange.
    4.1 The main construction elements of ion exchange filters.
    4.2 The filter of mixed activity (FMA).

12.1 The characteristic of the methods of removing impurities of the 4th group and spheres of its using

The impurities of the 4th group (Kulskiy's classification) are particles of ion sizes. The whole demineralization methods are divided into 3 groups [2, 19]:

1) softening methods;
2) water desalination methods;
3) desalting methods.

Water softening – the removing of hardness ions: Ca^{2+} and Mg^{2+}.

Desalination – the decreasing of total salt content (TSC) to the norms of drinking water (TSC to 1000 mg/L).

Desalting – the decreasing of TSC to conditions of distilled water – to 0,01 mg/L.

The methods of water softening are: thermal, reagent or chemical, physically-chemical (ion exchange), combined.

The methods of desalination and desalting are: distillation, reverse osmosis (hyper filtration), electric dialysis, freezing.

The methods of softening – the processes, causing the decreasing of water hardness.

The thermal softening of water by heating is based on carbon dioxide equilibrium shift into the side of $CaCO_3$ formation:

$$Ca(HCO_3)_2 \overset{T}{\Leftrightarrow} CaCO_3 \downarrow + CO_2 \uparrow + H_2O\,.$$

The shift of equilibrium occurs by decreasing of CO_2 dissolving, causing the temperature increasing. Carbon dioxide can have removed from water by boiling and, so, to decrease much the carbonate calcium hardness. However, this hardness can't be fully eliminated, because of $CaCO_3$, albeit slightly (13 mg / L at T = 18 ° C), but is still soluble in water.

$$Mg(HCO_3)_2 \overset{T}{\Leftrightarrow} MgCO_3 + CO_2 \uparrow + H_2O\,.$$

The hydrolysis reaction takes place at boiling:

$$MgCO_3 + H_2O \overset{T}{\Leftrightarrow} Mg(OH)_2 \downarrow + CO_2\,.$$

The solubility of $MgCO_3$ = 110 mg / L; $Mg(OH)_2$ = 8,4 mg / L.

The thermal method can have used for softening of water, containing mainly the carbonate hardness and costs for feeding boilers of low and middle pressure, and is also used as combined method at reagent softening methods. The disadvantages of the thermal method are increased cost by using electric energy for heating.

The methods of reagent softening – the method of transferring compounds of Ca^{2+} and Mg^{2+} into practically insoluble compounds by reagents treatment: CaO, Na_2CO_3, NaOH, $Ba(OH)_2$, Na_3PO_4 i $Na_2C_2O_4$ etc.

The following value of the residual hardness is reached at using reagents:

а) lime ($H_{res.}$ = 0,35 ÷ 0,7 mmole / L);

б) lime-soda ($H_{res.}$ = 1,4 ÷ 1,8 mmole / L);

The barium compounds are possible for using. Softening by barium compounds: $Ba(OH)_2$ and [$BaCO_3$ + $Ca(OH)_2$] ($BaSO_4 \downarrow$), but this makes more expansive cost of water treatment, besides, barium compounds are toxic.

Sodium phosphate (Na_3PO_4) provides the lowest residual hardness among all named reagents – to 0,035 ÷ 0,07 mmole / L; it is used only when the hardness of input water decreased by other reagent methods to 0,35 ÷ 0,7 mmole / L, it connects with high cost of sodium phosphate.

The distillation is the method, based on water evaporation with further condensation of its vapors.

It is carried in evaporators of different constructions. The distillation is used in cases, when TSC > 10000 mg/L. The disadvantage of the method is increased energy consumptions and, as consequence, the cost of softening water.

The reverse osmosis (hyper filtration) is the process of water passing through the semipermeable membranes. The water molecules pass through it, and molecules of dissolved substances are delayed. Th membrane methods win the technology market of water preparation, they are differed by such advantages, as constructions and exploitation simplicity, compact.

But the membranes technologies have such disadvantage, as the phenomenon of concentration polarization. Besides, unfortunately, the membrane elements aren’t produced in Ukraine.

The electric dialysis – the process of anions and cations transferring in water by the electric field through the membranes.

As whole electrochemical methods, it keeps to get practically purified acids and alkaline with water purification at the same time. It is used for desalting natural waters, the last time the deionization methods are used in pharmacy.

12.2 The essence of water demineralization by ion exchange

The essence of ion exchange – at water contact with special substances, named resins, the ion exchange between solution phase and resin phase is possible. This exchange is equivalence and described by the stoichiometric equation of the exchange chemical reaction. In accordance with the mark of exchanging ions charge, the cation exchangers and anion exchangers are differed (fig. 12.1)

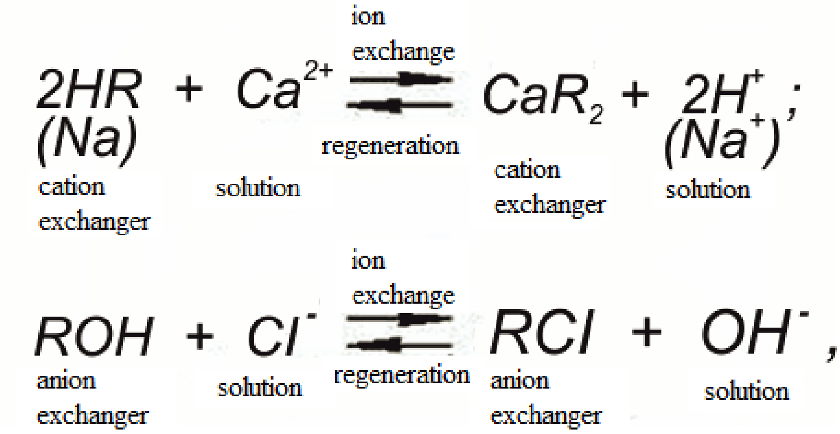


Figure 12.1 – The essence of ion exchange

R – the unmovable part (matrix) of resin

The essence of the process is in water filtration through the layer of resin. Herewith, the resin is, the most often, the unmovable layer. The apparatuses are used with resin (movable layer) or fluidized layer. So, the ion exchange is a sorption process, accompanied by the chemical reaction, and flows on ionic level. The forces of chemical interactions of the reactions are determinable, but not adsorption forces [1, 4].

There are 4 following stages can be isolated in apparatuses of filtering layer at ion exchange:

1) water filtration – actual ion exchange;
2) loosening of the resin layer;
3) regeneration of resin;
4) washing resin from the residues of regeneration solutions;

The concentration edges of using method: economically advisable at the content of hardness salts to 14 mmole / L, the total salt content – 2 ÷ 4 g / L, suspended substances – not more than 10 mg / L.

The advantages of the method:

1) the possibility of getting water with the residual salts content 0,01 ÷ 0,05 mg / L and practically absence of the hardness: ≈ 0,001 ÷ 0,002 mmole / L;
2) simplicity and reliability of the method.

The substantive disadvantage: at resins regeneration the large amount of wasted solutions can be got: acids, alkaline, salts, forming after loosening, regeneration and washing of ion exchange resins, and also after losing the exchange capacity (usually 5 – 8 years) – wasted resins.

12.2.1 The structure and properties of resins

More than 1000 kinds of resins are known, the single classification is absent, it is explained the complexing of composition and high difference of resins properties.

By the nature resins are divided into inorganic (mineral) and organic, natural or artificial (synthetic).

The inorganic natural resins are zeolites, clay minerals (alumina silicates), including bentonite clays (montmorillonite), glauconitic, feldspars, mica, phosphates and silicates Ti, Ca, Zr etc.

The zeolites are the alumina silicates of alkaline and alkaline earth metals with the general formula:

$$Me_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O \; .$$

The inorganic artificial resins are synthetic zeolites, hard soluble salts of heteropoly acids with the general formula $Me_3XY_{12}O_{40} \cdot nH_2O$ (X = P, As, Sb, Si; Y = Mo, W; Me – metal), ferrocyanides, phosphates, hydroxides, sulfides of Me (Zr , Al, Fe, Ti, Ni etc.).

The organic natural is stone and brown coal, peat, cellulose etc.

The synthetic organic resins, having the constant composition, strength, porosity etc., find a high using.

The resins in common meaning are solid, granular, powdered, fibrous or molded, mechanically strong and chemically resistant, insoluble substances, containing the functional (ionic) groups, capable to ionization and ion exchange with electrolytes. At ionization of functional groups two kinds of resins are formed:

1) fixed ions, mounted on the frame (matrix) of the resin and not able to leave the phase of resin and transfer into the outside solution;

2) counterions (exchangeable ions) of the resin, equivalency is fixed ions, but opposite in mark, capable to transfer into outside solution in the quantity, equivalent to the quantity of other ions of the same mark, transferring to the resin from outside solution (the exchanger of solution ions).

By its self-structure the resins are high-molecular compounds (polymers), getting by polymerization or poly condensation.

By its structure the resins have gel structure, crushing mechanically.

By chemical composition these are polymers, having the exchange functional groups. The polymer frame is the matrix and ionic groups. The functional groups: HCl, H_2SO_4, H_3PO_4, primary, secondary amino-groups etc.

The resins have following properties:

1) the ability to ion exchange, characterizing quantitatively by so-called ***exchange capacity.*** There is static exchange capacity (SEC) or TSEC (total static exchange capacity) – it is determined at equilibrium conditions (in solutions $CaCl_2$, HCl, NaOH) and dynamic exchange capacity (DEC) (to slippage) is determined at filtration (the dynamic exchange capacity is always less, than the static one).

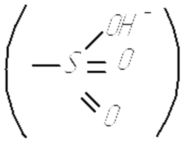
The following characteristics are for quantitatively characterization of ion exchange and sorption properties – total and working exchange capacity (the sorption ability of the resin to sorb ions).

The total exchange capacity is the total quantity of whole ionic groups, present in single volume of wet (swollen) or a mass of dry resin. The value of exchange capacity doesn’t affect the concentration and nature of exchangeable ions, is constant for this sample of resin and can have changed under the influence of ionization radiation, thermal or chemical influence,

At real conditions of many-time using of the resins in the cycle sorption – regeneration, the exchange capacity of resins isn’t used completely, but only some value, caused the process technology. For example, the traditional methods of water treatment at heat electric station (HES) keep to use ~ 50% of TSEC, in these cases, talk about renewable, active or working exchange capacity of the resin;

2) the acidity of cation exchangers or the alkalinity of anion exchangers. Depending on ability to ionization, the cation exchangers are divided into weak, medium, strong; the anion exchangers into strong- medium- and weak alkalinity.

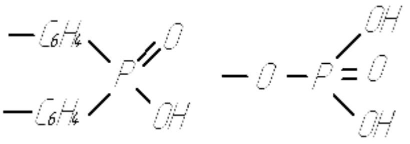
The strong acidity cation exchangers are that contain sulfuric groups.



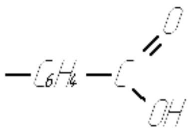
CEU (cation exchanger universal)-2-8 (the widest) CEU-2-2, CEU-2-3, Levatit (FRG), Daueks (USA), Umberlight JR (USA, Japan), Duolight (France, USA).

CEU-2-8 has gel structure, fixed ions – sulfuric groups. They are produced by sulfate or chlorine sulfonate acid of styrene copolymer grains with 8 % of divinyl benzene.

The cation exchangers of medium power are cation exchangers with groups of phosphoric acid, CEF (cation exchanger phosphate)-11 (in sodium form).



The weak acidity are resins with carboxyl groups: CB(carboxyl)-2, CB-2-4:



The strong alkalinity (high-alkalinity) anion exchangers – with quaternary alkyl-ammonia groups: AEH (anion exchanger high-alkalinity)-17-8 and its varieties.

$$-\left[N(CH_3)_3\right]^{+}OH^{-}.$$

The medium alkalinity anion exchangers contain ternary (≡ N), secondary (= NH), and primary (-NH_2) amino groups, connected to aliphatic circuit of the matrix: EDE-10P.

The weak alkalinity (low-alkalinity) anion exchangers are ternary and secondary amino groups, connected to aromatic radical: AEL (anion exchanger low-alkalinity)-2FN, AEL-31.

If the resin contains the one type of functional groups, it is called mono-functional, if several – poly-functional (SO_3H, COOH, phenolic groups).

There are poly-ampholytes – resins with amphoteric properties, for example, AELC-2.

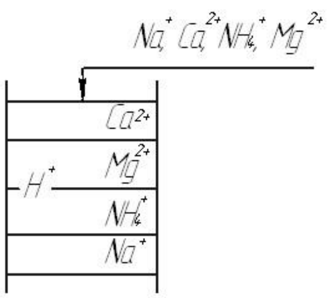
These properties (and selection of resins) are necessary, because water, incoming for purification, has different values of the pH;

3) the swelling of the resin (solvate properties) is ability, by hydration of functional groups, to hold water inside the resin grain. The resin grain is increased; the volume is increased too. The ratio of the resin volume in swelled state to the volume in air-dried is called the swelling coefficient (1,3 ÷ 1,5). The swelling of resins causes the increasing of diffusion rate. The twisted chain of polymer is straightened. The real pores are absent in gel structure of the resins. The availability of whole volume of resin grains for exchangeable ions is provided by its ability to swell in water solutions.

The swelling determines the technology parameter – water consumption for washing resin after regeneration. The ion exchangers are downloaded into filters in swelled state;

4) the selectivity of ion exchangers is the ability to adsorb preferably one an ion at presence of several ions. The higher affinity responds to its higher valence. There are selectivity rows. For natural waters the row of selectivity is:

$$Ca^{2+}>Mg^{2+}>NH_4^{+}>Na^{+}>H^{+};$$



$SO_4^{2-} > NO_3^{-} > Cl^{-} > CO_3^{2-} > HCO_3^{-} > OH^{-}$.

The selectivity of ion exchangers causes many-step of water desalting schemes;

5) the osmosis stability and abrasion strength. The grain «works» all times at variables conditions - expansion, compression. It causes to the ion exchanger destroying – the size and fractional composition are changed.

The osmosis stability is ability to save its fractional composition during a long time. It is determined after 150 hours of working.

The abrasion strength of the ion exchanger is determined by the life of the resin (usually 5 years). The ion exchanger is crushed, at loosening – the purification of clearance between grains from third party suspended and small particles is happened (particles appear by grains destroying).

Depending on the desalting scheme, the regeneration of ion exchangers is charged 1 ÷ 2 times per day (1-2 times per week, 1 time per 6 months).

The hard requirements are nominated to water: the content of suspended substances – not over 10 mg/L, at the outputting from filter – the transparency by «the type» – 50 cm (water for vapor) and 35 cm for drinking water;

6) particle size composition (fractional composition) is usually 0.5 ÷ 0.7 mm;

7) the chemical and thermal stability. The regeneration is carried by acids (to 25 %) and alkaline (15 %).

The plants-producers: Cherkassy «Azot», Kamenskoye «Smoly».

The ion exchange is subordinated many adsorption laws.

The static of ion exchange can be reviewed as at adsorption processes, using the same laws.

The kinetic – three stages are reviewed: inside, outside diffusion, and the actual ion exchange. The mechanism of mass transfer is subordinated the main laws and has much in common with adsorption. The same is related to the ion exchange.

The laws of dynamic at working of unmovable layer of the resin is also subordinated to the model of layered testing of the resin and, the adsorption laws can be used at studying the initial curve.

12.3 The regeneration of resins

After replacement exchangeable ions of the electrolytes to the ions, dissolved in water, the ion exchanger is exhausted and losses the ability of ion exchange, the regeneration of ion exchangers, namely the regeneration of its exchange capacity, is reached by passing exhausted resins of regeneration solutions through the layer. The following substances can be used as regeneration solutions:

at Na-cationization – NaCl;

at NH_4-cationization – NH_4Cl;

at H-cationization – HCl, diluted H_2SO_4 solution;

at OH-anionization – NaOH, NH_4OH;

at CO_3-anionization – Na_2CO_3, $NaHCO_3$.

The anion exchangers are downloaded the most often into standard pressure filters, usually using at chem-water purification stations.

The regeneration of resin is charged in 3 successive stages:

1 – loosening of the backfilling of the ion exchangeable material at loosening supply water up-down;

2 – passing of the regeneration solution (actual regeneration). Depending on passing the regeneration solution through the filter, the filters can be:

- *parallel-flow* (treated water and regeneration solution are passed through the filter in the same direction);
- *opposite-flow* (water and regeneration solution are passed through the filter in opposite directions);

3 – washing of filter's backfilling from the regeneration solution and products of regeneration.

The ion exchangeable filters, by the principle of working, are classified into following groups:

- cation exchangers;
- anion exchangers;
- mixing action (FMA).

The filters of mixing action are classified, in turn, in bulk with inside and outside regeneration and alluvial.

By the construction there are one-cell and two-cells ion exchangeable filter. In the last ones two filters, having the separate management, are connected in one corps.

The filters for continuous opposite-flow ion exchange with remote regenerations of resins can be used too. The process is carried in series of connected columns (working, regeneration, washing). The compact movable layer of the ion exchanger is used in working and regeneration columns, and in washing – the fluidized. At these installations the costs of initial water, regeneration solution, washing water are supported at a given level, and the circulation of the resin is regulated by changing the time of emptying the bunker of washing column. At changing the composition of the initial water, the rate of reactant introduction, regeneration solution and the resin circulation are changed respectively. The transporting of the ion exchanger is carried by the hydraulic method. Everyone column is calculated according to the characteristics of the process, carrying in it. The columns equipped the devices for liquid flows distribution in the layer of resin.

12.4 The main types of technological schemes of water purification by the ion exchange

Depending on the quality of initial water (hardness salts content Ca^{2+}, Mg^{2+}, Na^+, total salt content etc.) and requirements, nominating for the purified water, firstly by hardness, salts content and SiO_3^{2-}, the different schemes of water desalting can be used. There are following ways of the connections, by the character of connects of the filters and water incoming:

1) parallel (in comb) (fig. 12.2):

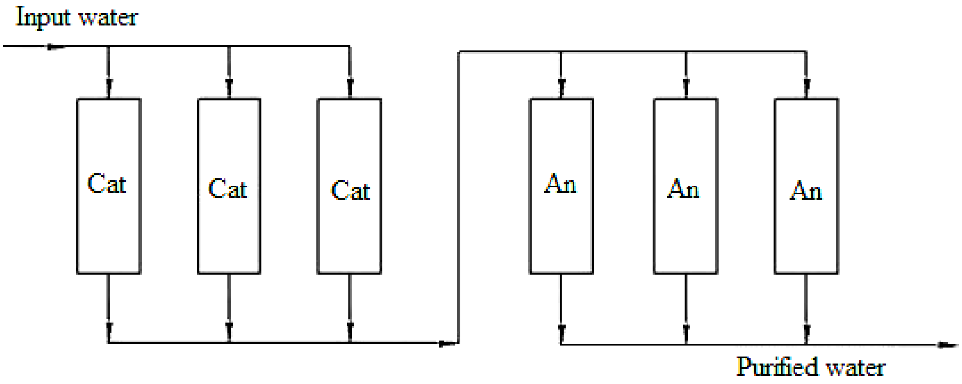


Figure 12.2 – The parallel scheme of the connection

2) block connection. The several filaments are established at the block scheme; everyone connects one all kinds of filters (fig. 12.3):

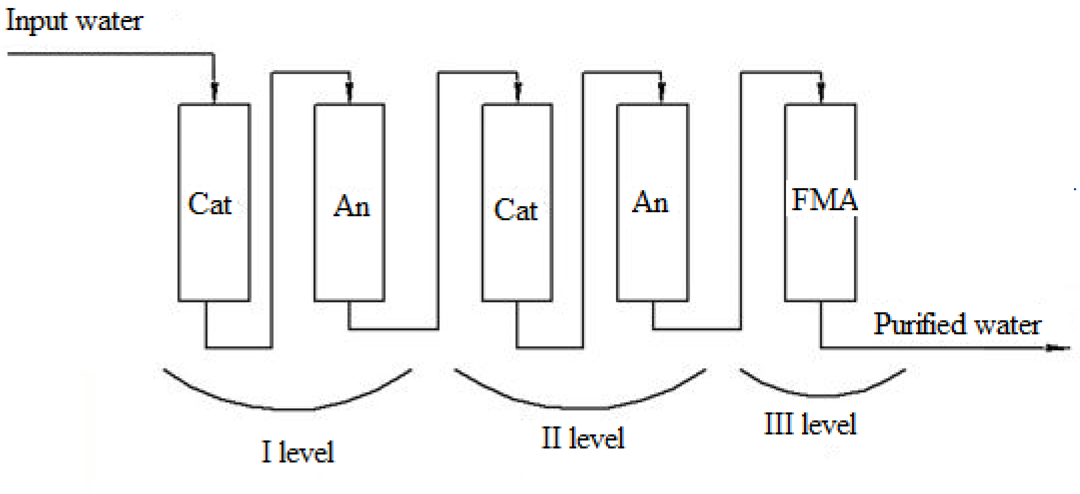
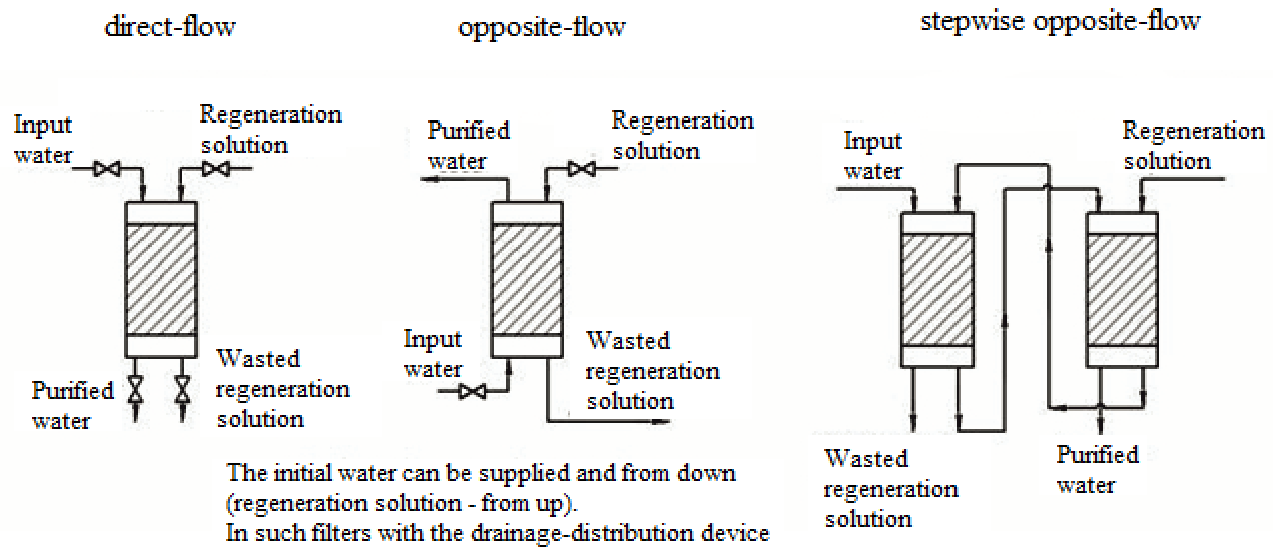


Figure 12.3 – The block scheme of connection

Such chains or filaments will be as long as necessary by the productivity.

The connections «in comb» are used in old systems, currently, HES and AES work by the block scheme, at such connection the quantity of apparatuses is increased comparing with parallel.



The initial water can be supplied and from down (regeneration solution - from up).
In such filters with the drainage-distribution device

Figure 12.4 – The methods of regeneration

There are following schemes used by the kind of supply direction (fig. 12.4):

- direct-flow (parallel-flow);
- opposite-flow;
- stepwise opposite-flow.

By the location of regeneration: the schemes with inside and outside (remoted) regeneration.

The inside regeneration is carried inside the apparatus, the outside – the resin is unloaded into the remote apparatus. The main apparatus is ion exchange filter.

There are following ion exchange schemes used for different aims:

1) Na-cationization is used for water softening with low carbonate hardness;
2) H-cationization is used for treatment of water with increased carbonate hardness;
3) H-Na-cationization is used for necessity of getting water with the residual alkalinity over 0,35 mmole/L (parallel, consistent and common H-Na-cationization);
4) two-steps schemes (H-OH [the 1st step] – calciner column – Na-OH [the 2nd step]) are used for waters with $H_{init.} = 6 \div 7$ mmole/L, at the output $H_{resid.} \approx 0,05$ mmole/L – the vapor producing in boilers at low pressure – to 10 MPa;
5) 3-stages schemes are used for getting water and vapor with over-critical parameters: ($T > 290\ ^\circ C$, $P \approx 20$ MPa). Herewith, the water is got with following parameters: $H_{resid.}$ to $0,001 \div 0,002$ mmole/L and the total salt content – to 0,05 mg / L. The noted schemes keep to get water, very close to the chemical compound, so-called high-omic water. The specific electric charging of such water is $4 \cdot 10^{-6}$ $Om^{-1} \cdot m^{-1}$.

The specific electric charging after the 2-steps scheme $0,4 \div 0,6$ µSm/cm, 3-steps $0,1 \div 0,07$ µSm/cm.

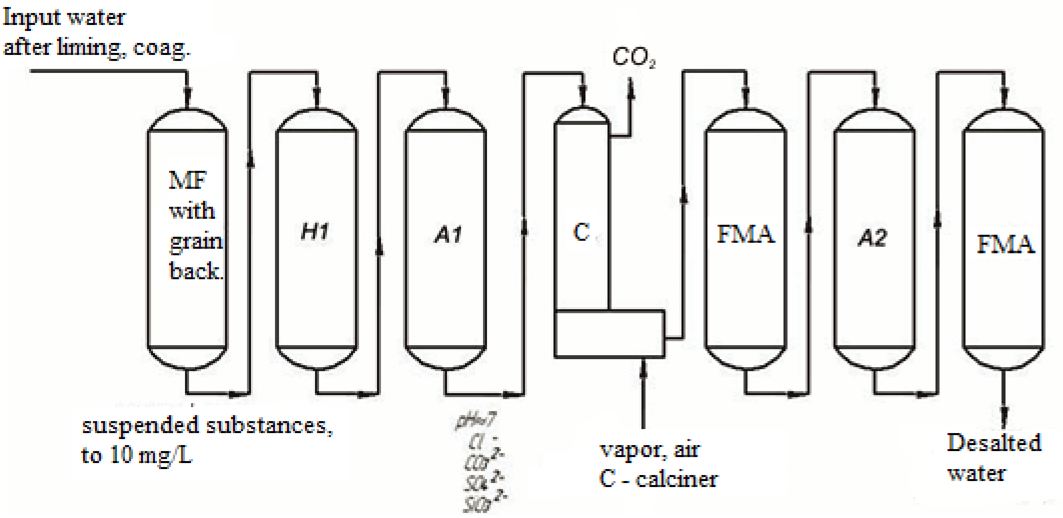


Figure 12.5 – The 3-stages scheme of water desalting

The water after liming and coagulation contains: suspended substances – 20 mg/L, TSC – 1000 mg / L, pH 9 ÷ 10, Ca^{2+}, Mg^{2+}, Na^{+}, SO_4^{2-}, Cl^{-}, CO_3^{2-}, SiO_3^{2-}.

After the mechanic filter the quantity of suspended particles is decreased to ≈ 10 mg/L.

The 1st stage.

At the 1st stage Ca^{2+} i Mg^{2+} are removed, that's why the filter is remoted by Na^{+}. After the 1st stage $H_{resid.} = 0,05 \div 0,1$ mmole/L, pH 5÷6.

The sulfuric coal is the most often used in H1, CEU-2-8, the exchange capacity of sulfuric coal is 300 mmole/L, of CEU – 800 mmole/L.

The anion exchanger for the 1st stage – low-alkalinity – is more profitably for download, for example, AEL-31; the anions of strong acids are removed, and remoted for regeneration by Cl^{-}. The water takes neutral reaction, herewith, the free carbon acid will be in water. It should be removed at the 2nd stage of anionization. For simplifying the loading on the 2nd stage, the calciner is established. It is designed for removing CO_2 by the aeration (to 5 mg/L). The calciner is the column-like apparatus with nozzle – for example, Rashig's rings.

After the 1st stage the partly desalted water is got (actually softened water). It is used in heat exchange equipment.

The 2nd stage.

After the 1st stage water incomes to the 2nd stage (pH ≈ 7), the residues Ca^{2+} and Mg^{2+} are removed and almost whole Na^{+}. The high-alkalinity cation and anion exchangers are established CEU-2-8 i AEH-17, EDE-10-P (they remove HCO_3^{-}i SiO_3^{2-}, and also Cl^{-}).

The 3rd stage.

All residues of cations and anions are removed by FMA (filters of mixing action). CEU-2-8 and AEH-17 are used.

The calculation of the 3rd stage scheme is begun from «the end» of the scheme, namely from FMA.

12.4.1 The main construction elements of ion exchange filters

Filters are cylindrical apparatuses with sphere bottom and cover. P ≈ 5 ÷ 6 atm. (to 0,6 MPa). The apparatuses are performed from steel; the lining is inside (rubber or anti-corrosion layer). Hatches – bottom for review and repair, top – if necessary, for downloading and unloading resin.

12.4.2 The filter of mixed activity

FMA has three drainage systems. At workable state the cation and anion exchanger's grains mixed, but the density of cation exchanger grains is more than anion exchanger's grains density, that's why at loosening the layers are placed, how shown in fig. 12.6. For FMA regeneration the same regeneration solutions are used. For anion exchanger regeneration NaOH is supplied through a top drainage device, the regeneration solutions are outcome through the top drainage device. The acid solutions for cation exchanger are income through the middle drainage device, coming out through the bottom. Firstly, the regeneration is charged by weaker solutions (1 ÷ 3%), for preventing the gypsum – oversaturation by [1, 2].

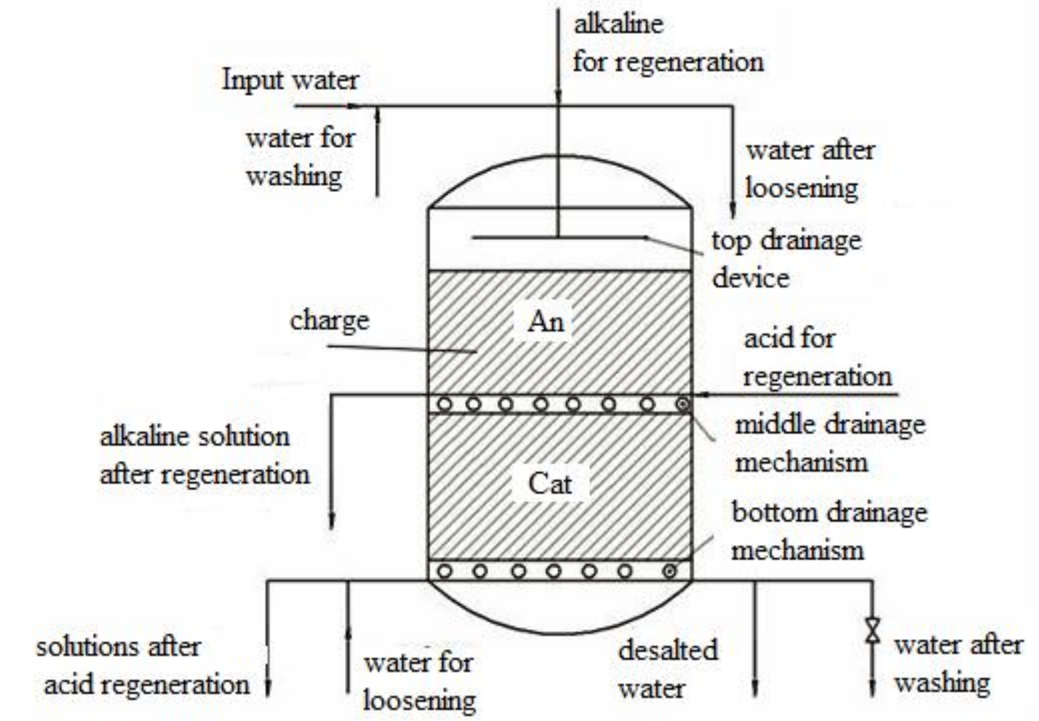


Figure 12.6 – The scheme of FMA

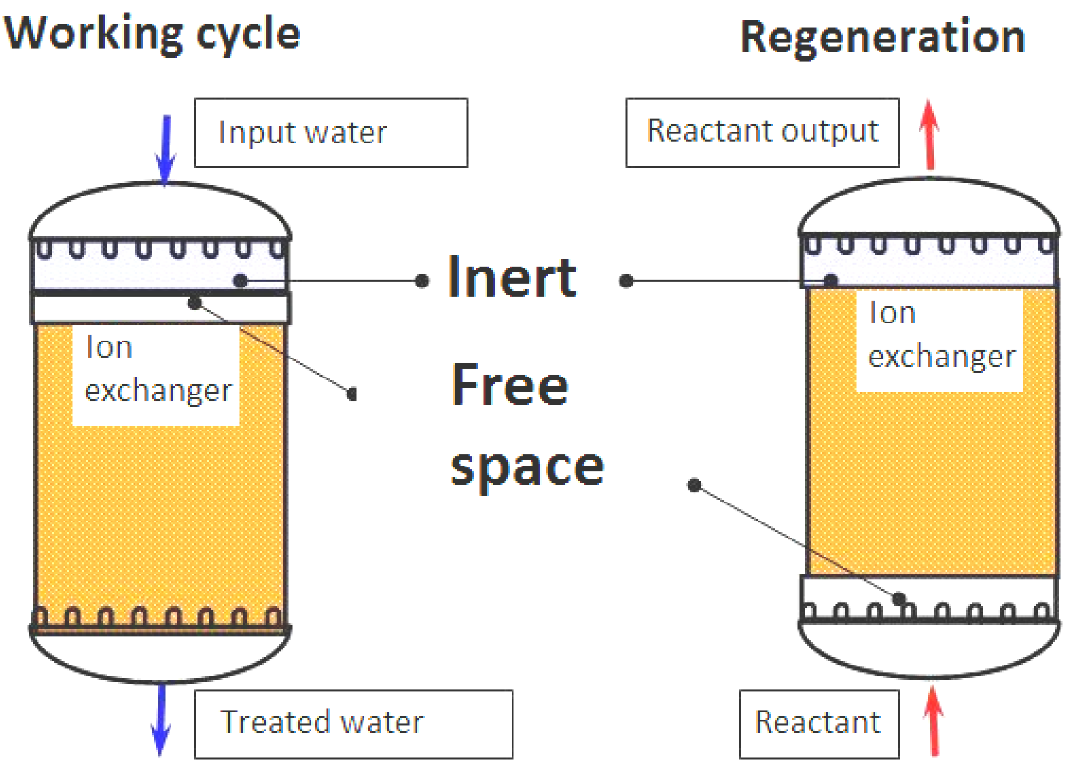


Figure 12.7 – The construction of ion exchange filter (“UPCORE” tech.).

The disadvantages of ion exchange – formation high quantity of regeneration solutions, containing 5 ÷ 6 g/L of salts. Unfortunately, using of these methods are very difficult, the separation of it is difficult too, at its treatment they are diluted by natural water or directed to canalization even without treatment. The solid wastes are formed too – wasted resins (the time of its working is limited by 5 – 8 years).

12.5 The utilization of wastes, formed at ion exchange

It’s possible to use following methods for solutions utilizations: freezing, distillation, electric dialysis; the dumping into special pools or sludge accumulators; the pumping regeneration solutions into underground horizons etc. [2, 20].

The first methods can be carried, if the cheap energy is presence at enterprise (for example, the heat of dumping gases).

The decreasing of water using – for washing and post-washing of the resins: the regeneration process is firstly charged by wasted regeneration solution, and then – by fresh regenerator – blowing water of evaporator or boiler (so-called developed regeneration). For decreasing the water cost for self needs it’s possible, for example, to direct waters, after loosening and washing, (the 3rd stage) into the 2nd stage for loosening of ion exchange charge.

Currently, Ukraine doesn’t use the special methods of solid wastes utilization – wasted resins. They are possible to use as backfilling of mechanical filters at processes of WW purification. But, including the chemical composition of synthetic resins, the perspective methods of its utilization should be the thermal treatment with further getting sorbents of the activated carbon type.

12.6 Deep desalination of water by membrane methods

12.6.1 Membrane processes

Methods of removal of finely- and hard-dispersed impurities from water by filtration are widely used in technology of water purification and water preparation for different branches. All of these methods can be divided on two large groups: filtration through the layer of grain backfilling or through the porous partitions.

Filtration through the porous partitions is carried out in different textile filters and is the base of all membrane processes. There are two possible mechanisms of delaying of particles are existed. If particles have size more than size of pores of porous partition, this is so-called seed mechanism (in case of micro- and ultra-filtration). If delaying of particles is carried out by diffusion mechanism of transition of solvent – this mechanism is typical for membrane processes of nano-filtration and reverse osmosis. So, the main distinctive feature of membrane processes is existing of membrane – selectively permeable (half-permeable) barrier between phases.

There is separation of membrane processes on groups, depending on driving force of process. Micro-filtration, ultra-filtration, nano-filtration and reverse osmosis are referred to the main group of membrane processes – so-called bar membrane processes. Their driving force is difference between pressures from different sides of membrane. Moreover, there are also electric membrane processes – electric dialysis and electric deionization. Their flowing is caused by gradient of electric potential, diffusion and membrane processes, flowing by difference of concentration of dissolved impurity from different sides of membrane (membrane decontamination), and processes, based on usage of difference of temperatures from different sides of membrane – membrane pervaporation and distillation.

For comparing of different membrane processes and understanding of the place of everyone among them, in modern water preparation its useful to use the diagram of filtration spectra (fig. 12.8).

The scope of membrane processes is very wide. The main branches of usage of membrane technologies in modern water preparation are following:

- Purification of water from surface origins – as preliminary preparation for next cleaning up, and as independent technology;
- Different technologies of waste water purification;
- Preparation of drinking water from different origins;
- Water preparation for nutritional industries, industries of non-alcohol and alcohol drinks;
- Getting of deeply desalinated water for different branches of industry – power engineering, micro-electronics, pharmacology industries;
- Desalination of sea water for getting of drinking or water for technological industry.

The principal scheme of the simplest membrane installation includes two main elements: membrane + membrane supporter and is illustrated in fig. 12.9.

However, such scheme has the main disadvantage – low output on permeate. Nonetheless, such scheme is used in household systems of purification of drinking water, and also for desalination of sea water.

Much more rational scheme includes recycle of concentrate (fig. 12.10), providing higher degree of conversion – in average, 75 %. But, it’s necessary to provide more power of pump. Often, for providing of necessary productivity, few membrane modules are used in such schemes. These modules are established parallel.

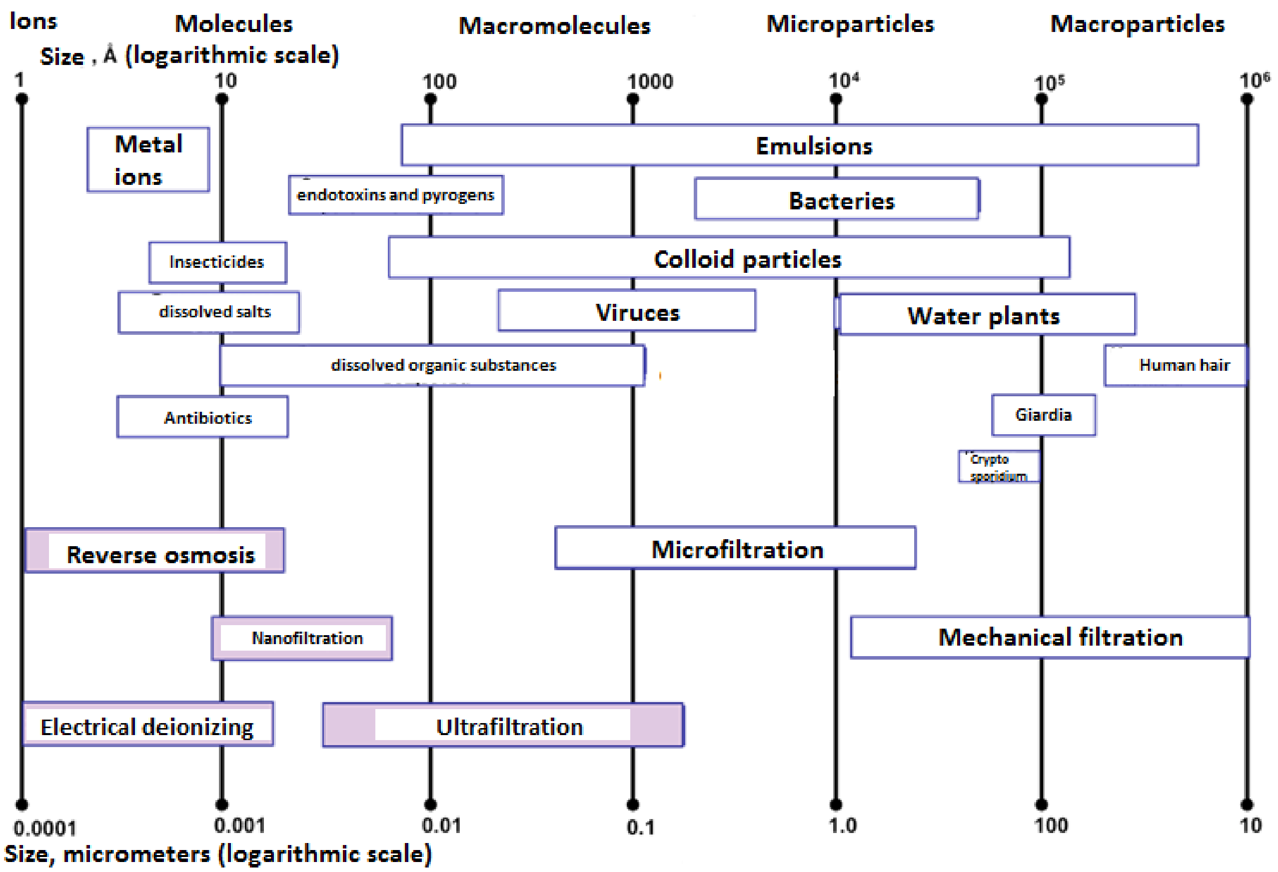


Figure 12.8 – Spectra of filtration of different membrane processes

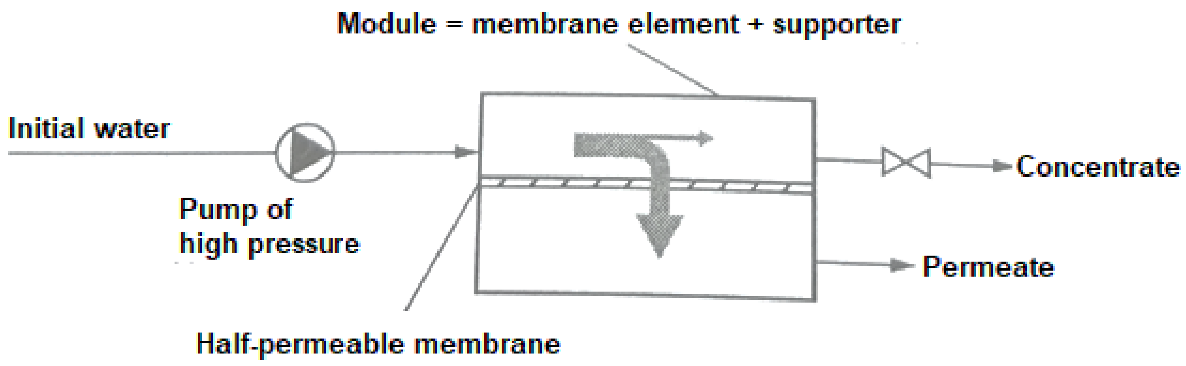


Figure 12.9 – The scheme of the simplest membrane element

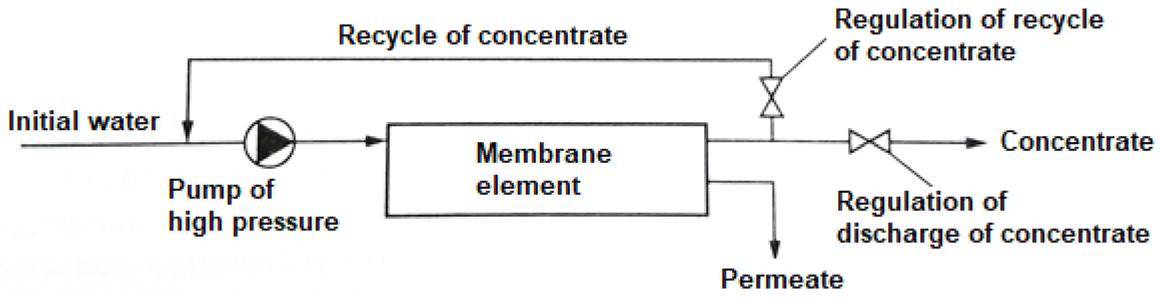


Figure 12.10 – The scheme of membrane element with recycling of concentrate

Questions for self-control to the section 12

1. Name the groups of water demineralization methods.
2. Characterize the methods of water softening, desalination and desalting.
3. What methods keep to make following processes: softening, desalination, desalting of water?
4. What the essence of the thermal method of water softening?
5. Compare the reagent methods of water softening.
6. What the essence of the membrane methods of water treatment?
7. What the essence of ion exchange method of water demineralization?
8. Name the stages of ion exchange.
9. Characterized the resins from the point of view of its origin.
10. What kinds of resins are formed at functional groups ionization?
11. Name the main properties of ion exchangers.
12. Compare the characteristics of resins – TSEC and DEC.
13. What the value of selectivity for creation of technological schemes of water desalting?
14. What aim and by what solutions does the regeneration of resins carry?
15. Name the main types of technological schemes of water purification by ion exchange.
16. Explain the principle of the 3rd stage scheme of water desalting by ion exchange.

17. What is the feature of FMA?

18. Name the possible ways and methods of utilization wastes, forming at ion exchange.

19. What the classification of membrane methods, using in water preparation?

20. What the simplest schemes of membrane modules do you know? Their advantages and disadvantages.

SECTION 13 LABORATORY WORKS

Laboratory work 1. Evaluation of the water quality physic indicators

The aim of work – to learn the standard methods of the determination water color, smell, temperature.

The theoretical theses

The physic indicators of water quality are: temperature, color, smell, flavor, transparency or turbidity.

The color of nature waters, first of all, caused of availability humites of iron (salts of humic acids). The water of rivers with the swamp type of nutrition has increased color (rivers of northern regions of Ukraine). The color evaluated in degrees of the platinum cobalt scale. According to THE STATE SANITARY NORMS AND RULES 2.2.4-171-10, it shouldn't exceed 20 degrees (in single cases, by agreement with organs of the sanitary supervision, color allowed to 30 degrees).

The quality evaluation conducted by comparison the sample of polluted water with distilled. For this in the glassfuls produced from the transparent glass, the experimentally and distilled water poured separately. At the background of white paper at the day light it viewed from above and from the side and color evaluated, namely, watching color noted (primrose, fulvous etc.). If the water hasn't color, it considered transparent. The color determined quantitatively from the platinum cobalt or dichromate cobalt scale.

The smell of water can be connected with live of water organisms (other water plants, seaweeds etc.), and also showed up when they die. These are natural smells. Is that the industrial waste waters fall to ponds with impurities of certain smell (phenols, formaldehyde, chlorine derivatives of benzene etc.) These are artificial smells.

First of all, the qualitatively characteristics given for water due to the smell according to the appropriate signs (fenny, earthy, putrefactive, fish, aromatic etc.). The power of smell evaluated form the five-mark scale (table 1).

The temperature of natural water depends on its origin. The water of underground sources differs temperatures constant, besides, that depth of water occurrence bigger, those diapasons of the season changing of the temperature is less. The temperature of opened ponds (rivers, lakes) experiences significant season changes. For example, the temperature of water in river Dnipro (near Kyiv city) changes during the year from 0 ^{0}C in winter to 28 ^{0}C in summer. Besides, in single places of opened ponds the temperature of water can be changed because of decay processes or underground water earning.

The optimal temperature for drinking water – 7…11 ^{0}C. Water with such temperature has the pleasant taste.

So-called organoleptic indicators up all physic indicators of water quality.

Table 13.1. The evaluation of water smell

Smell	Intensive	Mark
Absent	Not felt	0
Very weak	Only experienced researcher indicates	1
Weak	Consumer indicates, if attention paid	2
Notable	Consumer indicates easily	3
Clear	Strong smell and flavor make water unpleasant for drinking	4
Very strong	Water is unsuitable for drinking	5

The methodic of conducting work

Equipment: volumetric flasks (100 cm^3) – 15 ones; volumetric flask (500 cm^3); moderate cylinders (250 cm^3) – 2 ones; moderate pipette (10 cm^3); pipette (1 cm^3); sampler; bulbs – 4 ones; thermometer.

Reactants: dichromate cobalt solution; H_2SO_4 solution (1 cm^3 of acid in 1 L of water); sample of natural and industrial waste waters (students prepare solutions singly).

***Experiment 1.* The determination of water color by dichromate cobalt scale**

The preparation of main solution. In little volume of distilled water $K_2Cr_2O_7$ (0,0438 g) and $CoSO_4{\cdot}7H_2O$ (1 g) dissolved singly in two vessels. Salt solutions transferred quantitatively to the volumetric flask (500 cm^3), concentrated sulfuric acid added (0,5 cm^3) with density ρ = 1, 84 g/cm^3 and mark reached by distilled water.

The preparation of sulfuric acid solution. In single vessel, the sulfuric acid solution prepared by mixing 1 cm^3 of concentrated H_2SO_4 with 1 L of distilled water.

The preparation of scale. The main solution mixed with sulfuric acid solution. The main solution (1 cm^3) transferred to the volumetric flask (100 cm^3) and reached mark by sulfuric acid solution. This solution has color 5 degrees. For the preparation of solution with color 20 degrees it's necessary to mix 4 cm^3 of the main solution with 96 cm^3 of sulfuric acid solution. For the same methodic to prepare solutions with color 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 degrees.

The control samples of water compare with the scale and its color determined. Muddy water filtered in advance.

Experiment 2. The determination of water smell

In the bulb with ground glass stopper the investigated water pours (2/3 of volume) and shake off strongly. Then stopper opened and the character and intensively of smell determined. According to THE STATE SANITARY NORMS AND RULES 2.2.4-171-10, the intensively of smell at 20 ^{0}C shouldn't exceed mark 2.

Experiment 3. The determination of water temperature

The temperature of water determined directly in pond or in water sample taken. The thermometer used with division of the scale 0,1 ^{0}C.

The task: to determine the temperature of the tap water and samples proposed by teacher.

The control questions

1. What the water quality indicators belong to organoleptic?
2. What impurities of water give it color?
3. By what scale the intensively of water smell (flavor) can be evaluated?
4. What requirements does THE STATE SANITARY NORMS AND RULES 2.2.4-171-10 provide?

Literature: [1-6]; [17].

Laboratory work 2. Alkalinity, acidity and carbon (IV) oxide content in samples of natural water

The aim of work – to learn the standard methods of evaluation these water quality indicators.

The theoretical theses

The alkalinity of water from natural origins caused by weak acid anions and OH^- ions. The general alkalinity characterized the total concentration of ions OH^-, HCO_3^-, CO_3^- and anions of other weak acids.

The acidity of natural water with pH > 4,5 caused by free carbon (IV) oxide, humic and other weak organic acids; with pH < 4,5 – strong acids and salts of strong acids and weak bases. It's distinguished the total acidity, free acidity, free carbon (IV) oxide, aggressive carbon (IV) oxide and also acidity independent from other weak non-volatile acids.

The methodic of conducting work

Equipment: pipettes (100 cm^3) – 5 ones; bulbs for the titration (250 cm^3) – 5 ones; pH-meter.

Reactants: chlorine acid solutions – 0,05 M and 0,1 M; sodium hydroxide solution 0,1 M; indicators – methylene orange, phenolphthalein; water samples.

Experiment 1. The determination of water general alkalinity

If the sample contains suspended substances, before the determination they should be removed. It's necessary to mean, if total alkalinity less than 0,4 mmole/L, the determination should be repeated for specification by the titration of water samples by 0,05 M solution of acid. If the color of water is intensive, the titration conducted or by the pH-meter without indicator, or after bandwidth water through the layer of activated carbon.

At common determination of the alkalinity 100 cm^3 of the sample titrated by 0,1 M solution of chlorine acid with methylene orange availability to color transition from yellow to gold-rose. For increasing the accuracy of the alkalinity determination of water samples in the titration process, the sample blown by air.

The total alkalinity calculated by the formula

$$A_{tot} = \frac{C_{HCl} \cdot V_{HCl} \cdot 1000}{V},$$

where A_{tot} – the total alkalinity of water, mmole/L; C_{HCl} – acid concentration, mole/L; V_{HCl} – volume of acid solution spent for the titration, cm^3; V – volume of the water sample, cm^3.

Experiment 2. The determination of natural water samples total acidity

For the determination of total acidity 100 cm^3 of water sample titrated by 0,1 M solution of sodium hydroxide with 5-10 drops of phenolphthalein availability to the pale pink color appearance.

The total acidity calculated by the formula

$$Ac_{tot} = \frac{C_{NaOH} \cdot V_1 \cdot 1000}{V},$$

where Ac_{tot} – the total acidity, mmole/L; C_{NaOH} – sodium hydroxide concentration, mole/L; V_1 – volume of NaOH solution spent for the titration, cm^3; V – volume of the water sample, cm^3.

Experiment 3. The determination of free acidity in natural water samples

The investigated water (100 cm^3) titrated by 0,1 M solution of sodium hydroxide with 3 drops of methylene orange to the transformation of solution color to yellow. If at indicator adding to the sample of solution it becomes yellow, it means the free acidity is zero.

The free acidity calculated by the formula

$$Ac_{free} = \frac{C_{NaOH} \cdot V_2 \cdot 1000}{V},$$

where Ac_{free} – the free acidity, mmole/L; C_{NaOH} – sodium hydroxide concentration, mole/L; V_2 – volume of NaOH solution spent for the titration, cm^3; V – volume of the water sample, cm^3.

It’s necessary to mean that muddy and color of the water prevent the titration. These waters titrated without indicator, determining the finish of titration for the pH-meter.

Experiment 4. The determination of acidity in samples independent of weak non-volatile acids

The sample of investigated water (100 cm^3), neutral for the methylene orange, boiled during two hours for the removing of free carbon (IV) oxide, cooled rapidly and titrated by 0,1 M solution of sodium hydroxide with 5-10 drops of the phenolphthalein to the resistant rose color appearance.

The acidity, caused by weak acids, calculated by the formula

$$Ac_{weak} = \frac{C_{NaOH} \cdot V_3 \cdot 1000}{V},$$

where Ac_{weak} – the acidity, caused by weak acids, mmole/L; C_{NaOH} – sodium hydroxide concentration, mole/L; V_3 – volume of NaOH solution spent for the titration, cm^3; V – volume of the water sample, cm^3.

Experiment 5. The determination of free carbonic acid content in natural water

The investigated water (100 cm^3) titrated by 0,1 M solution of sodium hydroxide with 10 drops of the phenolphthalein to the resistant color appearance doesn’t disappear during 2-3 minutes. The solution of hydroxide added by little portions by closing the bulb by stopper every time and good mixing its content. After the first analysis the determination repeated by infusing almost all volume of sodium hydroxide solution at once, found during the first determination.

The content of free carbon (IV) oxide calculated by the formula

$$C_{CO_2(free)} = 44\left(\frac{C_{NaOH} \cdot V_4 \cdot 1000}{V} - Ac_{weak} - Ac_{free}\right),$$

where $C_{CO2(free)}$ – the content of free carbonic acid, mg/L; 44 – the molar weight of carbon (IV) oxide, g/mole; C_{NaOH} – the concentration of sodium hydroxide, mole/L; V_4 – NaOH solution volume, spent for the titration, cm^3; V – water sample volume, cm^3; Ac_{free} – free acidity, mmole/L; Ac_{weak} – acidity caused by weak acids, mmole/L.

Experiment 6. The determination of free carbonic acid content in natural water

The content of free and aggressive carbon (IV) oxide in surface natural water is usually little. This indicator has important value for the characterization of natural waters.

For the determination of free carbonic acid, it’s possible to use the special nomogram (fig. 1). Previously it’s necessary to determine the temperature of water, total salt content (TSC) in it, total alkalinity and pH.

Connecting by line on scales 1 and 3 lines responded by the temperature values and TSC (P), the point of crossing line with “dumbly” scale 2 noted. This point connected with alkalinity value on scale 4 and the point of crossing line with scale 3 noted. The point got connected with the respectively pH value on scale 5. The continuing of line to crossing with scale 6 determined mark responded the concentration of free carbonic acid.

Experiment 7. The determination of aggressive carbonic acid in natural water

This determination conducted using nomograms presented in pics. 2 and 3.

Having results of water chemical analysis, the accessory parameter A can be find by fig. 2. For this it’s necessary to connect points responded by the temperature values and TSC and to find mark on “dumbly” scale 4. Connecting it with point responded by calcium ions concentration on crossing with scale 3 gives accessory parameter A. Knowing the free carbonic acid content (from previously experiment) and alkalinity of analyzed water, the point 1 found by fig. 3 satisfied these parameters. If this point situated above curve responded the accessory parameter A, the water contains aggressive carbonic acid, if below – the water doesn’t content aggressive carbonic acid.

The concentration of free carbonic acid determined by letting down line from the point 1 parallel by sloping lines. The crossing of this line with curve responded by the accessory parameter A, gives the point 2, ordinate of which responded by the equilibrium concentration of carbonic acid:

$$C_{CO2(agr)} = C_{CO2(free)} - C_{CO2(eq)},$$

where $C_{CO2(free)}$, $C_{CO2(free)}$, $C_{CO2(eq)}$ – the concentrations of aggressive, free and equilibrium carbonic acid, mg/L.

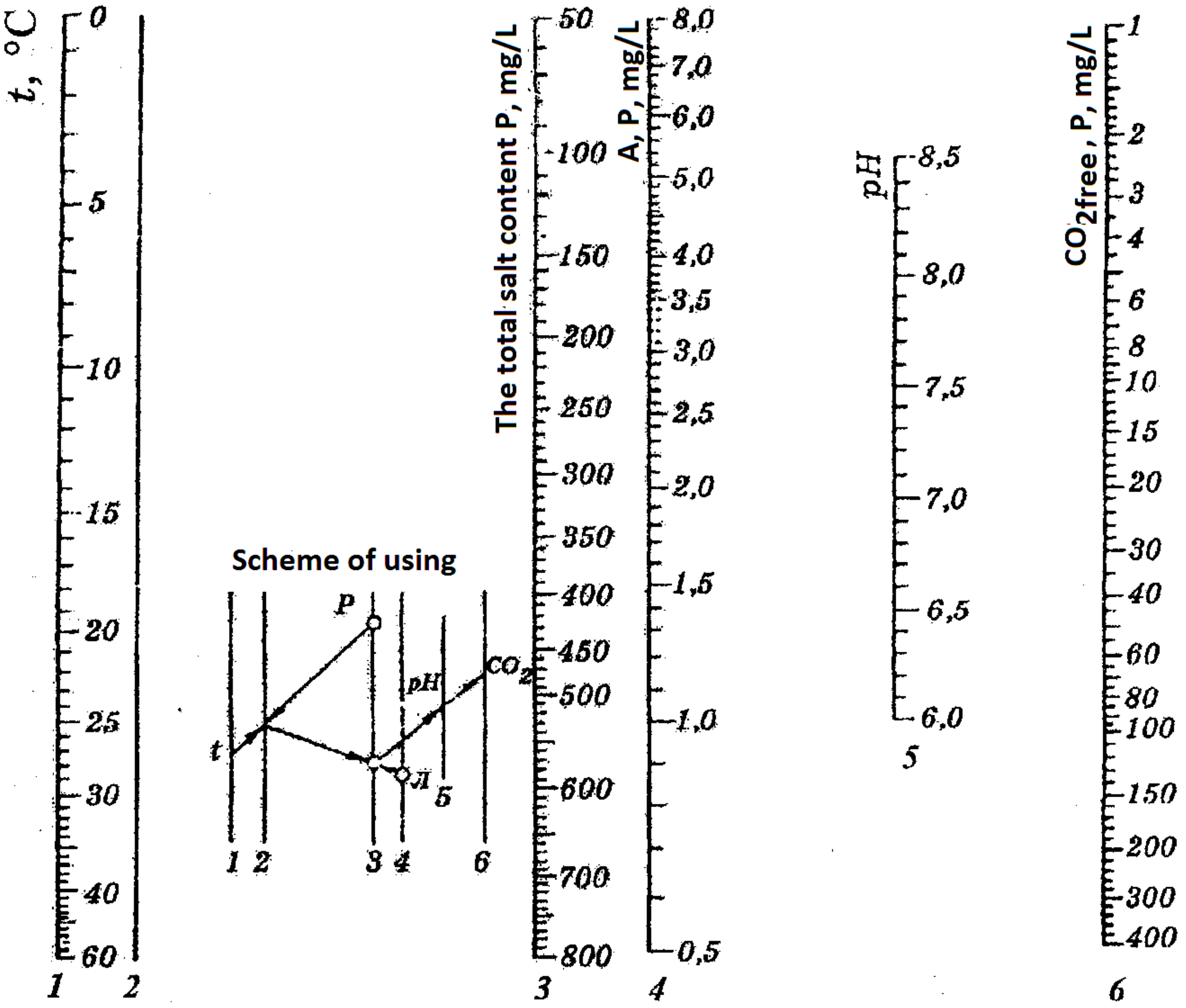


Figure 13.1 – Nomogram for the determination of free carbon (IV) oxide concentration in water

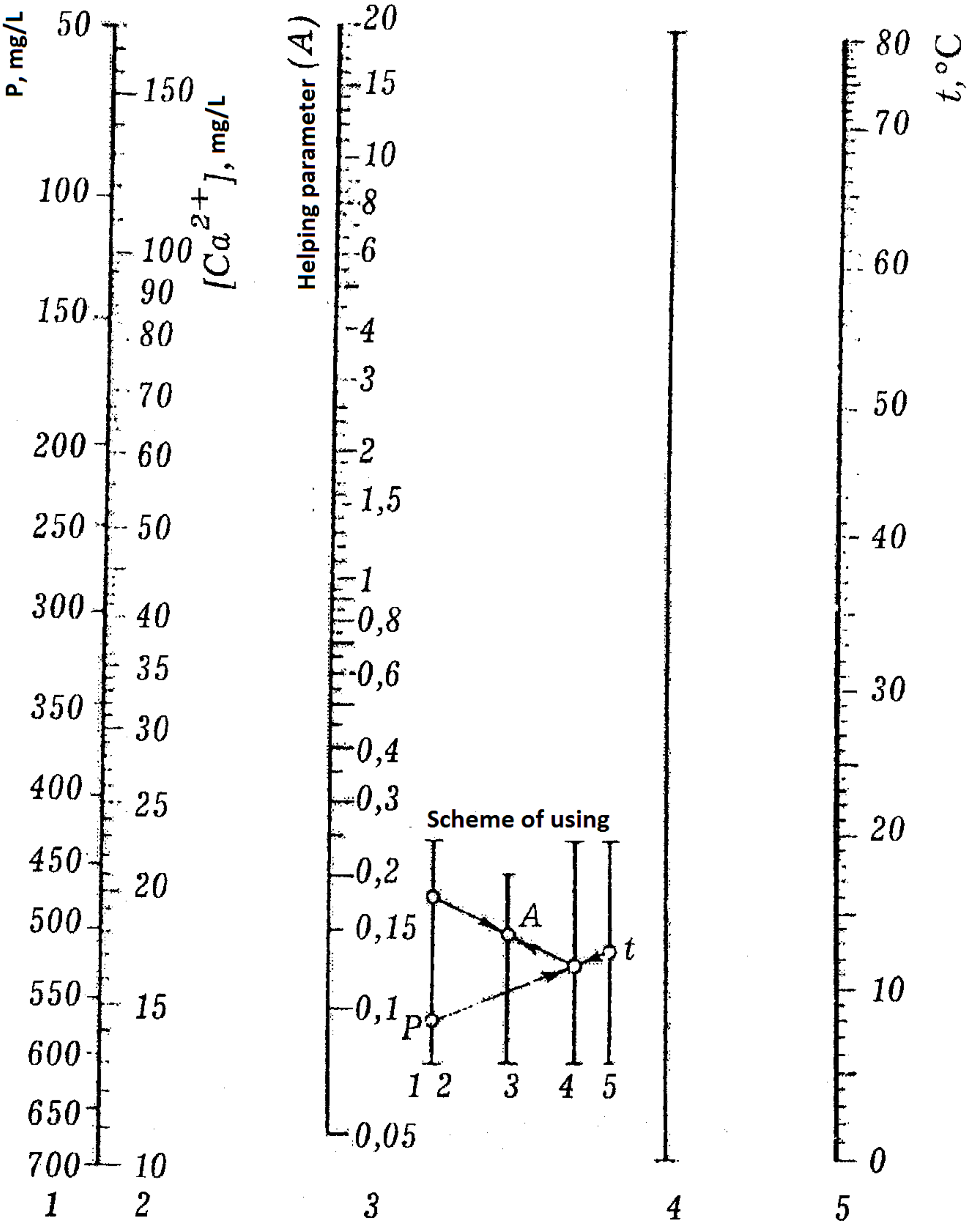


Figure 13.2 – Nomogram of the determination of helping factor for the calculation of aggressive carbon (IV) oxide concentration in water

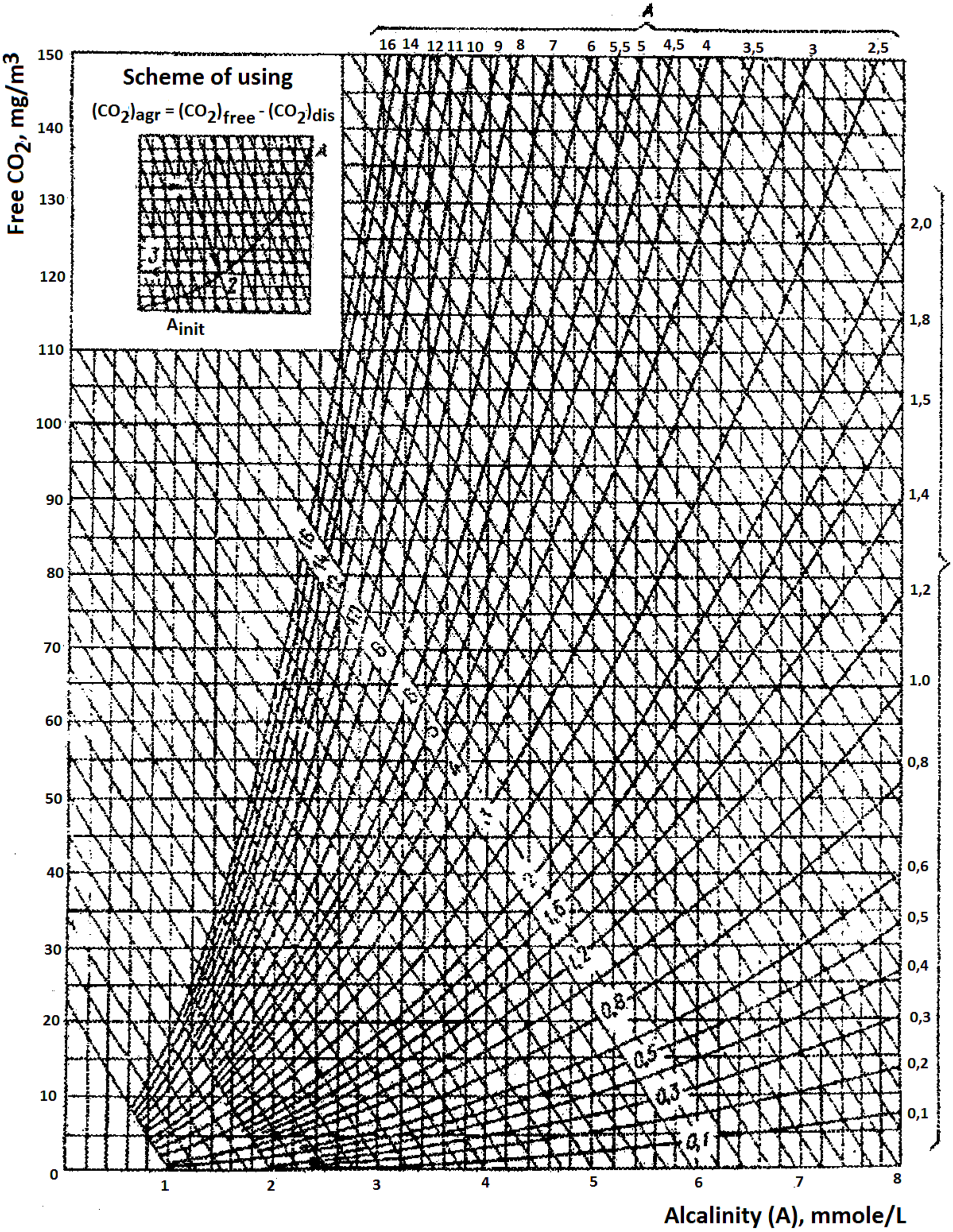


Figure 13.3 – Nomogram of the determination of aggressive carbon (IV) oxide concentration in water

The control questions

1. What substances caused the alkalinity of water?
2. What kinds of acidity can be distinguished in natural water?
3. What substances caused availability of free and aggressive carbonic acid in water?
4. What is the active water reaction?

Literature: [1-8]; [17].

Laboratory work 3. Dry residue, losses at calcination and oxidation in samples of natural water

The aim of work – to learn standard methods of the salt content evaluation and organic substances content in natural origins of water supply.

The theoretical theses

The salts quantity dissolved in natural waters can be determined by dry residue and losses at calcination. The dry residue formed at evaporation of some water volume, previously filtrated through the paper filter, consists of mineral salts and non-volatile organic substances. The organic part of water dry residue determined by residue losses at calcination process. It's necessary to pay attention, for waters with increased content of salts, the data about organic substances content in investigated water, taken by the way of dry residue calcination, can be something increased, because of at the calcination some salts partly decompose, formed volatile compounds. Especially, it concerns salts, content nitrogen, and also carbonates, chlorides, crystal hydrates etc. The water, usually contents to 1000 mg/L of dissolved salts, considered fresh.

The methodic of conducting work

Equipment: water bath; porcelain cups; conic bulbs; pipettes; paper filters; funnels; burettes; analytic balances; dry wardrobe; muffle furnace; desiccator.

Reactants: sulfuric acid solution (1:2) (one volume of H_2SO_4 96 % mas. and two volumes of distilled water); 0,01 M solution of potassium permanganate; 0,01 M solution of oxalate acid.

Experiment 1. The determination of dry residue in natural water sample

This determination usually conducted in a day of sample picking. Water filtrated through the paper filter. Porcelain cup dried to the constant mass, cooled and weighed on analytical balances. On water bath, filled by distilled water, 100 – 150 cm^3 (by the task of teacher) filtrated water evaporated. The cup with dry residue dried at 100 – 150 ^{0}C to the constant mass, cooled and weighed.

The content of dry residue calculated by the formula:

$$X = \frac{(m_1 - m) \cdot 100}{V},$$

where X – dry residue content, mg/L; m – the mass of cup, mg; m_1 – the mass of cup with dry residue, mg; V – water sample volume, cm^3.

Experiment 2. The determination of losses at the dry residue calcination

For the determination of this losses, the dry residue, got in previously experiment, calcined in muffle furnace at the temperature 600 ^{0}C during 1 hour, cooled in desiccator and the cup weighed on analytic balances. Losses calculated by the formula:

$$X_1 = \frac{(m_2 - m) \cdot 100}{V},$$

where X_1 – the content of calcined sample characterized mineral impurities in water, mg/L; m_2 – cup mass with residue after calcination, mg.

The content of impurities organic part found by the formula

$$X_2 = X - X_1,$$

where X_2 – the content of organic impurities in water sample, mg/L.

Experiment 3. The determination of natural water oxidation (Kubel's method)

The water sample (100 cm^3), picked by pipette or volumetric flask, poured to conic bulb with glass pellets on the bottom, diluted sulfuric acid (5 cm^3) and 10 cm^3 of 0,01 M solution of potassium permanganate added. The bulb should be heat-resistant. The bulbs content achieved to boiling and boiled exactly 10 min. Further the 0,01 M solution of oxalate acid (10 cm^3) added to the heat bulb with solution and heat solution titrated by 0,01 M solution of potassium permanganate to the pale pink color appearance. The temperature of the sample shouldn't be less than 80 ^{0}C. Then 10 cm^3 of 0,01 M oxalate acid solution pounded to the same bulb to another head liquid and titrated by 0,01 M solution of potassium permanganate to the same color doesn't disappear during one minute.

The oxidation calculated by the formula:

$$X_3 = \frac{(V_1 - V_2) \cdot 0{,}08 \cdot 1000}{V},$$

where X_3 – the permanganate oxidation of water, mg of O_2 on 1 L of water; V_1 – total content of 0,01 M potassium permanganate solution, taken for the titration, cm^3; V_2 – volume of permanganate solution, taken for the titration of oxalate acid (10 cm^3, the second titration), cm^3; K – aliquot coefficient (number 10 divided by the solution of potassium permanganate volume during the second titration); V – water sample volume, cm^3; 0,08 – oxygen quantity responded by 1 cm^3 of 0,01 M potassium permanganate solution, mg. (If the calculation of oxidation made in milligrams of the permanganate at 1 L of water, it's necessary to use 0,32 instead of 0,08 – the equivalent of potassium permanganate responded by its 0,01 M solution).

Attention! The determination should be repeat if water sample will become fulvous or transparent during boiling.

The control questions

1. What water indicators characterized dry residue and losses of residue at the calcination?
2. How determined the content of organic substances in natural water samples?
3. With what total content of salts the water considered suitable for drinking?
4. What indicator of water quality determined by the Kubel's method?
5. The availability of which impurities in water characterized the value of permanganate oxidation?

Literature: [1-8]; [17].

Laboratory work 4. Optimal coagulant doses

The aim of work – to determine the optimal coagulant dose for natural water purification.

The theoretical theses

The majority of substances, causing muddy of natural water, are in colloidal state. One of the most effective methods of water purification from colloidal impurities – coagulation. Its essence is: substances-coagulants added to water. The sulfates or chlorides of iron or its mixtures often used as coagulants. Coagulants are salts of weak bases hydrolyzed in water forming colloidal particles of hydroxides. The last ones adsorbed on its surface different impurities of water, increased (coagulated) and take out from water so colloidal as finely dispersed suspended impurities.

The hydrolysis of coagulants taking place by stages, its mechanism is enough difficult. Summary the hydrolysis reactions for example of iron chloride can be presented by following equations:

$$FeCl_3 + H_2O = FeOHCl_2 + HCl;$$

$$FeOHCl_2 + H_2O = Fe(OH)_2Cl + HCl;$$

$$\underline{Fe(OH)_2Cl + H_2O = Fe(OH)_3\downarrow + HCl;}$$

$$FeCl_3 + 3H_2O = Fe(OH)_3\downarrow + 3HCl.$$

The hydrolysis of aluminum sulfate taking place analogically:

$$Al_2(SO_4)_3 + 6H_2O = 2\ Al(OH)_3\downarrow + 3H_2SO_4.$$

Some value of the pH responds by each stage of hydrolysis. If the concentration of hydrogen ions in water increased from coagulants overdose, the hydrolysis equilibrium moved to left. This increases alumina or iron content in water because of its hydroxide compounds has enough high solubility. Using of these waters not recommends not in drinking water supply (hygiene considerations), not for industrial requirements via possibility of precipitate forming on the apparatus.

The optimal coagulant dose D_{opt} is the least its dose provides the transparency of purified water 30 cm “by type” according to THE STATE SANITARY NORMS AND RULES 2.2.4-171-10 for drinking water. If the optimal dose has been selected truth, the purified water shouldn’t contain alumina or iron. The optimal dose of coagulant depends on many factors, that’s why it determined experimentally, gradually increasing coagulant quantity, added to the water.

The passing of coagulation processes significantly depends on type of the coagulant, using in process. If alumina sulfate used, at low temperatures (1 – 2 ^{0}C) the processes of forming and precipitation of flakes become slower. The residual quantity of alumina accumulated in water, which is the consequence of forming precipitate in ditch water. That’s why in winter it’s rationally to use iron chloride, because the process of forming its flakes is little sensitive to water temperature. Simultaneously, iron chloride has some shortcomings too, for example, after the precipitation of the main mass of big flakes of hydroxide, some quantity of little flakes is in water during long time. For elimination of this shortcomings, mixed coagulants used, which give, in particular, possibility to save 30 – 60 % of coagulants.

The methodic of conducting work

Equipment: volumetric cylinders (500 cm^3) with stoppers – 7 ones; pipettes (1, 5, 10, 25, 100 cm^3); cylinder with diameter 20 – 25 mm with height not more 350 mm for the determination of water transparency; volumetric flasks (50, 100, 250, 1000 cm^3); text with letters height 3,5 mm; glass for picking sample.

Reactants: the solution of alumina sulfate or chloride, samples of polluted water.

Experiment 1. The determination of optimal coagulant doses

For the investigation, the sample of water with knowing transparency used. The investigated water (400 cm^3) poured to seven cylinders. Then such quantity of the coagulant added to cylinders by volumetric pipette (iron sulfate or chloride solution) its content in water would be 10, 25, 50, 100, 200, 300, 400 mg/L. Adding coagulant, water mixed by three-ones canting of cylinders closed by stoppers. The time of entering coagulant into water noted. After two hours from each cylinder 250 – 300 cm^3 of clarified water for analyses picked by helping of water flow pomp. It's necessary to pick water carefully for avoiding of making precipitate muddy. In samples of the clarified water transparency established or height of the precipitate layer measured (duration of coagulation determined by teacher).

At water creaming in cylinders the time of the beginning flakes forming, time of precipitation beginning, height of precipitation layer and height of clarified water pillar fixed, and also type of flakes (loose, big, small). The observation charged after every 10 min.

Experiment 2. The determination of water transparency "by type"

The water transparency is edge height of water pillar in centimeters, through which it's possible to read the text written by standard type with letters height 3,5 mm.

Table 13.2. Indicators of water purification by the way of coagulation

Indicator	**Cylinder number**						
	1	**2**	**3**	**4**	**5**	**6**	**7**
Coagulant type							
Coagulant dose, mg/L							
Coagulant quantity, cm^3							
Time of the beginning flakes forming, min							
Time of the beginning flakes precipitation, min							
Transparency of purified water, cm							
Optimal coagulant dose, mg/L							

Table 13.3. Precipitate layer height, mm

Cylinder number	**Time of process passing, min**								
	10	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**
1									
2									
3									
…									
7									

Table 13.4. Height of clarified water layer, mm

Cylinder number	**Time of process passing, min**								
	10	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**
1									
2									
3									

For the determination of transparence investigated water poured to cylinder with transparent bottom and tap underneath. Cylinder put on height 4 cm above type and water poured through tap until single words of the text become visible. The height of water layer in cylinder responsible by transparency in centimeters.

Input, experimental and calculated data recorded to tables. For data got graphics in coordinates “water transparency – coagulant dose”, “precipitate layer height – coagulation time” or “height of clarified water layer – time of the process” built (experiment with optimal coagulant dose). The optimal coagulant dose determined by the graphic “water transparency – coagulant dose”.

The control questions

1. Explain, what the principle of the coagulation water purification?
2. Write down equation of the reaction forms hydroxides at the coagulant solution adding to water.
3. Explain, why at overdosing of coagulant the processes of forming and precipitating flakes of hydroxides become slower.
4. Define the concepts: water transparency, optimal coagulant dose.

5. Explain, why the purified water shouldn't have residual quantities of alumina and iron.
6. Call stages of the micelle forming.
7. Explain the double electric layer forming.
8. Give the characteristics of the electric kinetic potential.

Literature: [1-8]; [17].

Laboratory work 5. Dynamic exchange capacity of cation exchanger

The aim of work – to determine the dynamic exchange capacity of cation exchanger CU-2 until the moment of penetration Ca^{2+} ions into the filtrate. To regenerate cation by the solution of sodium chloride and to wash up it by distilled water.

The theoretical theses

The essence of ion exchange is the solid (liquid) substance (resin) absorbs anions or cations from electrolyte solution changing it on equivalent quantity of other ions with the same charge signal. According to the charge signal of exchanged ions it classified on cation exchangers, anion exchangers and ampholytes.

Ion exchange resins are artificial high molecular organic, poly electrolytes almost undissolved in water and other solvents and has ion exchange properties. The possibility to ion exchange caused by availability of active ion groups with moveable ions (counter ions) in ion exchangers. They can be exchanged on ions of another environment. If this active groups have acidity character (ankers or fixed ions $–SO_3^-$, $- COO^-$, $-PO_3^-$ etc.), ion exchangers (cation exchangers) capable to change moveable hydrogen or sodium ions on other cations from electrolyte solution. If the functional groups have alkalinity properties (anker ions $–NH_3^+$, $=NH_2^{3+}$, $\equiv S^+$ etc.), ion exchangers change moveable hydroxide ions on other anions.

The certain polymer determines space structure of ion exchanger. Cells consist of the matrix – high molecular, almost insoluble in water and other solvents ion exchange material and moveable ions. The last one's cause charge of certain signal.

The ion exchange process can be described by reversible equilibrium heterogeneous chemical reactions of double exchange:

$$H[Kat] + Na^+ = Na[Kat] + H^+;$$
$$2Na[Kat] + Ca^{2+} = Ca[Kat]_2 + 2Na^+;$$
$$[An]OH + Cl^- = [An]Cl + OH^-;$$
$$2[An]OH + SO_4^{2-} = [An]_2SO_4 + 2OH^-;$$

where [An] – anion exchanger; [Kat] – cation exchanger.

The most important characteristic of ion exchange sorbents is full exchange capacity – the theoretic number of ionic groups contained in the single mass or volume of the ion exchange material.

The capacity (sorption by given ion) is quantity of sorbed ion by the single mass or volume of the ion exchanger in equilibrium conditions (mmole/g, mmole/L). It can be determined so in static, as in dynamic conditions. The static exchange capacity determined by the way of contacting the mass of ion exchange material with certain volume of the investigated solution during the time enough for equilibrium establishment. The dynamic exchange capacity – by ions quantity absorbed by the same mass of ion exchange material in conditions of continuous flowing of the electrolyte solution through the layer of ion exchange resin until the moment of ions penetration. The full dynamic exchange capacity determined by flowing solution through the column of knowing quantity of the ion exchanger until the composition of filtrate and input solution becomes analogical.

The ion exchange reactions are reversible. That's why, if the concentration of ions H^+, Na^+, OH^- increased extremely, the equilibrium moves to the left. This property used at the regeneration of ion exchangers.

The methodic of conducting work

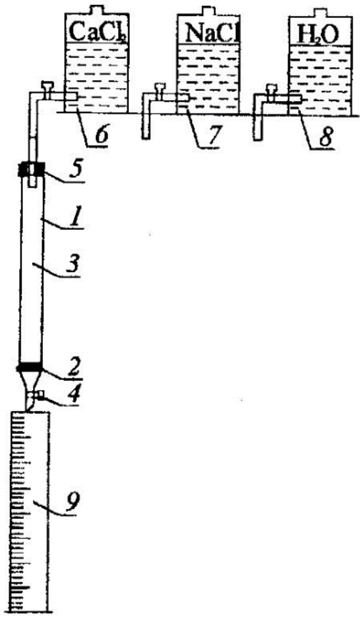
Equipment: volumetric flasks (100 cm^3); volumetric cylinders (250 cm^3) – 2 ones; pipettes (100 cm^3); glass columns; bulbs for the titration (volume 250 cm^3).

Reactants: cation exchanger CU-2; working solutions of $CaCl_2$ and NaCl; ammonia buffer solution; the indicator – chrome dark blue; 0,01 M solution of Trilon B; argentum nitrate solution.

The installation of the dynamic exchange capacity of cation exchanger determination (fig. 4) consists of ion exchanger column-filter 1 presented by glass tube (diameter 15 – 25 mm), the bottom part of it includes glass diaphragm 2 for supporting of ion exchange resin layer 3. The cation exchanger quantity in column – 30 g. For the regulation of liquid moving rate in the bottom part of column the glass tap and Mor's clamp on resin tube designed. From above the column hermetically closed by resin tube with hole 5. For giving to column the investigated solution of $CaCl_2$, NaCl solution for ion exchanger regeneration and washing up water, the glasses 6 – 8 set up. From it reactants given for score of hydrostatic pressure. For the determination of solution quantity moving through column in one time, the volumetric cylinder 9 used.

Experiment 1. Ion exchange filtration of calcium chloride solution

The filtration rate of solution through the cation exchange filter regulated at the beginning. For this distilled water given through the filter from above to bottom by regulation of pouring by helping of regulated device 4. The time determined of pouring 20 – 25 cm^3 of water, accumulated in volumetric cylinder 9. When liquid flow achieves necessary rate of giving, it cut off by the tap, but not by regulated device. The linear rate of filtration should be approximately 5 m/h.



1 – column-filter; 2 – glass diaphragm; 3 – ion exchange resin; 4 – clamp or tap; 5 – stopper with hole; 6 – 8 – glasses with solutions and water; 9 – volumetric cylinder

Figure 13.4 – Scheme of installation for the determination of dynamic exchange capacity of cation exchanger

When the speed of liquid pouring determined, the solution of calcium chloride with molear concentration of equivalents 3,5 mmole/L filtrated. For this to the column with ion exchanger, instead of glass with distilled water 8, the glass 6 with $CaCl_2$ connected, the tap opened and filtrate picked up by portions (100 – 110 cm^3), the concentration of calcium cations determined in it by complexonometric method. The filtration stopped when the concentration of calcium ions in filtrated achieves above 0,05 mmole/L. After this the summary volume of filtrate has been passed through the ion exchange layer can be determined.

Experiment 2. The conducting of regeneration and washing up of the cation exchanger

For conducting the cation exchanger regeneration, instead of glass 6 with solution of calcium chloride, the glass 7 with solution of sodium chloride (mass fraction – 8 %) connected to the column and passed through the ion exchange layer. The volume of NaCl solution should equal the summary volume of $CaCl_2$ solution passed through the column with the same rate. Then excess of salt solution washed up by connecting glass

8 with distilled water to the column. It washed up, while washing water doesn't contain chloride ions (sample with argentum nitrate). For this construction of column, it's necessary usually not less than 1000 cm^3 of distilled water.

The control methods

The determination of calcium ions content in filtrate based on the reversible reaction

$$Ca^{2+} + H_2Y^{2-} = CaY^{2-} + 2H^+,$$

where H_2Y^{2-} - Trilon B anion.

For moving the equilibrium in the hand of complex compound CaY^{2-} forming, the reaction charged in environment of alkaline buffer mixture (at pH 10), which neutralized hydrogen ions.

In conical bulb with capacity 250 cm^3 by pipette or volumetric flask 100 cm^3 of the filtrated picked up (from portion of 105 – 110 cm^3), 5 cm^3 of ammonia buffer solution and 2 – 3 drops of indicator added. The liquid mixed and titrated by Trilon B solution to transition of color from crimson to violet blue.

The ions of calcium content calculated by the formula:

$$C_{Ca^{2+}} = \frac{V_1 C_{H_2Y^{2-}} \cdot 1000}{V},$$

where C_{Ca2+} - the concentration of calcium ions in filtrate, mmole/L; V_1 – volume of Trilon B solution spent for the titration, cm^3, C_{H2Y2-} - the concentration of Trilon B solution, mole/L; V – water sample volume, cm^3.

The experimental data recorded to the table 5.

By the experimental data it's necessary to build filtration curve in coordinates "electrolyte volume passed through the filter – calcium ions concentration in filtrate". By the graphic it's necessary to determine the filtrate volume until calcium ions penetration. The penetration concentration of calcium ions equals 0,05 mole/L.

Table 13.5. The experimental data

Sample number	**Sample volume, cm^3**	**The volume of electrolyte passed through the filter, cm^3**	**The concentration of calcium ions in filtrate, mmole/L**

The dynamic exchange capacity calculated by the formula

$$DEC = \frac{V_{pen} C_{Ca^{2+}}}{1000m},$$

where DEC – the dynamic exchange capacity of cation exchanger, mmole/g; V_{pen} – the filtrate volume until calcium ions penetration, cm^3; C_{Ca}^{2+} - the concentration of calcium ions in filtrate, mmole/L; m – cation exchanger mass, g.

The control questions

1. Explain the essence of ion exchange. Write down equations of process reactions.
2. Describe building and properties of synthetic ion exchangers (moveable ions, exchange capacity, swelling, acidity-alkalinity properties, osmotic stability etc.).
3. How determined the dynamic exchange capacity of ion exchangers?
4. What is the regeneration of ion exchangers, what is this?
5. Call the spheres of using ion exchange in water treatment processes. What is its preferences and drawbacks comparing with other methods?
6. Present the principal scheme of softening and desalination of water by ion exchange method. What are requirements to water quality in different branches of industry?

Literature: [1-8]; [17]; [22].

Laboratory work 6. Natural water softening

The aim of work – to make softening of natural water with helping of soda-lime method, to induct with the methodic of water hardness determination.

The theoretical theses

The water softening is process decreasing its hardness. The hardness of water caused by salts of calcium and magnesium. Several kinds of water hardness distinguished: carbonate and non-carbonate, and together they up total hardness.

The carbonate hardness caused by availability in water of calcium and magnesium hydro carbonates. This kind of hardness called temporary, because of it can be fully removed by water boiling. Herewith hydro carbonates decomposed forming carbon (IV) oxide and carbonates precipitated:

$$Ca(HCO_3)_2 \xrightarrow{T=373\ K} CaCO_3\downarrow + CO_2\uparrow + H_2O;$$
$$Mg(HCO_3)_2 \xrightarrow{T=373\ K} MgCO_3\downarrow + CO_2\uparrow + H_2O;$$
$$MgCO_3 + H_2O \xrightarrow{T=373\ K} Mg(OH)_2\downarrow + CO_2\uparrow.$$

Non-carbonate (permanent) hardness caused by availability in water of calcium and magnesium compounds (first of all – salts of strong acids), remained dissolved at boiling. The hardness expressed by milli mole concentration of calcium and magnesium equivalents (mmole/L).

By the value of hardness water classified on very soft (until 1,5 mmole/L), soft (1,5 – 3,0 mmole/L), water of medium softening (3,0 – 4,5 mmole/L), enough hard (4,5 – 6,0 mmole/L), hard (6,0 – 11,0 mmole/L) and very hard (above 11,0 mmole/L). For requirements of commercial-drinking water supply at THE STATE SANITARY NORMS AND RULES 2.2.4-171-10 the water considered suitable with hardness not more 7 mmole/L. Salts, caused water hardness, don't harmful for human, but large quantity of it in water makes it unsuitable for commercial- household needs.

Water, contains calcium and magnesium salts, is impossible for using for getting vapor because the formation of dense layer of scale, caused overheating of boiler and its rapid destroying. The water hardness, used in vapor generators, shouldn't be above 0,0002 mmole/L. Water with increased carbonate hardness can't be used in cooling systems.

For water softening the thermal, reagent, ion exchange and combine methods usually used. The thermal methods based on water heating, its distillation and freezing.

The reagent methods keep to transform calcium and magnesium compounds, soluble in water, to almost insoluble. Lime, calcined soda, sodium or barium hydroxides, oxalate acid, sodium phosphates etc. used as reagents for water softening. Among reagent methods the most widely used lime-soda method. Its essence is in processes described by following equations:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O;$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O;$$
$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaSO_4\downarrow.$$

Soda removes non-carbonate calcium water hardness:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl;$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4.$$

The water hardness can't be fully removed by reagent methods because of such compounds, as $CaCO_3$ and $Mg(OH)_2$ has very low solubility in water. That's why, lime-soda method used, if it's necessary to soft natural water to relatively shallow residual hardness (approx. 1 mmole/L). The phosphate method gives deeper softening (almost until fully desalination) among reagent methods, and also ion exchange method.

The essence of ion exchange method is: the solid substance (ion exchanger) has property to exchange ions, entered to its structure, with equivalent quantity of ions with the same signal, presented in solution. The ion exchanger often presented in apparatus in non-moving state, and water passed through ion exchanger layer (filtered). Ion exchangers are solid (sometimes – liquid), insoluble in water substances of the natural or artificial origin. Ion exchangers include natural minerals (zeolites, glauconitic etc.), artificial substances (permutes) and also synthetic resins, sulphated coal etc. In water preparation processes artificial ion exchangers, used the most often, are high-molecular resins. Depending on ion signal, taking place in ion exchange, cation and anion exchangers distinguished. Ion exchange is reversible process. This property is one more preference of process, because gives possibility to regenerate ion exchanger.

If ion exchanger has moveable cation group in view of Na^+ (then it will call cation exchanger), the ion exchange process runs by the schemes:

$$Na_2[Kat] + Ca(HCO_3)_2 = Ca[Kat] + NaHCO_3;$$
$$Na_2[Kat] + MgSO_4 = Mg[Kat] + Na_2SO_4;$$

if cation exchanger is in H-form, that

$$H_2[Kat] +MgCl_2 = Mg[Kat] + 2HCl;$$

if ion exchange runs among anions, the process placed

$$An[OH] + HCl = [An]Cl + H_2O.$$

The regeneration of exhausted ion exchangers conducted with helping of sodium chloride, sulfuric or chloride acid solutions, alkaline solutions. Herewith the following processes placed:

$$Ca[Kat] + 2NaCl = Na_2[Kat] + CaCl_2;$$
$$Mg[Kat] + H_2SO_4 = H_2[Kat] + MgSO_4;$$
$$[An]Cl + NaOH = [An]OH + NaCl.$$

Ion exchange used not only for softening natural, but also for purification of waste (the most often – industrial) waters, keeping to utilize valuable, harmful and toxic water impurities. Herewith waste waters can be purified until the edge allowable concentration (EAC), and then they can be used in technology processes or in systems of reversible water supply. Ion exchange method widely used for purification of waste waters of metallurgical, chemical, coke-chemical, machine-building enterprises and other branches of industry.

The methodic of conducting work

Equipment: pipettes; volumetric cylinder (250 cm^3); conical bulbs for the titration (250 cm^3); heat-resistant bulbs for boiling; funnels; paper filters.

Reactants: 0,1 M solution of chloride acid; 0,04 mmole/L solution of sodium hydroxide; 0,1 mmole/L solution of calcined soda; 0,05 M solution of Trilon B (disodium salt of ethylenediaminetetraacetate acid); ammonia buffer solution (pH 10); indicators – methylene ornge, phenolphthalein, chromic dark-blue.

In water sample, proposed by teacher, firstly by analytic way all kinds of hardness determined. Then the quantity of reagents calculated, for softening water, the properly softening process conducted, the residual hardness of water sample determined and the softening degree calculated.

Experiment 1. The determination of carbonate hardness of water

In majority of natural water ions HCO_3^- connected only with Ca^{2+} and Mg^{2+} ions. For the determination off carbonate hardness, it's enough to determine the content of HCO_3^- ions and to form neutral salts by water titration by chloride acid. At the same time, except HCO_3^- ions, water can contain OH^- and CO_3^{2-} ions. They also form neutral salts at the titration by chloride acid. HCO_3^-, OH^- and CO_3^{2-} ions caused total water alkalinity, determined by chloride acid expenses for titration of water until pH 3,6 at availability of methylene orange. OH^- and CO_3^{2-} ions content determined by expenses of chloride acid for titration until pH 8,6 with phenolphthalein availability. If the alkalinity by phenolphthalein equals zero, the total alkalinity will equal carbonate hardness, namely $A_{tot} = H_c$. If the alkalinity by phenolphthalein is above zero, that

$$H_c = A_{tot} - A_{ph},$$

where A_{ph} the alkalinity by phenolphthalein.

For the determination of carbonate water hardness, 100 cm^3 of certain water sample picked up by pipette or volumetric flask and transited to conical bulb (250 cm^3), then 2 - 3 drops of phenolphthalein added. If water gets pale pink color, it titrated by 0,1 M solution of chloride acid until transparency. Then 2 -3 drops of phenolphthalein added to this bulb and titration continued by chloride acid until color transition from tallow to rose.

The carbonate hardness of water determined by the formula

$$H_c = \frac{(V_{tot} - V_{ph})}{V} C_{HCl} \cdot 1000,$$

where H_c – the carbonate hardness of water, mmole/L; C_{HCl} – the concentration of chloride acid, mole/L; V_{tot} --- total volume of chloride acid solution spent for the titration, cm^3; V_{ph} – volume of chloride acid spent for the titration only with phenolphthalein, cm^3; V – volume of water sample taken for analysis, cm^3.

Experiment 2. The determination of non-carbonate and total water hardness

The total water hardness determined by helping of the complexometric method. Herewith calcium and magnesium ions form complex compounds with Trilon B:

$$Me^{2+} + H_2Y^{2-} = MeY^{2-} + 2H^+.$$

100 cm3 of analyzed solution picked up by pipette or volumetric flask, transited to conical bulb for titration (volume 250 cm^3), 5 cm^3 of ammonia buffer solution and 3 -5 drops of indicator chromic dark blue added. Herewith, if water contains Ca^{2+} and Mg^{2+} ions, the solution gets violet-crimson color. The solution slowly titrated by 0,05 M solution of Trilon B until forming of grey-blue color.

The total water hardness calculated by the formula

$$H_{tot} = \frac{V_1 C_1 \cdot 1000}{V},$$

where H_{tot} – the total water hardness, mmole/L; V_1 – volume of Trilon B solution spent for the titration, cm^3; C_1 – the concentration of trilon B solution, mole/L; V – volume of water sample taken for analysis, cm^3.

The non-carbonate hardness of water determined as difference between total and carbonate hardness:

$$H_{nc} = H_{tot} – H_c.$$

The calculation of reagents quality for water softening

If water hasn't magnesium hardness, the volume of lime milk calculated considering carbonate water hardness:

$$V_{Ca(OH)_2} = \frac{H_c V_{H_2O}}{1000 C_2},$$

where $V_{Ca(OH)2}$ – volume of lime milk, cm^3; H_c – the carbonate hardness of investigated water, mmole/cm^3; V_{H2O} – water volume needed for softening, cm^3; C_2 – the concentration of $Ca(OH)_2$ in lime milk, mole/L.

The quantity of soda solution for softening water calculated considering non-carbonate hardness:

$$V_{Na_2CO_3} = \frac{H_{nc} V_{H_2O}}{1000 C_3},$$

where V_{Na2CO3} – volume of soda solution, cm^3; H_{nc} – the non-carbonate hardness of investigated water, mmole/cm^3; C_3 – the concentration of soda solution, mole/L.

Experiment 3. The softening of water and determination of residual hardness

Some volume of the sample transferred by volumetric cylinder to the bulb (volume 500 cm^3) (should be produced from heat-resistant glass), calculated quantities of lime milk and soda solution added and boiled 10 – 15 min. (from the beginning of boiling). Then bulb cooled good until room temperature, water filtrated through the paper filter. 100 cm^3 picked up by pipette to the titration flask and residual hardness of water determined after softening. The analysis and calculations charged analogically until the determination of total water hardness.

The degree of water softening calculated by the formula

$$x = \frac{H_{tot} - H_{res}}{H_{tot}},$$

where x – the degree of softening, share units; H_{tot} – the total hardness of water until softening, mmole/L; H_{res} – the residual hardness of water after softening, mmole/L.

The control questions

1. The availability of what substances caused hardness and alkalinity of water?
2. What kinds of water hardness can be classified on?
3. What methods of water softening used in industry?
4. What the essence of reagent and ion exchange methods of water softening?

Literature: [1-12]; [17-22].

SECTION 14 PRACTICAL WORK

14.1 Calculation of horizontal tank

1) Total area of water clarification

$$F = \frac{Q}{U_0},\ m^2,$$

2) Total length of sedimentation part (L, m):

$$L = \frac{V \cdot H}{U_0 \cdot K},\ m,$$

where V – average linear rate of water in flow part of tank (35 mm/s); H – depth of sedimentation zone, m (2,5 – 3,5 m);
U_0 – hydraulic size of particles, mm/s (see the table for calculation of sand trap);
K – coefficient, depending on the type of tank (for horizontal K = 0,5).

14.2 Calculation of vertical tank

1) Area of water mirror:

$$F = \frac{Q \cdot \beta}{V_f},\ m^2,$$

where β – coefficient, taking into account volume usage of the tank, $\beta = 1{,}3 \div 1{,}5$;
V_f – rate of water flow,
$V_f = 0{,}8$ (low muddy water) – 1,5 (muddy water), mm/s.

2) Total number of vertical tanks

$$N = \frac{F}{f},$$

where f – area of one standard tank, $f = \pi d^2/4$.
The diameter of vertical tank is usually selected in range of 5, 6, 7 *m*.

14.3 Calculation of radial tank

1) Total area of sedimentation:

$$F = \frac{Q}{q},\ m^2,$$

where Q – productivity of station, m^3/h;

q – loading of water per 1 m^2 of mirror per hour, $m^3/(m^2 \cdot h)$, usually 2 – 3,5 $m^3/(m^2 \cdot h)$.

2) Quantity of tanks is calculated by the formula:

$$N = \frac{F}{f},$$

where f – area of one standard tank, m^2.
Standard radial tanks have diameters: 18, 24, 30, 36, 42 to 60 *m*.

14.4 Calculation of sand trap

One of the simplest and ancient facility, working by creaming, are sand traps. They are used for delaying of heavy insoluble impurities (mainly sand) at the productivity of purification facilities more than 100 m^3/day. This facilitates of next successively connected purification facilities. Substances of organic origin are creamed with mineral impurities in sand traps. Hydraulic size of these particles is close to hydraulic size of sand. Quantitative ratio between delayed mineral and organic substances depends on the category of waste water and conditions of exploitation. At purification of household waste water, sand traps delay particles with diameter 0,25 mm and more. Quantity of organic compounds in delayed mass is 15...20%.

Depending on direction of main flow of waste water, sand traps are:

- horizontal (water moves horizontally, with straight-line or round motion;
- vertical (water moves vertically up);
- aeration and tangential with helical (progressive-rotating) motion of water.

1) Length of flow part:

$$L = \frac{V \cdot H \cdot K}{U_0}, m,$$

where V – rate of horizontal moving of water, 0,15 – 1,3 *m/s*;
U_0 – hydraulic size of particles (rate of sedimentation, *mm/s*);
H – rate of flow part of sand trap (not more than 1,2 *m*);
K – coefficient, depending on particles size, type of sand trap and ratio “width: depth” of sand trap.

For horizontal sand traps:
K = 1,7 (U_0 to 18 *mm/s*);
K = 1,3 (U_0 > 18 *mm/s*).

2) Required area of water mirror for all types of sand traps:

$$F = \frac{Q}{U_0}, m^2.$$

Table 14.1. Dependence of sedimentation rate of particles on their geometrical size (D)

D, mm	0,1 – 0,2	0,25 – 0,35	0,4 – 0,5
U_0, *mm/s*	5,12 – 8,7	24,2 – 35,1	40,7 – 51,6

14.5 Calculation of clarifier with suspended layer of precipitate

Total area of precipitation:

$$F = \frac{Q \cdot K_p}{V_s},\ m^2,$$

where K_p – distribution coefficient of water between clarification zone and zone of separation of precipitate;

V_s – rate of rising of water in clarification zone, *mm/s*.

It's necessary to use table for calculation of clarifier (*M* – muddy of water).

Table 14.2. Data for calculation of clarifier

M, mg/L	**K_p**	**V_s, mm/s**	
		in winter	**in summer**
0 – 100	0,7 – 0,8	0,5 – 0,6	0,7 – 0,8
101 – 400	0,8 – 0,7	0,6 – 0,8	0,8 – 1,0
401 – 1000	0,7 – 0,65	0,8 – 1,0	1,0 – 1,1
1001 – 1500 and more	0,64 – 0,06	1,0 – 1,2	1,1 – 1,2

14.6 Calculation of volume of tank for dissolution (preparation of solution of coagulant)

1) Volume of tank:

$$V_t = \frac{Q \cdot \tau \cdot D_c}{C_c \cdot \rho},\ \text{m}^3,$$

where τ – time of full cycle of preparation solution, 10 – 12 h;

D_c – dose of anhydrous coagulant, kg/m^3;

C_c – concentration of solution of coagulant (for anhydrous substance), fraction of one;

ρ – density of coagulant solution, tons/m^3.

For calculation:

D_c = 3,5 – 15 kg/m^3;

C_c = 0,1 – 0,2;

P = 1,03 – 1,06 tons/m^3.

14.7 Calculation of mechanic filter

1) Total area of filtration:

$$F = \frac{Q}{\tau \cdot V - n \cdot q - n \cdot \tau_1 \cdot V}, \text{ m}^2,$$

where τ – time of working of water purification station per day, h/day;
V – calculation rate of filtration on different filters at different modes, m/h;
n – quantity of rinsing of one filter per day;
q – marginal outlay of water per one rinsing, m^3/m^2;
τ_1 – time of idle of filter at rinsing, h.

Filtration mode	**Single-layer**	**Double-layer**
Normal	5 – 10 m/h	7 – 10 m/h
Forced	6 – 12 m/h	8,5 – 12 m/h

2) Quantity of filters

$$N = 0{,}5 \cdot \sqrt{F_f}\ .$$

14.8 Calculation of grids

Grids are the first device in scheme of purification facilities. They are metallic rods, fixed on frame, with transparencies of different width, depending on necessary degree of purification. Rods can be rectangular, less often – round. Rod is installed vertically or obliquely on the road of moving of waste water. Angle of inclination of grid to horizon is 60 – 80°.

Grids can be moveable or non-moveable. By the method of their purification – the simplest and mechanized. Following table contains main parameters of grids-crushers.

The simplest grids are installed at the concentration of pollutants – lower than 0,1 m^3. They are purified manually by metallic rake. Impurities are dumped into drainage areas or gutters with holes. Then they are exported in closed containers into special places and disinfected.

Number of transparencies:

$$n = \frac{Q}{b \cdot h \cdot V} \cdot K,$$

where n – number of transparencies;

Q – productivity of station, m^3/s;

b – width of transparencies between rods, 16 – 20 *mm*;

h – depth of water near grid, 0,8 – 1,5 *m*;

V – rate of water, passing through the grid, 0,5 – 1 *m/s*;

K – coefficient of reserve, taking into account compression of transparencies and delaying of impurities (usually 1,05).

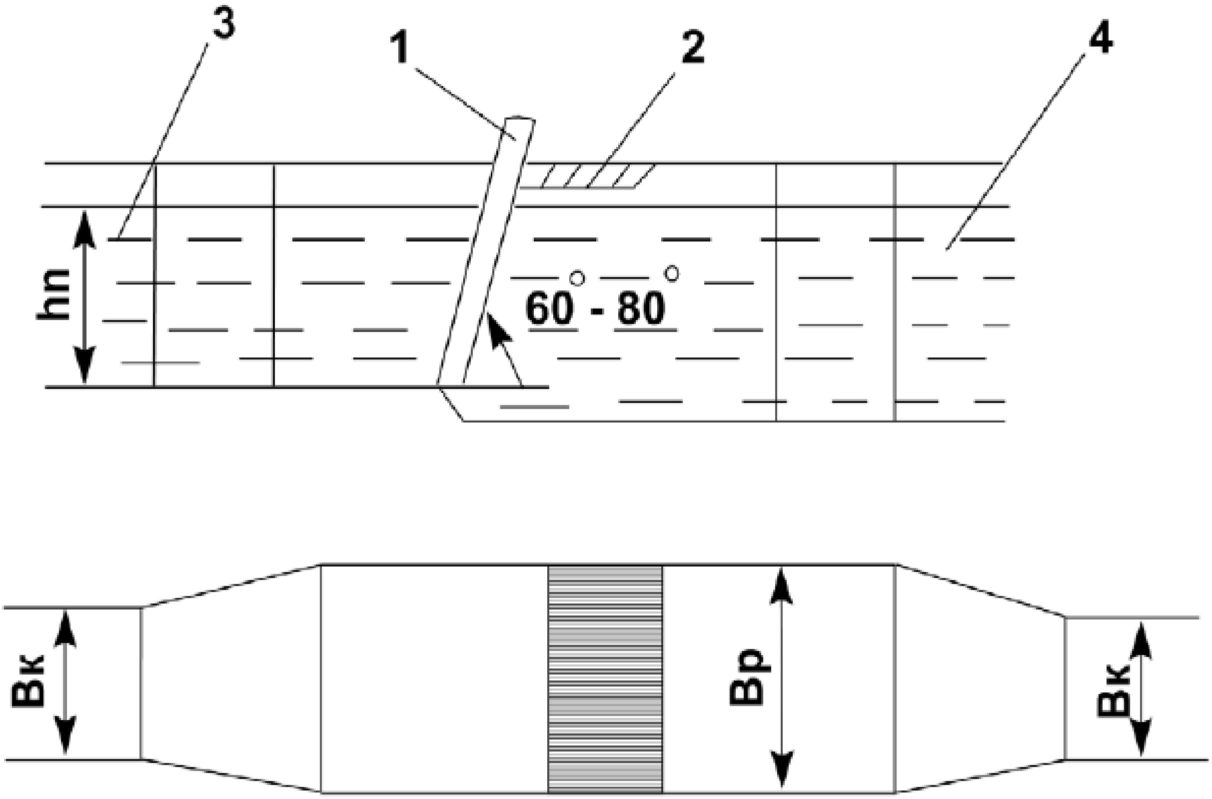


Figure 14.1 – Scheme of the simplest grid:
1– grid; 2 – coverage; 3 – supplying channel; 4 – dumping channel

Total width of all grids

$$B = S \cdot (n-1) + b \cdot n,$$

where S – width of rod of grid, 8 – 10 *mm*.

Number of grids for installation:

$$N_p = \frac{B_p}{B},$$

where B – width of standard grid, *m*.

Table 14.3. Overall dimensions of standard grids

Q, m^3/s	**Characteristic of grid B (width) * H (height), mm**
0,028 – 0,11	1000*1000
0,28 – 0,38	1000*1000
0,61 – 1,14	800*1400
1,39 – 2,20	1400*2000
2,45 – 2,70	1400*2000

14.9 Calculation of bulkhead cell of flakes formation

1) Total volume of cell:

$$V = Q \cdot \tau,$$

where τ – time of stay of water in cell of flakes formation. For color water τ = 30 min, for muddy – 20 min.

2) Total area of cell in plan

According to the altitude scheme of water purification station, height of cell of flakes formation is selected as equal to height of tank.

$$F = \frac{V}{h},$$

h = 2,5 – 3,5 *m*.

14.10 Calculation of aerotanks

1) Duration of aeration in aerotanks of all types (τ_a):

$$\tau_a = \frac{BOD_{in} - BOD_{fin}}{a \cdot (1 - s) \cdot w}, h;$$

BOD_{in}, BOD_{fin} – biological oxygen demand in initial and purified water, respectively, mg O_2/L;

a – dose of active silt, *g/L* (for aerotanks with aeration *a* = 2 – 4,5 *g/L*);

s – ash content of silt (usually *s* = 0,2 – 0,4);

w – average specific rate of oxidation, mg *BOD/(g·h)*, 85 ÷ 100 *mg/(g·h)*.

2) Degree of recirculation of active silt in aerotanks (R_{rec}):

$$R_{rec} = \frac{a}{\left(\frac{1000}{I}\right) - a}, \text{ parts of one;}$$

where I – silt index, depending on specific load, for household waste water and some kinds of industrial waste water, $I = 70 \div 130$ cm^3/g.

3) Volume of aerotank (V_a):

$$V_a = \tau_a \cdot (1 + R_{rec}) \cdot Q, m^3.$$

4) Increase of active silt (Inc):

$$Inc = 0{,}8 \cdot C_{sus} + K_p \cdot BOD_{in}, mg/L;$$

where C_{sus} – concentration of suspended particles in initial water, *mg/L*;

K_p – reserve coefficient of active silt, $K_p = 0{,}3 \div 0{,}5$.

14.11 Calculation of ion exchange filters

Total area of filtration

$$F = \frac{Q}{V_f}, \text{ m}^2,$$

where V_f – rate of filtration, m/h, for first and second stage of ion exchange $V_f = 10 \div 30$ m/h.

Quantity of ion exchange filters

$$N = \frac{F}{f},$$

where f – area of one standard filter, m^2; it is calculated, selecting diameter of filter:

D, mm	1000	1400	1500	2000	2600	3000

Volume of ion exchange resin for loading into all filters:

$$V_i = N \cdot f \cdot H, m^3,$$

where H – height of layer of ion exchange resin, m, usually $H = 1{,}5 \div 2{,}5$ *m*.

14.12 Calculation of adsorption installation

Outlay of sorbent for one-stage scheme (G_c):

$$G_c = Q \cdot D_c, \text{ kg/h},$$

where Q – productivity of station, m^3/h;

D_c – dose of sorbent, kg/m^3.

Outlay of sorbent for several stages of purification:

$$G_i = \frac{G_c}{i}, \ kg/h,$$

where I – quantity of stages (most often $I = 2 \div 3$).

For calculation of quantity of sorbent $D_c = 0{,}8 \div 1{,}3$ kg/m^3.

14.13 Calculation of extraction installation

For one-stage installation quantity of reactant is calculated by the formula:

$$C_{res} = C_{in} \frac{1}{K \cdot \eta + 1}, \ mg/L,$$

where C_{in}, C_{res} – concentration of pollutant in initial water and water after purification, respectively, mg/L;

K – coefficient of extraction:

$$K = \frac{C^e}{C^w},$$

where C^e, C^w – concentration of pollutant in extractant and in water, mg/L; value $K \cdot \eta$ is called “factor of extraction”; η – ratio between volume of extractant and water.

$$\eta = \frac{V_e}{V_w}.$$

Following extractants are used for removing of phenol and its compounds from water: benzene, butyl acetate, amylaceous alcohol, toluene, chloroform etc.

It’s recommended to take butyl acetate for calculation of extraction installation ($K = 50$). Value η is determined from equation, then value of extractant volume; value of water is productivity of station, m^3/h.

14.14 Calculation of horizontal oil trap

1) Area of section:

$$F = \frac{Q}{V},\ m^2,$$

where Q – productivity of station, m^3/h;

V – horizontal rate of water flow in oil trap, 0,4 ÷ 0,6 m/s.

2) Length of sedimentation zone of oil trap:

$$L = \frac{a \cdot V}{U} \cdot h,\ m,$$

where a – coefficient, taking into account turbulence of water flow, a = 1,5 ÷ 1,75;

h – working depth of oil trap, m, h = 1,8 ÷ 2 m;

U – rate of emersion of particles, m/s, U = 0,04 ÷ 0,06 sm/s.

3) Duration of emersion:

$$\tau = \frac{L}{V},\ \text{s}.$$

TASKS FOR COURSE WORK

ORIGIN AND APPOINTMENT OF WATER

Version	Water origin passing purification	Purified water appointment
1	Natural water (surface pound)	Drinking water
2	Natural water (underground pound)	Drinking water
3	Natural water (surface origin)	Technic water for vapor producing
4	Industrial waste waters	Recycle using
5	Household waste waters	Slope to pound
6	Mixture of industrial and household waste waters	Slope to biological pounds
7	Industrial waste waters	Recycle using
8	Natural water (surface pound)	Technic water for vapor producing
9	Industrial waste waters	Recycle using
10	Industrial waste waters	Technic water
11	Industrial waste waters	Slope to pound
12	Mixture of industrial and household waste waters	Slope to city canalization
13	Industrial waste waters	Recycle using
14	Natural water (surface origin)	Technic water for vapor producing
15	Household waste waters	Slope to pound
16	Industrial waste waters	Recycle using
17	Industrial waste waters	Slope to plant canalization
18	Natural water (surface pound)	Technic water for cooling systems
19	Mixture of industrial and household waste waters	For recycle using by enterprise
20	Industrial waste waters	Recycle using
21	Household waste waters	Slope to pound
22	Natural water (underground origin)	Technic water for cooling systems
23	Industrial waste waters	Slope to plant canalization
24	Household waste waters	Slope to pound
25	Industrial waste waters	Recycle using

CHARACTIRISTICS AND INDICATORS OF TREATING WATER QUALITY

Version	Power of station, m^3/h	pH	Suspended substances, mg/L		Color, degrees	Smell, mark	OCC, mg of oxygen in 1 L	OBC, mg of oxygen in 1 L	Dissolved Gases, mg/L	Pollutants, mg/L	Total salt content, mg/L	Coli-index
			hard dispersion	colloidal								
1	1600	6,5	120	80	50	4	7	5	8 (CH_4)	-	800	140
2	1200	8,0	2	-	20	2	12	-	10 (H_2S)	10 (Fe total)	3600	270
3	600	7,0	1500	600	80	4	15	-	-	2,0 (Mn)	1200	1000
4	300	2,0	260	300	150	-	150	-	-	120 (Cr)	4000	-
5	2000	6,5	250	180	360	4	200	180	-	70 (SAS)	1800	10000
6	800	7,2	150	70	500	5	400	250	-	250 (oil-products)	1500	-
7	400	4,5	80	50	22	5	200	130	-	6500 (phenols)	800	-
8	2200	6,5-7,5	120	40	35	4	80	45	12 (CH_4)	40 (organic comp.)	2100	4000
9	500	7,0	150	40	6	3	122	80	-	85 (Ni, Co)	4700	-
10	180	2,5	75	30	130	5	60	-	-	8 (Fe^{2+})	6000	10
11	1100	3,7	145	70	35	5	250	180	-	320 (heavy met.)	12700	-
12	1600	8,5	60	35	15	4	280	120	-	150 (albumen subs.)	8300	3000
13	150	4,2	40	28	58	3	160	75	24 (NH_3)	85 (nitrates)	4200	-
14	125	7,5	310	45	43	3	100	60	-	50 (plankton)	3800	-
15	85	9,0	200	80	27	5	510	450	-	65 (synt. wash)	2300	1200
16	80	4,0	120	100	380	5	200	120	-	500 (oil-products)	1800	-
17	60	2,0	180	65	33	3	30	20	-	12 (mercury comp.)	5000	-
18	140	6,5	190	70	12	2	44	25	-	-	2200	1000
19	200	8,0	95	50	15	4	680	550	-	-	3700	10000
20	1100	5,0	65	40	17	5	300	80	-	4900 (aniline)	700	-
21	800	11,0	400	85	5	3	440	370	-	180 (fats)	1300	1000
22	420	8,0	5	-	-	3	32	15	-	12 (fluoride comp.)	11300	8
23	130	5,5	27	15	45	5	180	85	-	50 (org. solvents)	2900	-
24	170	6,5	500	150	30	5	280	220	-	140 (SAS)	1450	10000
25	700	6,0	70	30	40	5	140	90	-	1100 (phenol)	600	-

INDICATORS OF WATER QUALITY AFTER TREATMENT

Version	pH	Suspended substances, mg/L		Color, degrees	Smell, mark	OCC, mg of oxygen in 1 L	OBC, mg of oxygen in 1 L	Dissolved Gases, mg/L	Pollutants, mg/L	Total salt content, mg/L	Coli-index
		hard dispersion	colloidal								
1	6,5 – 7,0	-	5	2	1	-	-	-	-	500	3
2	6,5 – 8,0	-	-	1	1	2	-	-	0,300	800	3
3	7,5 – 8,0	-	-	-	-	-	-	-	0,050	10	-
4	6,5 – 8,5	10	5	5	-	10	-	-	2,000	200	-
5	6,5 – 8,5	30	15	12	4	30	25	-	2,000	500	100
6	6,5 – 8,5	40	20	10	3	40	25	-	25,000	500	-
7	6,0	15	10	8	5	40	20	-	100,000	400	-
8	6,5 – 7,5	-	2	-	-	5	-	-	-	0,25	-
9	6,0 – 8,0	12	10	3	3	25	15	-	2,500	220	-
10	6,5 – 7,0	-	-	2	1	3	-	-	0,300	1000	3
11	6,5 – 8,5	40	30	8	5	20	15	-	until EAC	1600	-
12	6,5 – 8,5	20	15	6	4	30	25	-	20,000	2000	150
13	6,5 – 8,5	15	15	5	2	30	15	2	10,000	1000	-
14	7,5	-	-	2	-	-	-	-	-	0,5	-
15	6,5 – 8,5	20	10	2	3	40	15	-	2,000	1000	100
16	6,5 – 8,5	30	15	12	5	40	25	-	25,000	1000	-
17	6,5 – 8,5	20	10	4	3	25	10	-	0,005	1000	-
18	6,5 – 8,5	5	5	3	2	12	5	-	-	50	10
19	6,5 – 8,5	15	5	3	2	30	15	-	-	100	30
20	6,5 – 8,5	10	5	3	2	20	15	-	15,000	25	-
21	6,5 – 8,5	40	20	5	3	30	15	-	5,000	1300	100
22	6,5 – 8,5	-	-	2	3	30	15	-	0,750	1200	3
23	6,5 – 8,5	10	5	5	5	10	5	-	until EAC	150	-
24	6,5 – 8,5	10	5	5	2	38	15	-	1,500	150	100
25	6,5 – 8,5	20	10	15	5	25	15		20,000	80	-

WATER IMPURITIES CLASSIFICATION FOR ITS PHASE AND DISPERSION CHARACTERISTICS AND RECOMMENDED METHODS OF WATER TREATMENT

Processes	**Technological methods of water treatment**	**Sphere of using**	**Reactants (and its consumption per 1000 m^3 of water in kg**	**Equipment of water preparation stations**	**Removal degree of impurities from water**
1	2	3	4	5	6
Removing methods of impurities of the first group (particle size – above 10^{-5} cm)					
Mechanic non-reagent separation	Creaming	Hard-dispersive impurities (above 500 mg/L), color until 50 deg.	-	Decanters	50…70 %
	Filtration	Suspended substances (until 50 mg/L), color until 50 deg.	-	Slow filters	95…99 % of microorganisms until drinking water norm
	Filtration	Suspended substances (until 1000 mg/L), color until 50 deg.	-	Previous filters	60…80 %
	Microfiltration	Plankton (above 1000 cells per 1 L), suspended substances	-	Micro filters	70…95 %
	Centrifugation	Hard- and small-dispersive impurities	-	Centrifuges, hydro-cyclones	80…90 %
Adhesion on high-dispersive and grain materials	Filtration of coagulated suspension through the layer of grain backfilling	Coagulated suspension (10…15 mg/L)	Flocculants: PAA [0,01…0,04], AC [0,2…1,0]	Rapid filters, two- or multilayer filters	Until norms of drinking water
	Filtration by using contact coagulation	Suspended substances (until 150 mg/L), color until 150 deg.	$Al_2(SO_4)_3$ or $FeCl_3$ [10…120], PAA [0,2…0,6], AC [0,1…2,0]	Coagulators, contact filters	

1	2	3	4	5	6
Adhesion by alumina or iron hydroxides or clay materials	Water treatment by coagulants	Suspended substances and color without limits, pathogen bacteria, spores	$Al_2(SO_4)_3$ [40…250], $FeCl_3$ or $FeSO_4$ [20…150], lime, soda	Equipment for preparation and dosage of reactants, mixers, cameras of forming flakes, decanters, filters	Until norms of drinking water
	Treatment by clay materials	Pathogen bacteria, spores etc.	Clay materials (palygorskyte, montmorillonite) [100…500]		98…99,9 %
Adhesion by flocculants	Water treatment by coagulants and flocculants with following creaming and filtration	Suspended substances and color no-limited, pathogen bacteria	$Al_2(SO_4)_3$ [40…250], $FeCl_3$ or $FeSO_4$ [20…150], PAA [0,01…3 % from quantity of suspended substances] AC [20 % from dose of waterless coagulant]	The same	Until norms of drinking water
Flotation	Non-reagent flotation	Oil, butters, non-filterable mass (until 2000 mg/L)	Air	Floaters and devices for air desperation	0,9
	Reagent flotation		Air, fatty alcohols [10], $Al_2(SO_4)_3$ or $FeCl_3$ [25…50], AC [10]	Floaters and devices for air desperation and reagents dosage	90…99 %
Bactericide influence on pathogen microorganisms	Water treatment by oxidants: chlorination	Bacteria pollution	Chlorine [1…20] or chlorine (IV) oxide [1…5]	Chlorine storages, chlorinators, mixers	Standard by coli-index
	Ozonation		Ozone [0,5…50]	Ozonation devices, contact tanks	
	Ionization		Metallic silver	Ionization devices	
	Water treatment by radiation: ultrasound	Pathogen bacteria	Electric energy	Ultrasound installations	0,95
	UV-rays		Electric energy	Bactericide installations	98…99,9 %

1	2	3	4	5	6
Removing methods of impurities of the second group (particle size $10^{-5}…10^{-6}$ cm)					
Oxidation	Chlorination	Increased content of colloidal suspended substances and HMC caused color (35…250 deg.) and water oxidation	Chlorine [1…20] or chlorine (IV) oxide [1…5]	Chlorine storages, equipment for getting chlorine (IV) oxide, chlorine, chlorinators, mixers, contact tanks	Water of standard quality
	Ozonation		Ozone [0,5…20]	Ozone devices and devices for inputting ozone into water	
Adsorption by alumina and iron hydroxides or high-dispersive clay materials	Coagulation in free volume with following decantation and filtration	The same	$Al_2(SO_4)_3$ [40…200], $FeCl_3$ [30…200], lime, soda, NaOH	Equipment for preparation and dosing of reagents, cameras for flakes forming, decanters, coagulators; filters	Water of standard quality
	Water treatment by high-dispersive muddies and coagulants	Low muddy, water pollution by viruses	$Al_2(SO_4)_3$ [40…200], $FeCl_3$ [30…200], lime, soda, NaOH, adding bentonites or palygorskyte [50…200] etc.		
	Contact coagulation	Colloidal particles and high-molecular substances (35…150 deg.) in conditions of low concentrations of suspended substances	$Al_2(SO_4)_3$ [10…120], PAA [0,2…0,6], AC [0,1…2,0]	Equipment for preparation of solutions mixers, cameras for flakes forming	
Adhesion by flocculants	Water treatment by flocculants		High-molecular poly electrolytes [2…15]	The same	Water of standard quality

1	2	3	4	5	6
Viruses removing action	Water treatment by oxidants: chlorination	Water pollution by viruses	Chlorine [5…20], chlorine (IV) oxide [1…10]	Chlorine storages, chlorinators, mixers	Water of standard quality
	ozonation		Ozone [0,5…20]	Ozone and contact tanks	
	ionization (ions of silver and other metals)		Metallic silver [0,05…0,5]	Ionization devices	
Removing methods of impurities of the third group (particle size $10^{-6}…10^{-7}$ cm)					
Desorption of gases and volatile organic compounds	Aeration	Gases and volatile organic compounds offer unpleasant flavors and smells to water	Air	Sprinkle basins, cooling tanks, gas removing devices	From CO_2 – 65…80 %, H_2S - until 0,3…0,5 mg/L
Oxidation	Chlorination	Non-volatile organic compounds, H_2S (0,3…0,5 mg/L)	Chlorine [1,5…10] or chlorine dioxide [0,5…1,2]	Chlorinators, mixers, devices for chlorine dioxide getting	H_2S, other – depending on compound
	Ozonation	If chlorination efficiency isn’t enough	Ozone [2…4]	Ozone devices, contact tanks	Depending on compounds
	Treatment by potassium permanganate	If pollutions are little	$KMnO_4$ [3…10]	Devices for preparation and dosage of $KMnO_4$	Depending on compounds
Adsorption on activated carbon and other materials	Coal treatment	Unpleasant flavors and smells of natural origin and also in waste waters	Coal of different marks [5…20]	Devices for mixing water with coal suspension	80…95 %
	Water purification on coal filters and adsorbers with suspended layer of coal	Aromatic compounds (until 2000 mg/L)	Granulated coal	Adsorbers, furnaces for coal activation and regeneration	80…95 %
Extraction by organic solvents	Phenol removing phenol from water	Phenols (above 2000 mg/L)	Butil acetate, etil acetate, benzene etc.	Extraction devices	80…90 %
Evaporation	Vapor-circulation method	Volatile organic substances, phenols	Vapor at t = 100…105 ^{0}C	Columns for removing by volatilization	90…95 %
	Azeotrope stripping	Azeotropic mixture forming		Columns for removing by volatilization	90…95 %

1	2	3	4	5	6
Biochemical decomposition	Aerobic method	Waste waters pollution	Active silt, bio layer, air	Aero-tanks, bio-filters, decanters	90…98 %
	Anaerobic method	Concentrated waste waters, precipitates	Anaerobic microorganisms	Methane-tanks	90…98 %
Thermal oxidation methods	Flame calcination in gas phase	The same	Air	Cyclone furnaces	90…95 %
	Liquid-phase oxidation		Air	Devices for liquid phase oxidation	90…95 %
Removing methods of impurities of the fourth group (particle size – until 10^{-7} cm)					
Hyperfiltration	Ions removing by reverse osmosis	TSC 20…30 g/L	Electric energy [5…10 kW·h per 1 m^3 of water]	Devices with half-injection membranes	95…98 %
Transferring of ions into low-dissociated substances	Neutralization (by adding acid or alkaline)	pH 6,5…9	CaO, Na_2CO_3, NaOH, H_2SO_4, HCl, CO_2	Devices for preparation and dosage of solutions, mixers	Until necessary parameters
	Complex ions forming (stabilization)	Index of water saturation I>0	Sodium hexametaphosphate, sodium threepoliphosphate [2…20]		Prevention of forming corrosion
Softening (forming of low-soluble compounds of calcium and magnesium)	Thermal method	Carbonate hardness, calcium sulphate, muddy less than 50 mg/L	Heating	Thermal softer of water	Carbonate hardness – until 0,018 mmole/L
	Lime-soda method	Total hardness 2,5…15 mmole/L, muddy until 50 mg/L	Lime, soda	Mixers, rotor reactor, coagulators, decanters	Hardness – until 0,018 mmole/L
	Phosphate method	Total hardness until 1 mmole/L	Na_3PO_4		Hardness until 0,02…0,025 mmole/L
Forming of low-soluble metal hydroxides	Removing of color and heavy metals and also magnesium hardness	Ions of color and heavy metals, high magnesium hardness	Lime and NaOH	Devices for preparation and dosage of solutions, mixers, decanters, coagulators, filters	Until edges of metal hydroxides solubility

1	2	3	4	5	6
Fixing of ions by solid phase of sorbents: H-, Na-cation xchanging	Softening (by using of unmovable layer of cation exchanger	Total hardness until 7 mmole/L, suspended substances 8…10 mg/L	Cation exchangers, sulphated coal, NaCl, H_2SO_4, HCl	Cation exchanger filters, devices for preparation of regeneration solutions, adsorbers	Hardness until 0,0025…0,025 mmole/L
	Color metals removing	Waste waters			Hardness until 0,0025…0,025 mmole/L
Fixing of ions by solid phase of sorbents: H-, OH-ion exchanging	Freshness	TSC 3…4 g/L, suspended substances – until 8 mg/L, color – until 30 deg.	Cation exchangers, anion exchangers, sulphated coal, NaOH, H_2SO_4	Ion exchange filters, devices for preparation of regeneration solutions	75…90 % (until TSC 500…1000 mg/L)
	Desalting				99,5…99,9 % (until TSC 1…15 mg/L)
Separation in different phase states of water	Transferring water into gas phase (distillation)	TSC 20…35 g/L	Vapor, fuel	Evaporators of different types	99,9 % (until salt content of ditilled water 20…50 mg/L)
	Ions recombination in non-mixing liquids (extraction)	TSC 3…4 mg/L, calcium and magnesium salts absent	Secondary and third amines [2…4]	Extraction and rectification columns	95…99 %
	Transferring water into solid phase (freshness by freezing)	TSC until 35 g/L	Different cooling agents, natural cold	Devices by using artificial cold, areas for freezing	92…97 %
Using of ions moveable in electric field	Electric dialysis	TSC 3…10 g/L, muddy until 2 mg/L, iron content – until 0,3 mg/L	Electric energy expenses – 20 kW·h per 1 m^3 of water, ion exchange membranes	Devices by electrochemical water desalting	TSC until 500…1000 mg/L

INDEPENDENT WORK OF STUDENTS

№	Name of topic of independent work
1	Influence of impurities on the quality of natural waters
2	Technological methods of improving the quality of surface and groundwater
3	Modern hardware equipment of the stage of flakes formation
4	*Physical methods of disinfection of water*
5	Equipment for reverse cooling water
6	Water losses in recycling cycles of water supply
7	Cooling devices for reversible systems
8	Cooling water treatment
9	Existing methods for preventing salt deposits
10	Types of corrosion and ways of its elimination in the processes of water treatment
11	Preparation of water for artificial enrichment of groundwater reserves
12	Fluorination and non-fluent inlets for drinking and technical purposes
13	Stabilization treatment of water. Magnetic and acoustic water treatment

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