

Treatment of methanol-containing wastewater at gas condensate production

Andrey Ivanov¹⁾ , Alexey Strizhenok¹⁾ , Gabriel Borowski²⁾ 

¹⁾ Saint-Petersburg Mining University, Faculty of Mining Engineering, 21st Line of Vasilyevsky island, 2, 199106, Saint-Petersburg, Russia

²⁾ Lublin University of Technology, Faculty of Environmental Engineering, Poland

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Abstract: The purpose of the study was to assess the impact of industrial wastewater on the concentration of methanol in the considered section of the Ob River basin, present proposals for the implementation of a new treatment system and analyse the implementation results. On the basis of the results of the analysis of the known methods for reducing the concentration of methanol in water, a new technological scheme for post-treatment of effluents using biological treatment with methylotrophic *Methylomonas methanica* Dg bacteria was proposed. The calculation of the dilution of treated wastewater using the “NDS Ecolog” program was carried out on the basis of the detailed calculation method of Karashev, the results of which showed a decrease in the concentration of methanol in the control section to 0.0954 mg·dm⁻³ (permissible concentration is 0.1 mg·dm⁻³). During the period of the flood of the Glukhaya channel, it ceases to be a separate water body and, in fact, becomes part of the flood channel of the Ob River. Certain parts of the flooded areas, due to elevation changes, communicate with the channel only during a short period of time when the water level rises, i.e. 3–5 weeks during the flood period, and in fact remain isolated reservoirs for the rest of the time, potentially acting as zones of accumulation and concentration of pollutants.

Keywords: biological treatment, gas condensate, hydrates, methanol, rectification, regeneration, wastewater

INTRODUCTION

The considered condensate stabilisation plant is one of the largest gas condensate processing plants in the Russian Federation. The plant processes oil and gas condensate mixture and produces commercial products: motor gasolines, diesel fuel, jet fuel, liquefied gases, gas condensate distillate, light and stable condensate [LITVINENKO 2020; LITVINENKO, MEYER 2017; QUIROZ CABASCANGO, BAZHIN 2020]. The company’s environmental policy is based on ensuring the reduction of negative impact on the environment, resource conservation, taking the measures to preserve the climate, biodiversity and compensation for the possible damage to the environment [BABENKO *et al.* 2020; FILATOVA *et al.* 2021]. In the gas industry, methanol is used as a hydrate inhibitor [DVOYNIKOV *et al.* 2021a]. It enters the plant together with the oil and gas condensate mixture.

Methanol is very important for the plants of the North [SHARIKOV *et al.* 2020]. This substance is used as a hydrate

inhibitor. Gas hydrates are solid crystalline compounds that are formed under certain temperature and pressure conditions from water and low molecular weight gases [BABENKO *et al.* 2020; ZOU *et al.* 2021]. Methanol, which belongs to the class of thermodynamic inhibitors of hydrate formation, reduces the activity of water in water solution, which results in changing equilibrium conditions for the formation of hydrates [KITAEV *et al.* 2021; MONDAL *et al.* 2016; QURESHI *et al.* 2020].

Thus, the injection of methanol into the bottomhole zone of the well of gas hydrate fields not only causes the decomposition of gas hydrates at the bottom of the well, but also improves the filtration characteristics of the bottomhole zone, i.e., the section of the formation adjacent to the wellbore. In addition, the high adsorption capacity of methanol is used to remove water after hydrostatic testing of gas pipelines, as well as in low-temperature processes for removal of carbon dioxide (CO₂), hydrogen sulphide (H₂S) and other sulphur-containing organic compounds from natural gas [DIDMANIDZE *et al.* 2020].

The widespread use of methanol, especially at gas production plants of the Far North, is due to a number of reasons, including its relatively low cost compared to other inhibitors of hydrate formation (glycols, surfactants, water-soluble polymer compositions), the highest antihydrate activity among the known inhibitors, even at low temperatures, very low freezing point of concentrated methanol solutions and their extremely low viscosity even at temperatures below -50°C [OHLSTRÖM *et al.* 2001; SEMENOV *et al.* 2021; ZAGASHVILI *et al.* 2020]. Environmental risks in the form of accidental emissions or spills of methanol can arise during its production, transportation, use and wastewater accumulation of this substance [DEMIRBAS 2008; FERNANDEZ *et al.* 2007; MATVEEVA *et al.* 2017; TRICKEY *et al.* 2020]. The water of the Ob River and water bodies of its basin, are characterised by high methanol concentrations due to the presence of developed natural gas fields and gas condensate industries in this area.

Methanol is supplied to the plant along with the oil and gas condensate mixture [GRAAF, BEENACKERS 1996]. During the production and transportation of hydrocarbons, a droplet liquid is formed in the flow. When it freezes, hydrate plugs (ice) are formed, which reduces the flow permeability or leads to a complete stop of pumping [WANG *et al.* 2019]. The addition of a water-methanol mixture in the fields ensures the absence of hydrate deposits on the walls of main pipelines [LIU *et al.* 2016].

The main purpose of the wastewater recovery unit with methanol recovery and wastewater treatment is to recover methanol from a water-methanol mixture by rectification [DAVANI *et al.* 1986]. The methanol mixture is first separated from the condensate and then from the water by heating [BONDAREV *et al.* 2018]. The boiling point of methanol (65°C) is lower than that of water. The end product of the plant is 98% methanol, which is shipped by rail for reuse by mining companies. The aim of the study was to evaluate the degree and nature of the impact of one of the condensate plants on the methanol content in surface waters based on an analysis of the available production data and a review of open sources, as well as to develop a new treatment system that will reduce the technogenic impact of the methanol-containing wastewater to standard indicators.

MATERIALS AND METHODS

The basin of the Ob River below the confluence of the Irtysh is divided into two regions: Sredneobsky and Nizhneobsky. The river flows along its entire length in a flat valley, the width of which is greater than 50 km. The Ob River is characterised by a multi-arm channel. In the area of the city of Surgut, it is divided into two main branches (Ob and Yuganskaya Ob). The Sredneobsk region is the place where other large rivers flow into the river: Vakh, Bolshoi Yugan, Bolshoi Salym, as well as many small rivers. The main source of water for rivers in this place is large sediments, but also groundwater and liquid sediments.

The chemical composition of the river waters of the Ob-Irtysh basin enables to categorise them as waters of the calcium group of the hydrocarbonate class. Relatively weak slope of the terrain, as well as a large tortuosity coefficient (3–4) of the territories of the Khanty-Mansi Autonomous Okrug lead to a rather slow flow of rivers.

The Ob River and its large tributaries are characterised by spring-summer floods, low summer-autumn runoff, with rain floods in the warm season (which are insignificant in size and duration) and low runoff in winter. The duration of the flood varies from 100 to 130 days.

The terrain is very swampy, and the marshes are unevenly distributed throughout the territory. This is due to the flat topography, shallow river slopes and extremely slow runoff, as well as shallow river incisions and poor drainage. There are a large number of lakes in the region of the West Siberian Lowland. This is caused by a combination of two factors, i.e. excessive moisture and flatness of the surface. There are also drainless reservoirs with bitter salt water. There are also several large reservoirs in this area. Most of the water bodies of Western Siberia are fisheries. Large rivers and floodplain lakes are the main source for commercial fishing.

The taiga zone is usually characterised by alternating swamp and forest landscapes. In the region, there are mainly low-lying moss-grass and raised sphagnum bogs. Low-lying bogs are usually located in the floodplains of rivers, and their vegetation is represented by sedges, willows and forbs (*Scutellaria galericulata*, *Stellaria longifolia*, *Equisetum palustre*, *Galium uliginosum*). The landscape of raised sphagnum bogs is mainly characterised by ridge-lake and ridge-hollow complexes with dwarf-sphagnum and dwarf-sphagnum-pine vegetation. Shrubs are represented by *Betula nana*, *Myrtus*, *Andromeda*, *Oxycoccus* and *Vaccinium myrtillus*. The tree layer is represented by pines. Their height is from 4 to 10 m, and the crown density does not exceed 0.2–0.3 m. The moss cover is continuous, of sphagnum mosses.

The trees of the forest landscape are represented by *Picea*, *Cedrus*, *Alnus*, *Pinus*, *Larix*, *Abies* and *Betula*. Forests are stretched out in narrow bands along river floodplains or arranged in a mosaic pattern. The forestry regulations provide for the following forest categories in the area where the plant is located: valuable (protected forest belts located along water bodies; spawning forest belts) and operational [Prikaz № 59-np ... 2018]. The fauna of the region is represented by 60 species of mammals, 260 species of birds, 4 species of reptiles, 42 species of fish, as well as 6 species of amphibians (3 of which are in the Red Book by BAYKALOVA *et al.* [2013]).

The following mammals have spread throughout the area: *Canis lupus*, *Ursus arctos*, *Mustela nivalis*, *Lepus timidus*, *Rattus norvegicus*, *Mus musculus*. *Rangifer tarandus* is a rare species. Among birds, the most widespread are *Falco* (*Falco peregrinus*, *F. columbarius*, *F. subbuteo*), *Bubo bubo*, *Larus* (*Hydrocoloeus minutus*, *Chroicocephalus ridibundus*, *Leucophaeus modestus*), *Grus* (*Grus communis*, *G. monacha*, *G. leucogeranus*) and geese (*Branta ruficollis*, *Plectropterus gambensis*). The ichthyofauna of the Middle Ob is represented by 22 species of fish. The most important fishing objects in this part of the basin are representatives of the following species: *Acipenser*, *Stenodus leucichthys nelma*, *Coregonus muksun*, *Coregonus peled*, *Acipenser ruthenus*, *Lota lota*, *Esox lucius*, *Leuciscus idus*, *Rutilus*, *Carassius carassius*, *Leuciscus leuciscus*, and *Perca fluviatilis*.

In winter, the rivers are fed by swamp waters, which are almost devoid of oxygen, but contain many organic substances, which in turn increase the productivity of water bodies. In addition, oxygen is consumed for the oxidation of ferrous iron compounds that enter rivers from swamps. Mass death of fish is

rarely observed in the Ob: under normal conditions, the fish have time to escape into non-clogged water bodies [STARIKOV 2012].

In order to calculate the concentration in the control section, a normative method was used, namely, a detailed method (numerical method) for solving the turbulent diffusion equation, developed by A.V. Karaushev, makes it possible to obtain a concentration field of a substance within the entire calculated area from the point of release to the section under consideration. The equation of turbulent diffusion for the conditions of the spatial problem has the following form:

$$\frac{\partial_x S}{\partial X} = \frac{D}{V_r} \left(\frac{\partial_y^2 S}{\partial Y^2} + \frac{\partial_z^2 S}{\partial Z^2} \right) \quad (1)$$

where: D = the coefficient of turbulent diffusion, V_r = average flow velocity in the considered section of the watercourse ($\text{m}\cdot\text{s}^{-1}$), $\partial X, \partial Y, \partial Z$ = coordinate change along the length, width and depth of the watercourse, respectively, relative to the origin of coordinates – the place of discharge, $\partial_x S, \partial_y S, \partial_z S$ = change in the concentration of the considered polluting component along the length, width and depth of the watercourse relative to the concentration of the polluting component in waste water ($\text{mg}\cdot\text{m}^{-3}$).

The entire computational flow area was divided by the planes parallel to the coordinate planes into computational cells. The following relationships were established between the longitudinal and transverse dimensions of the design elements:

$$\partial X = \frac{0.25 V_r \partial Z^2}{D} \quad \text{and} \quad \partial Z = \frac{0.5 Q_{ww}}{H_a V_r} \quad (2)$$

where: Q_{ww} = the maximum wastewater discharge ($\text{m}^3\cdot\text{s}^{-1}$), H_a = the average depth in the considered section of the watercourse (m).

Determination of the coefficients of turbulent diffusion was conducted by using the Karaushev method:

$$D = \frac{g H_a V_r}{M C} \quad (3)$$

where: g = gravitational acceleration ($g = 9.8 \text{ m}\cdot\text{s}^{-2}$), M = dimensionless parameter equal to $M = 0.7C + 6$, C = the Shezy coefficient.

The Shezy coefficient is determined when there is data on the composition of bottom sediments or the roughness coefficient of the bed of a water body. In the presence of the data on the granulometric composition of bottom sediments, the Strickler–Manning formula is applied:

$$C = 33 \left(\frac{H_a}{d_e} \right)^{\frac{1}{6}} \quad (4)$$

where: d_e = the effective diameter of bottom sediments, determined by the granulometric curve.

If there is data on the roughness coefficient of the bed of a water body, the Pavlovsky formula is applied:

$$C = \frac{H_a^{1.6}}{n_r} \quad (5)$$

where: n_r = the roughness coefficient of the bed of the water body.

If there is data on the slope of the water surface, the Equation (6) is applied:

$$C = \frac{V_r}{\sqrt{H_a i}} \quad (6)$$

where: i = the slope of the water surface (%).

As a result of calculations performed from cross-section to cross-section, a concentration field was obtained in the area below the place of discharge of pollutants. The detailed method of Karaushev is a numerical method for solving the turbulent diffusion equation and makes it possible to obtain a field of concentration of a substance within the entire computational region from the place of wastewater discharge to the control section. There are no limitations to the applicability of this method.

RESULTS AND DISCUSSION

The initial water-methanol mixture is supplied to the unit from the tank farm. The plant includes the following structures and systems: rectification unit, pretreatment unit, steam condensate pumping station, control room, ventilation chambers, individual heating points, and household premises. The technological process is controlled from the control room located in the building of the auxiliary block.

The plant has three outlets used for the discharge of wastewater of the following categories.

1. Industrial stormwater, resulting from the use of water for the technological needs of the plant: washing of tanks and equipment; steaming containers and equipment; hydraulic testing of tanks and equipment; testing of fire extinguishing systems; wet cleaning of technological premises. Moreover, this runoff contains the industrial stormwater from sites and landfills where technological equipment is located.
2. Domestic and domestic untreated sewage resulting from the discharge from plumbing fixtures and showers; wet cleaning of household premises.
3. Methanol-containing wastewater generated as a result of the production activity of the low-pressure waste gas utilisation unit; prevention of hydrate formation; production activities of the wastewater utilisation unit with methanol recovery and wastewater treatment.

The approved standards of permissible discharge by discharge are presented in Table 1.

The plant has a sewerage system. All types of wastewater are collected in sewage pumping stations, and then they are transmitted to treatment facilities. The plant has three sewerage systems.

1. **Household wastewater.** Domestic wastewater is discharged to sewage pumping stations for domestic wastewater. Then it is transmitted to the pumping station, and from it to the treatment plant. From the pumping station of the household wastewater of the plant, the wastewater first enters the mechanical grate, which retains large pollution of organic and mineral origin. After passing through the mechanical grate, the wastewater enters the primary clarifier. It is required for pre-clarification of wastewater. Mechanical sedimentation of suspended solids takes place in it. From the primary sedimentation tank, wastewater enters the aeration tank for removal of organic matter, as well as nitrogen and phosphorus compounds. Further, the wastewater enters the secondary

Table 1. Data on wastewater discharges at the plant

Wastewater outlet number	Wastewater generation volume in 2020 (m ³)	Name of substance	Actual concentration in 2020 (mg·dm ⁻³)	Permissible concentration (mg·dm ³)	Actual wastewater discharge in 2020 (Mg)	Approved standard of permissible discharge (Mg·y ⁻¹)
1	453227	petroleum products	19.25	0.45	7.191	0.2436
		sodium alkyl sulphate	0.50	0.13	0.187	0.0706
		methanol	4.60	0.50	1.718	0.271
2	167271	petroleum products	0.37	0.45	0.101	0.162
		sodium alkyl sulphate	0.33	0.314	0.090	0.107
		methanol	0.22	0.50	0.060	0.179
		phosphates by P	0.303	1.51	0.082	0.532
3	4205	methanol	no data			

Source: own elaboration.

clarifier. It is necessary to clarify the sludge mixture with the subsequent return of sludge to the treatment systems and, if necessary, remove it from the system. After passing through the secondary sedimentation tank, the wastewater enters the clarified water tank. From there, it is fed to the adsorption filter for final post-treatment. The filter contains a load represented by a sorbent. In order to improve the retention of pollutants on the filter media, a coagulant is supplied to the filters. Its supply is carried out from the coagulant tanks using metering pumps. After passing through the adsorption filter, water enters the filtrate tank and it is supplied to wash the filters. The water from the filtrate tank is also used for technical needs. From the filtrate tank, water is supplied to the ultraviolet disinfection unit, after which the purified water is fed to the discharge.

- 2. Production wastewater.** Industrial wastewater is discharged to sewage pumping stations; then, it enters the pumping station of industrial effluents of the plant, and from it to treatment facilities. The treatment facilities include, in series, mechanical grids, an underground homogeniser-settling tank for water purification from suspended solids and oil products, as well as flow averaging, a block of adsorption filters of two-stage purification, and an ultraviolet disinfection unit. After treatment facilities, water is supplied for discharge.
- 3. Industrial wastewater,** contaminated with methanol. The industrial wastewater contaminated with methanol is discharged to sewage pumping stations for the methanol-containing effluents. Then, they are transmitted through the pressure sewerage network to the treatment plant. The treatment facilities for methanol-containing effluents are represented by a bottom

water recovery unit with methanol recovery and wastewater treatment.

The main purpose of the unit is the recovery of methanol from a water-methanol mixture by rectification. The methanol mixture is first separated from the condensate and then from the water by heating [Li 2003]. The boiling point of methanol (65°C) is lower than that of water. The end product of the plant is 98% methanol, which is shipped by rail for reuse by mining companies. According to the company, the permissible concentration of this alcohol in the discharged water is 2200 mg·dm⁻³. The actual concentration data are not provided. In this regard, an approximate calculation was performed. The production capacity of the plant is 3·10⁹ kg of gas condensate per year. The mass of methanol per 1000 m³ of gas condensate is 1 kg. The density of gas condensate is 700 kg·m⁻³. The consumption of methanol-containing wastewater at the plant is 4204 m³·y⁻¹. On the basis of these data, the mass of methanol generated at the plant over the year was found, i.e. 4285 kg·y⁻¹, and then the concentration of methanol in industrial wastewater contaminated with methanol was found, amounting to 1024.5 mg·dm⁻³. The efficiency of wastewater purification from methanol at the rectification plant is 98%; thus, the methanol content in the purified water was calculated, reaching 20.49 mg·dm⁻³.

The media have repeatedly reported that the maximum permissible concentration for methanol was exceeded downstream the Ob River. The Ob River communicates with the Glukhaya channel, into which methanol-containing wastewater is discharged. In connection with the above, the calculation of the rate of dilution of wastewater in the “NDS Ecolog” program was performed according to the detailed method of Karaushev. The location of the discharge of methanol-containing wastewater into

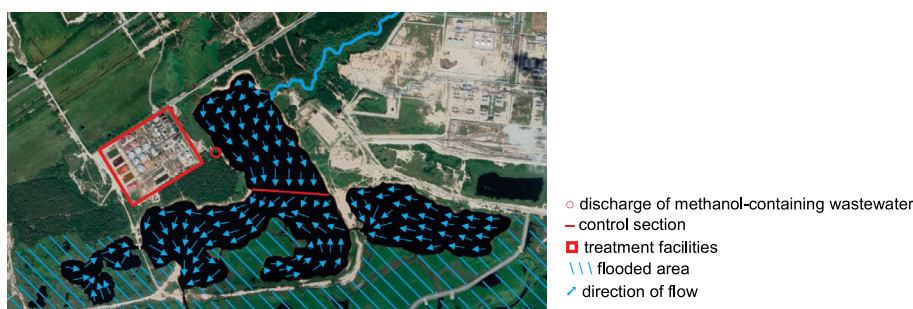


Fig. 1. Field of flow directions in the Glukhaya channel; source: own elaboration

the Glukhaya channel, the location of the control section and the direction of the flow are shown in Figure 1.

The following discharge parameters were used in the calculation: discharge type – scattering, number of discharge heads – 2, estimated wastewater flow rate – $0.00013 \text{ m}^3 \cdot \text{s}^{-1}$, wastewater flow rate – $0.8 \text{ m} \cdot \text{s}^{-1}$, average outlet diameter – 0.5 m, the distance from the point of release to the shore is 2 m, the distance from the outlet to the surface of the water body is 0.5 m, the distance from the point of release to the control section is 500 m. The parameters of the water body at the point of release were also used in the calculation: the object is a river, the average depth in the section under consideration is 5 m, the estimated flow rate is $1 \text{ m} \cdot \text{s}^{-1}$, the estimated water flow rate of the water body is $8.5 \text{ m}^3 \cdot \text{s}^{-1}$, the average width of the water body in the section under consideration is 450 m, the tortuosity coefficient of the river section is 1.2.

The calculation showed that when the concentration of methanol in wastewater is $20.49 \text{ mg} \cdot \text{dm}^{-3}$ in the control section, the concentration is $2.12 \text{ mg} \cdot \text{dm}^{-3}$. This water body belongs to the highest fishery category, for this category of water bodies the maximum permissible concentration for methanol is $0.1 \text{ mg} \cdot \text{dm}^{-3}$, which indicates the possibility of more than 20-fold excess of the standard concentration, in connection with the introduction of measures for the additional treatment of methanol-containing wastewater.

Typically, in gas processing plants, wastewater contains not only methanol, but also other pollutants (hydrocarbons, phenols, and others). A possible method for the disposal of such effluents is combustion in gas flares [CHEIN *et al.* 2021; GHOSH *et al.* 2019; TEIXEIRA *et al.* 2018; 2019; TIMOSHENKO, SHPAK 1989]. Wastewater is injected via nozzles into a combustion chamber filled with flue gases heated to temperatures above 1000°C . Water instantly evaporates, and impurities dissolved or suspended in it burn out. This method is convenient, but it also has many disadvantages. Therefore, with relatively high fuel consumption reaching $100\text{--}200 \text{ kg} \cdot \text{m}^{-3}$ of wastewater, the temperature in the combustion chamber is still insufficient for the complete decomposition of pollutants [MATANI, MALI 2019]. As a result, gases and dusty impurities are formed, requiring thorough additional cleaning in special devices, including electrostatic precipitators, scrubbers, adsorbers, multicyclones, etc. At the same time, the more powerful the plant, the higher the degree of environmental hazard from emissions into the atmosphere and the more obvious the need to use new, more advanced cleaning methods and more reliable measures to protect the environment. In addition, this method is very expensive.

Another method of wastewater management, widely practiced in the gas industry, is its underground disposal [DVOINIKOV *et al.* 2021b]. It is carried out by pumping wastewater into deep, reliably isolated aquifers that do not contain fresh, balneological, mineral and thermal waters. Underground disposal of wastewater in the area of the depression funnel in the water pumping system of the developed natural gas field can be carried out if it is impossible to purify wastewater from methanol and other components to the required maximum permissible concentration [MA *et al.* 2020]. Geological formations that can limit the area of influence of waste and meet a number of requirements for the conditions of occurrence and properties of rocks can be used for such a deep placement of wastewater. Compliance of the geological environment with the established requirements is

assessed by conducting special comprehensive geological exploration, the subject of which is the suitability for deep disposal of waste, depending on the type, composition and properties of waste, technology of preliminary preparation for liquidation.

The physicochemical method for purifying the water containing methanol using ultraviolet radiation from excilamps (gas-discharge lamps) in the presence of nitric acid (HNO_3). In this case, under the influence of ultraviolet radiation, the photolysis of water and nitric acid occurs with the formation of highly reactive radicals, i.e. OH, H, NO_2 and NO, which subsequently enter into reactions with methanol with the formation of the final products, namely CO_2 , H_2O and NH_3 . Under the experimental conditions, it was found that in the methanol-containing water with the addition of nitric acid (at a $\text{CH}_3\text{OH}:\text{HNO}_3$ ratio of 10: 1) under the action of ultraviolet radiation with a wavelength of $\lambda = 172 \text{ nm}$ (Xe2 is an excilamp), the methanol concentration in water in 16 min decreased from 35.0 to $2.6 \text{ mg} \cdot \text{dm}^{-3}$, i.e. 13.5-fold, and when using similar radiation with a wavelength $\lambda = 222 \text{ nm}$ (KrCl – excilamp) decreased from 338.0 to $14.6 \text{ mg} \cdot \text{dm}^{-3}$, that is, by a factor of 23 [MEDVEDEV *et al.* 2005].

There is a method for extracting methanol from industrial wastewater of gas condensate fields, which consists in the regeneration of this substance by rectification, followed by deep catalytic oxidation of its residual amounts in the bottom residue (non-evaporated liquid) [KUZHAJEVA *et al.* 2019a, b; SALIKHOV *et al.* 2020; YANG *et al.* 2019]. In this case, 100% oxidation of methanol in the bottom residue in a concentration of up to 1.5% is achieved using a copper-chromium-magnesium and chromium-magnesium catalyst on an alumina carrier (Al_2O_3). The duration of contact of methanol-containing water with the catalyst is not less than 0.9 s at a temperature not lower than 450°C .

The work aimed at developing a technology for separating methanol from the wastewater from gas condensate fields and returning the main part of methanol to the technological cycle, followed by bringing the residual concentration of methanol in discharged process waters to the maximum permissible concentration, which is very relevant [SCHABER, IVANOVA 2017; ZAPOROZHETS, SHOSTAK 2019; ZHOU *et al.* 2014]. Regeneration of methanol can be carried out by rectification, as the most reliable and efficient technology that allows extracting up to 99 wt. % methanol with a residual concentration of about 1 wt. % and above [BRENCHUGINA *et al.* 2007; NIASAR *et al.* 2019]. The wastewater containing methanol is neutralised with phosphoric acid, enriched with nitrogen sources, and subsequent treatment is carried out with the *Methylomonas methanica* Dj microorganisms. Using this method, the recommended pH should be 6.0–7.0, and the temperature of the wastewater should be between 20 and 37°C [MURZAKOV *et al.* 2005].

Comparative characteristics of the considered methods of wastewater treatment from methanol are presented in Table 2.

The rectification unit is used at the plant. Its efficiency is 98%, which is insufficient. On the basis of the results of the assessment of the methods (Tab. 2), it is proposed to carry out additional treatment of the methanol-containing wastewater leaving the production water disposal unit with methanol regeneration and wastewater treatment by using the biological treatment method.

Unlike chemical and physicochemical methods of purification, “reagents” (microorganisms) that carry out biological

Table 2. Comparative characteristics of methods of utilisation and treatment of methanol-containing wastewater

Method name	Advantage	Disadvantage
Burning	convenient for many types of wastewater, including methanol-containing ones	high cost, not environmentally friendly
Underground disposal	reducing the negative impact on surface water, eliminating the need for complete wastewater treatment	the impossibility of proper control over the spread of wastewater in formations, irreversible pollution of underground formations
The use of ultra-violet radiation	the ability to purify methanol-containing wastewater to maximum permissible concentrations	necessity of adding nitric acid, high cost
Rectification	the ability to recover methanol for reuse, high purification efficiency (up to 98%)	high cost, the need for additional treatment to maximum permissible concentrations
Biological treatment	the ability to purify methanol-containing wastewater to maximum permissible concentrations, low cost compared to other methods	the need to maintain the pH value within 6–7, the need to maintain the wastewater temperature in the range from 20 to 37°C

Source: own study.

purification are not added to water, but spontaneously develop in treatment facilities, forming microbial cenoses consisting of hundreds of different types of microorganisms [GUPTA, GOEL 2019]. Therefore, for the stable and effective functioning of biological treatment systems, it is important to maintain a certain technological regime, in which the necessary microbial cenosis is formed, capable of purifying water, and cell aggregates are formed that are easily separated from the purified water.

The *Methylomonas methanica* Dg strain is obtained selectively from the actual methanol-containing wastewater. In order to implement the method, selection of methanol-assimilating culture is carried out [CHEN *et al.* 2017]. For this purpose, the soil contaminated with methanol is placed in a vertical glass

funnel and industrial methanol-containing wastewater, initially diluted with a nutrient medium to a methanol concentration in the effluent of 1 g·dm⁻³, is passed through it. Further, the concentration of methanol is increased to the values approximately equal to 10 g·dm⁻³, and the dilution with the nutrient medium is gradually reduced. At the stage of supplying wastewater containing 10 g·dm⁻³ of methanol and its absence in the effluent leaving the column, a pure culture of bacteria is isolated by seeding the contents of the column onto an agar mineral nutrient medium of the given composition and containing 2.0 g·dm⁻³ of methanol [GVOZDYAK *et al.* 1986]. As a result, the desired strain of *Methylomonas methanica* Dg is obtained, capable of purifying the methanol-containing wastewater to maximum permissible concentrations [MURZAKOV *et al.* 2006].

For the possibility of reproduction of these microorganisms, the following conditions must be met: pH value of 6–7, wastewater temperature from 20 to 37°C [KALYUZHNYAYA *et al.* 2015].

The average consumption of wastewater leaving the bottom water recovery plant with methanol regeneration is 0.48 m³·h⁻¹, the methanol content is 20.49 mg·dm⁻³, the wastewater temperature is 24°C, the pH value is 7. While analysing the data above, it can be concluded that the conditions necessary for the reproduction of microorganisms of the species *Methylomonas methanica* Dg are met. In order to carry out biological treatment, the following technological units are required: wastewater homogeniser; aeration tank; sump; and clarifying sorption filter [ALI SHAH *et al.* 2014; ZHANG *et al.* 2010]. An enlarged technological scheme of these treatment facilities is shown in Figure 2.

After the installation of bottom water utilisation with methanol recovery, the wastewater is pumped into the equaliser by means of a pump. Then, with the help of submersible pumps, the averaged flow enters the aeration tank. The wastewater from the aeration tank enters the settling tank. The sludge of the settler, represented by the excess sludge, is pumped out to the sludge treatment unit of the domestic wastewater treatment plant [CLAUSEN *et al.* 2010]. The required amount of return sludge is fed back to the aeration tank by means of a pump.

Further, for additional treatment from suspended solids, represented by activated sludge, wastewater is pumped to clarification-sorption filters. From them, the purified water is supplied to the filtrate tank. Then, with the help of a pump, the required amount of water is supplied to flush the filter. After the filter, the purified water is fed by gravity to discharge. From the

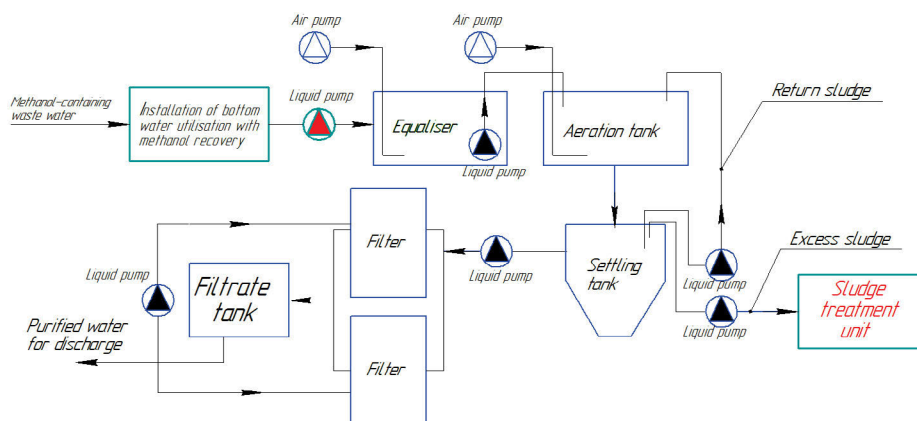
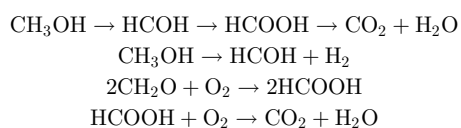


Fig. 2. Technological scheme of biological wastewater treatment from methanol; source: own elaboration

wastewater utilisation unit with methanol regeneration, wastewater flows by gravity into the equaliser. The homogeniser is a tank with an aeration system for mixing and a pump for pumping wastewater into the aeration tank, which allows reducing the volume of the remaining tanks up to 20%, preventing the removal of activated sludge from the aeration tanks, and ensuring a uniformly high cleaning efficiency.

From the homogeniser, the water is pumped into the aeration tank for biological treatment of wastewater from methanol. The aeration tank is a rectangular tank with an aeration system. The methylotrophic *Methylomonas methanica* Dg bacteria are used in the aerotank for the biochemical conversion of methanol. Wastewater is purified from methanol by microbiological transformation (oxidation) of this substance through formaldehyde and formic acid to carbon dioxide and water:



After passing the aeration tank, the wastewater flows by gravity into the sump. Mechanical sedimentation takes place in it, as a result of which the activated sludge is separated from the wastewater [GAI, LIU 2017].

In this case, it is a vertical sump with a thin layer module. It contains a pump for pumping return sludge, as well as a pump for pumping out sludge, represented by excess sludge. The sludge is transferred for processing to the sludge treatment unit of the domestic wastewater treatment plant. After passing through the sump, the wastewater enters the clarified water tank, and from it, with the help of a pump, it is supplied to the clarification-sorption filter. This is necessary for the final post-treatment from suspended solids represented by activated sludge. The filter contains a load represented by a sorbent. After passing through the filter, water enters the filtrate tank; then, water is supplied from it to wash the filter. From the filtrate tank, wastewater flows by gravity to the discharge. At the plant under consideration, the consumption of methanol-containing wastewater is $0.48 \text{ m}^3 \cdot \text{h}^{-1}$. The daily flow rate is 11.52 m^3 per day. The volume of the flow average (m^3) is calculated by the following formula:

$$V = Q_{ah} \cdot \tau_{reg} \quad (7)$$

where: Q_{ah} = average hourly consumption of wastewater ($\text{m}^3 \cdot \text{h}^{-1}$); the value of τ_{reg} is determined according to [SP 32.13330.2018]; $V_y = 1.59 \text{ m}^3$ (0.48·3.3).

The volume of the average equal to 2 m^3 was chosen. In order to mix water, an aeration system was installed in the homogeniser. It includes a perforated aeration pipe and a blower. A Zenova 2RB 210-M004 single-stage vortex blower was used to supply air to the aeration system with the following characteristics: maximum air flow $80 \text{ m}^3 \cdot \text{h}^{-1}$, maximum air pressure 12 kPa, operating point $20 \text{ m}^3 \cdot \text{h}^{-1}$ at 12 kPa, power 0.37 kW at 2900 rpm.

A Pedrollo NGAm 1B centrifugal pump was selected to supply waste water to the aeration tank, it is characterised by the following parameters: maximum water flow $18 \text{ m}^3 \cdot \text{h}^{-1}$, maximum water pressure 17 m of water column, operating point $12 \text{ m}^3 \cdot \text{h}^{-1}$ at 13 m of water column, power 0.55 kW at 2900 rpm. From the

homogeniser, water enters the aeration tank. The volume of the aeration tank is determined by the Equation (8):

$$V_a = \frac{\tau_x \cdot 0.35 BOD_5 \cdot Q_d}{1000 X_a} \quad (8)$$

where: τ_x = the total age of activated sludge, $\tau_x = 12$ (days), Q_d = daily wastewater consumption ($\text{m}^3 \cdot \text{d}^{-1}$), X_a = the dose of activated sludge taking into account biofilm on dry matter, $X_a = 4 \text{ g} \cdot \text{dm}^{-3}$; BOD_{5A} = the value of BOD_5 removed in the aerotank ($BOD_{5A} = 450 \text{ mg O}_2 \cdot \text{dm}^{-3}$); $V_a = 5.45 \text{ m}^3$ ($12 \cdot 0.35 \cdot 450 \cdot 11.52 / 4 \cdot 1000$).

The volume of the aeration tank was taken as equal to 6 m^3 . In order to saturate the water with oxygen, an aeration system is installed in the aeration tank. For this purpose, a fine-bubble aeration system manufactured by one of the Russian companies was selected.

An air blower is required to supply air to the aeration system of the aeration tank. The air consumption required for aeration is $20 \text{ m}^3 \cdot \text{h}^{-1}$. A Zenova 2RB 410-013 single-stage vortex blower was selected with the following characteristics: maximum air flow $80 \text{ m}^3 \cdot \text{h}^{-1}$, maximum air pressure 12 kPa, operating point $20 \text{ m}^3 \cdot \text{h}^{-1}$ at 120 kPa, power 0.37 kW at 2900 rpm.

In order to increase the efficiency of biological treatment, a flat loading was placed in the aerotank. Flat loading is designed to intensify the processes of biological wastewater treatment in aeration tanks. It is produced in the form of flat and corrugated sheets of resistant polymeric materials with a mesh structure for

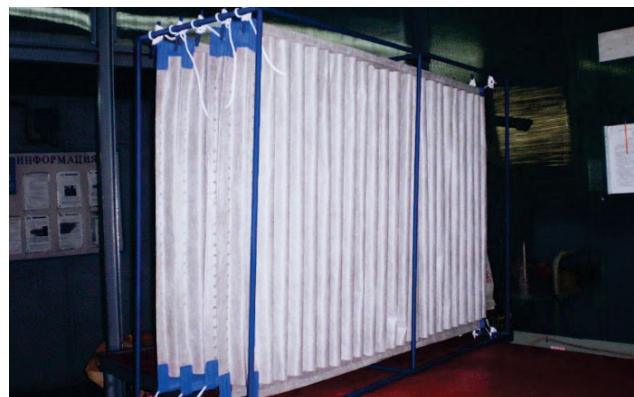


Photo 1. Flat loading produced by one of the Russian companies (phot: A. Ivanov)

effective attachment of microorganisms and the formation of stable biofilms. For this purpose, a flat loading made by one of the Russian companies was selected (Photo 1).

After passing the aeration tank, the wastewater flows by gravity into the sump. In it, the activated sludge is deposited along with the wastewater from the aeration tank. On the basis of the average hourly flow rate of wastewater equal to 0.48 m^3 , a PVO-ON-2.5 thin-layer sedimentation tank by one of the Russian companies was selected. It has a productivity of $2.5 \text{ m}^3 \cdot \text{h}^{-1}$, which works as follows: wastewater, passed through the aeration tank, flows into the settler flow distributor by gravity; then, the water is directed to thin-layer modules operating on the principle of counter-current water and sediment, suspended solids settle on an inclined surface, and then descend into the conical part of the

settler. An overflow partition is located in the upper part, through which water falls into the clarified water tank by gravity.

Further, with the help of a submersible pump, the sludge is transferred to the unit for processing the sludge of domestic wastewater. For this purpose, a centrifugal pump is installed. Part of the sludge is fed back to the aeration tank via a return sludge pump. After passing through the settling tank, wastewater enters the clarified water tank, and from it, with the help of a pump, goes to the clarification-sorption filter for cleaning.

On the basis of the average hourly flow rate of wastewater equal to $0.48 \text{ m}^3 \cdot \text{h}^{-1}$, a clarification-sorption filter was chosen with the following characteristics: loading volume 110 dm^3 , productivity $1.1\text{--}2.6 \text{ m}^3 \cdot \text{h}^{-1}$, pressure $20\text{--}40 \text{ kPa}$, filtration area 0.129 m^2 , backwash $4.5 \text{ m}^3 \cdot \text{h}^{-1}$. Two filters were installed. This is necessary so that while flushing one of them, the second continues to work, as well as in case of a malfunction of one of the filters. A centrifugal pump was used to supply wastewater to the filters.

After passing through the filter, water enters the filtrate tank and water is supplied from it to wash the filter. The water from the BF is also used for technical needs. The volume of the filtrate tank is determined by the Equation (9):

$$V_{\text{FT}} = \frac{Q_{\text{FT}} \cdot 20}{60} \quad (9)$$

where: Q_{FT} = the flow rate of water required to flush the filter ($\text{m}^3 \cdot \text{h}^{-1}$); $V_{\text{FT}} = 1.07 \text{ m}^3$ ($3.23 \cdot 20 / 60$).

One filter rinsing usually takes 10 min. A minimum of two flushes is required, so the flush time is 20 min. The water consumption for washing the filter is determined by the Equation (10):

$$Q_{\text{FT}} = S \cdot v_w \quad (10)$$

where: v_w = the washing speed ($v_w = 25 \text{ m} \cdot \text{h}^{-1}$), S = filtration area (m^2); $Q_{\text{FT}} = 3.23 \text{ m}^3 \cdot \text{h}^{-1}$ ($0.129 \cdot 25$).

Thus, the required volume of the filtrate tank is 1.1 m^3 .

In order to supply water for washing filters, a centrifugal pump was used. Sorbent was selected as the filter loading. After passing through the filter, the purified water from the filtrate tank flows to the discharge by gravity. Container-type block-modular

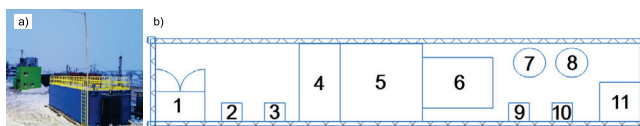


Fig. 4. Block-modular container-type treatment facilities: a) general view, b) arrangement of equipment in a container: 1 = control cabinet, 2, 3 = air pumps, 4 = equaliser, 5 = aeration tank, 6 = settler, 7, 8 = filters, 9, 10 = liquid pumps, 11 = filtrate tank; source: own elaboration

treatment facilities (standard sea container pallet wide $12192 \times 2438 \times 2591 \text{ mm}$) were selected (Fig. 4a) to reduce capital costs and save territorial resources, with the equipment layout shown in Figure 4b.

The cleaning efficiency according to the proposed scheme is 96%. After the implementation of this biological treatment of methanol-containing wastewater, the concentration of methanol in the treated water will decrease to $0.82 \text{ mg} \cdot \text{dm}^{-3}$, while the

concentration of methanol in the water of the Glukhaya channel in the control station will decrease to $0.0954 \text{ mg} \cdot \text{dm}^{-3}$, which is lower than the maximum permissible concentration for water bodies of fishery appointment ($0.1 \text{ mg} \cdot \text{dm}^{-3}$).

CONCLUSIONS

A method for biological treatment of methanol-containing wastewater was proposed. The purification efficiency of the proposed method was 96%. Thus, the concentration of methanol in the discharged water is equal to $0.82 \text{ mg} \cdot \text{dm}^{-3}$. In turn, after the discharge and dilution of wastewater, the concentration of methanol in the control section of the Glukhaya channel is $0.0954 \text{ mg} \cdot \text{dm}^{-3}$, which does not exceed the established standard concentration for this water body. It was concluded that the proposed method of biological wastewater treatment from methanol can be implemented at the plant in question. What is typical, the permissible concentration of methanol in wastewater declared by the company is $2200 \text{ mg} \cdot \text{dm}^{-3}$, nevertheless, the calculated concentration of methanol in wastewater that has undergone rectification, i.e. $20.49 \text{ mg} \cdot \text{dm}^{-3}$ leads to the concentration of $2.12 \text{ mg} \cdot \text{dm}^{-3}$ in the control section (maximum permissible concentration is $0.1 \text{ mg} \cdot \text{dm}^{-3}$), which may indicate incorrect accounting of data on the parameters of the water body for dilution.

During the period of the flood of the Glukhaya channel, it ceases to be a separate water body and, in fact, becomes part of the flood channel of the Ob River. If the Ob River is considered as a water body for dilution, then the permissible concentration of methanol in wastewater can be as high as those declared by the company. However, as is known, all calculation methods consider negative dilution conditions, and in the absence of a flood, the Glukhaya channel is considered as an independent water body; moreover, isolated by the natural relief from the main channel of the Ob River. In addition, certain parts of the flooded areas, due to elevation changes, communicate with the channel only during a short period of time when the water level rises, i.e. 3–5 weeks during the flood period, and in fact remain isolated reservoirs for the rest of the time, potentially acting as zones of accumulation and concentration of pollutants. This is aggravated by the fact that a network of technological roads on embankments has been built in the flooded areas.

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