WATER TREATMENT AND WATER CHEMISTRY

Biological Pollution of Technological Equipment and the Chemically Desalting Water Treatment Plant at a TPP (Review)

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Abstract—At thermal power plants, installations in contact with the water coolant are subject to biological contamination. This is due to a number of factors: the maintenance of favorable temperature regimes, the formation of stagnant zones, the constant supply of nutrients, the presence of large areas of equipment surfaces (pipelines, water storage tanks, the pipe surface of the condenser), the presence of various materials (ionexchange resins, membranes), and changing climatic conditions. The fight against the formation of such pollution of thermal power equipment is very relevant today, although almost all TPPs carry out thorough preparation of additional and feed water. It should be noted that the control of the concentration of organic impurities in the liquid and vapor phases, as well as continuous monitoring, are rather laborious processes. Organic deposits and the presence of biofilms on the process equipment of circulating cooling systems (CCS), water treatment plants (WTP), and chemically treated water storage tanks lead to various production failures, emergencies, and a general decrease in the efficiency of heat and electricity generation. In this paper, foreign and domestic studies on the features of the formation and development of biofilms were reviewed. Current methods for detecting and assessing biological pollution are considered and traditional chemical, physical, electrochemical, acoustic, electromagnetic, and other methods of combating microorganisms and bacteria are described. It has been shown that the growth of bacteria significantly complicates the equipment-cleaning procedures and accelerates the process of scale formation. To effectively solve the problems of biological deposits, the development of methods for monitoring and controlling the formation of bacterial deposits, the preparation of additional water, and the maintenance of a water-chemical regime must be carried out differentially based on the identification of colonies of microorganisms using test systems. The previous works of the team of authors concerning the issues of pollution of the coolant of circulating cooling systems and water treatment plants at TPPs of the Republic of Tatarstan in the period from 2009 to 2022 are noted.

Keywords: thermal power plants, water treatment plants, biological pollution, biofilm, steam turbine condenser, ion-exchange resins, membrane technologies, UV irradiation, ozonation **DOI:** 10.1134/S0040601523090021

In the water coolant used for various technological needs at thermal power plants, there are a large number of bacteria and microorganisms that settle on different surfaces and release polymeric substances that form a biofilm. Such surfaces are usually called substrates and consist mainly of bacteria, suspended solids, corrosion products, algae, protozoa, and mollusks. The factors influencing the development of biological pollution are shown in Fig. 1.

The biofilm formed by the biocenosis is very resistant to external influences, including biocidal treatment [1]. The effectiveness of the biocide depends on the age of the biofilm as well as on its specific physical and chemical structure.

The composition of the biofilm includes directly bacterial or microbial cells and the extracellular polymeric substances secreted by them, consisting of proteins, polysaccharides, and deoxyribonucleic acid [2]. Under natural conditions, several types of microorganisms and bacteria coexist in a biofilm, which provides the system with physiological and functional stability and increases the survival of microorganisms.

The process of formation and development of a biofilm is carried out in several stages. At the first stage, microbial cells attach to various surfaces: adhesion. This stage is reversible since the fixed cells can, under the influence of certain factors, return to a free (planktonic) form of existence.

The second stage, called fixation, is characterized by the final attachment of bacteria and microorganisms to the surface. At this stage, irreversible attachment of microorganisms and bacteria to the surface and the release of extracellular polymeric substances are carried out. Attachment occurs due to short-range bonds, such as dipole-dipole, hydrogen, ionic, covalent, and hydrophobic interactions [3].



Fig. 1. Factors affecting the development of biofilms.

At the third stage, microcolonies are created, which then unite, due to the presence of polymeric substances, and, thus, a biofilm is formed, which has a spatial three-dimensional structure.

The authors of [4–6] analyzed the adhesive properties of microbial cells and proposed a physicochemical approach to the study of biofilms based on the concept of short-range interaction. The bacteria are in direct contact with the substrate, and the Gibbs free energy is estimated from the interfacial tension. When the bacterium reaches the surface of the equipment, forces of mutual attraction and repulsion between the two cells begin to act. Initial adhesion also occurs due to the presence of electrostatic forces and hydrophobic and van der Waals interactions [7].

In the 1980s, biofilms were studied in natural and industrial systems [2] and it was found for the first time that the bacteria and microorganisms included in the biofilm are able to show resistance to bactericidal and antimicrobial reagents. At the same time, bacteria and microorganisms often use biofilm as a protection against changing environmental conditions.

The authors of [8, 9] studied the process of formation of biological contaminants and laid the theoretical foundation for their subsequent study. In [10], the ability of iron- and mucus-forming bacteria to create biofilms was noted. Using dynamic modeling, the authors of [11] found that, due to biological contamination of heat-exchange surfaces, their thermal resistance increases to $1.35 \times 10^{-4} \text{ (m}^2 \text{ K)/W}$.

In [12], a model for predicting biological pollution based on the algorithm of the nonlinear space of physical states is proposed. The advantage of this model is that it uses a method for detecting biological contamination of heat-exchange equipment in transient operating modes.

In 1990, the author of [13] presented a method for online detection of biological contaminants in a shelland-tube heat exchanger based on intelligent monitoring technology. In 2014, in [14], an equation was derived for predicting the characteristics of biological pollution using the partial least squares method. The wall thermal resistance was taken as an output variable, and the wall temperatures at the heat-exchanger inlet and outlet were taken as input variables. Using the MatLab and LabView software packages, the authors of [15] developed a real-time system for accurate and efficient prediction of biological contamination of a heat exchanger.

Bacterial activity can lead to corrosion reactions on the surfaces of power equipment or enhance them [16, 17]. Corrosion processes caused by the activity of bacteria are usually called bioinduced corrosion or biocorrosion (microbiologically influenced corrosion: MIC) [18]. Biocorrosion accounts for approximately 10% of all types of metal corrosion [19]. According to studies [20], microorganisms and bacteria that are part of biofilms affect corrosion in the following way:

1. absorption of oxygen, which leads to the creation of anode zones and entails the formation of localized corrosion cells;

2. causing of degradation of protective coatings applied to metal surfaces;

3. absorption of hydrogen as a result of the cathodic reaction, which depolarizes the cathode and increases the rate of metal loss at the anode;

4. contribution to the degradation of chemical reagents dosed into the coolant for the protection of metals in industrial water supply systems, corrosion inhibitors or descalers;

5. by-products of bacterial metabolism can lead to the precipitation of metal ions such as iron to form FeS, which promotes corrosion processes.

According to studies [21], biocorrosion can be considered as a result of the following processes:

1. attachment of bacteria and microorganisms to the metal surface;

2. bacterial and electrochemical transformation in a biofilm and on a metal surface.

These processes affect the corrosive activity of the microenvironment at the biofilm-metal interface.

BIOLOGICAL POLLUTION OF TECHNICAL WATER SUPPLY SYSTEMS AND WATER STORAGE RESERVOIRS

In the circulating cooling systems of thermal power plants, due to the maintenance of a favorable temperature range ($10-40^{\circ}$ C), a large amount of nutrients and a high saturation of circulating water with dissolved oxygen, microorganisms, and bacteria intensively develop. Biological deposits contaminating an CCS are a collection of various bacteria and microorganisms that enter the system both with make-up water and from the air. Bacteria are able to use scale and scale inhibitors as nutrients.

Biological contamination of heat-exchange surfaces leads to a decrease in the efficiency of the heattransfer process and an increase in operating costs for maintenance and cleaning of power equipment. The analysis of sediments in the CCS shows that from 4 to 30% is due to biological pollution [22]. The appearance and development of biofilms formed by colonies of anaerobic bacteria (iron-oxidizing, sulfate-reducing, nitrifying, etc.) contribute to bioinduced corrosion. Complex biocidal treatment is used to suppress biological pollution [23, 24].

In 2015, the employees of KSPEU conducted a study of the CCS with an evaporative cooling tower for biological contamination of the Naberezhnye Cheln-inskaya CHPP plants [25]. Extensive contamination

of condensing equipment and the evaporative cooling tower was detected. Anaerobic bacteria dominated in the samples taken. This was facilitated by an elevated ambient temperature, saturation of water with oxygen in the cooling tower, and unstable maintenance of the water chemistry regime.

In [26], a study was made of the biological contamination of recycled water used to cool the equipment of a 450 MW CCGT. According to the results of the research, it was revealed that the total microbial count (TMC) in the water samples of the CHPP's CCS was at the level of 10^4-10^5 CFU/mL, which slightly exceeds the normalized value of 10^4 CFU/mL for open cooling systems. The presence of yeast and fungi was also detected at level 10^3 CFU/mL, which is unacceptable.

In [27], the object of study of biological pollution was a CCS with an evaporative cooling tower, which was operated for approximately 2.5 years. Water samples were taken from the cooling tower catchment area and biofilms. Based on the analysis of bacteria and microorganisms found in these samples, a library of 16S rRNA gene clones was created. Most of the free-living bacteria (99.0%) were bacteria of the species *Betaproteobacteria*. The predominant bacteria were as follows, %:

Alphaproteobacteria	47.9
Betaproteobacteria	11.7
Acidobacteria	13.1
Gemmatimonadetes	11.3

Water-storage tanks (tanks of clarified water, partially desalinated and chemically purified water) are also subject to biological contamination. The authors of [28] studied a tank of demineralized water at one of the thermal power plants in Hungary. Water samples taken at the tank inlet and outlet were analyzed for the presence of biological contaminants in demineralized water. The number of aerobic heterotrophic bacteria was 1.05×10^1 and 3.90×10^2 CFU/mL in samples taken at the tank inlet and outlet, respectively.

In [29], the reaction of iron bacteria (IB) and sulfate-reducing bacteria (SRB) was analyzed in a laboratory setup simulating the operation of a TPP network heater. The influence of temperatures, coolant flow rate, and the concentration of artificially introduced bacteria on the development of biological pollution of the network heater was determined. As a result of the experiment, it was found that, with an increase in temperature to 40°C, the total amount of biological contaminants increased, while the growth rate of iron bacteria decreased with an increase in the coolant flow rate and two types of bacteria showed synergistic interaction.

The traditional approach to estimating condenser tube fouling is to calculate heat transfer from condenser backpressure, cooling water flow, and temperature. With an increase in backpressure in the condenser by only 0.67 kPa, caused by biological contamination of the tubes, the efficiency of heat and power generation decreases by 0.5%, which corresponds to 3 MW of generated power [30].

Estimating the development of biological contamination in the condenser tubes from plant parameters is a difficult task, mainly due to the large number of variables that affect heat transfer. In 2002, electrochemical sensors for biofilm formation were tested at an operating thermal power plant in Italy [31]. Several TPPs have implemented a special system called BIOX to control biofilm formation in condensing units [32].

BIOLOGICAL CONTAMINATION IN WATER TREATMENT PLANTS

In [33], studies of biological contamination of a water treatment plant at a thermal power plant were carried out, the scheme of which includes preliminary cleaning and chemical desalination using mixed bed filters (MBF) as the third stage. No biological contaminants were found on the filters of the first and second stages, while the filter material loaded into the MBF was subject to the greatest biological contamination. In water samples after MBF, the number of bacteria was comparable to that in initial water samples and varied in the range $(2 - 8) \times 10^4$ CFU/mL. In [33], various biocides were also tested: Bronopol (Merck KGaA, Germany), ProClin (Merck KGaA, Germany), Kathon WT (Dow Chemical Company, United States). The effectiveness of the applied biocide with a concentration of 25 ppm appeared already after 8 h. Scanning electron microscopy studies of ionexchange resins showed that the ion-exchange resin grains were covered with visible organic and inorganic deposits. The authors also noted the cracking of the grains of anion and cation exchangers, the latter being even partially destroyed and microorganisms present on their surface. On ion-exchange resins from MBF, a complex biofilm was found, consisting of almost all types of microorganisms/bacteria (spherical, rod-like, and filamentous), and biofouling was also present in the intergranular space.

In [34], a comprehensive study of feed water was carried out in order to establish the presence of organic impurities and their structure using infrared and ultraviolet spectroscopy, potentiometry, and elemental analysis and to determine the physicochemical properties of organic impurities with the prediction of their behavior in the waste heat boiler. As a result of the analysis of the passage of humic substances through the purification stages of the WTP, the content of organic substances in the steam condensate of the waste heat boiler was measured by the concentration of total organic carbon (TOC), which amounted to $100-150 \text{ }\mu\text{g/dm}^3$.

In 2020, the authors of [35] studied the bacterial contamination of the block diagram of chemical desalination at Kazan CHPP-1. A step-by-step analysis of water samples at the WTP was carried out using BART-test biodetectors containing various nutrient media: slime-forming bacteria (SLYM-BART), sulfate-reducing bacteria (SRB-BART), and heterotrophic aerobic bacteria (HAB-BART). The TMC was determined for all elements of the WTP. A high degree of microbiological contamination was found in water samples after MBF; the number of bacteria was $(6.89 - 6.35) \times 10^6$ CFU/mL.

The paper [36] presents the results of studying the biological contamination of WTP, which also includes MBF. In contrast to the results of the experiments of previous authors, bacterial reproduction was not recorded on the surface of the grains of ion exchangers of the studied resin samples.

The authors of [37] studied the biological contamination of the coolant in WTP systems by cultivation methods. It was noted that, when measuring the number of bacteria by epifluorescence microscopy, the CFU values are one to two orders of magnitude higher than when counting plates, regardless of the culture medium used.

In [38], a significant amount of biological contaminants was found on the surface of the grains of anion exchangers of the ion-exchange resin of WTP filters at power plants in the city of Shoubra El-Khiema (Egypt). Most of the observed bacteria belonged to the genus *Bacillus*, which are relatively resistant to biocidal treatment. As a result of studies of samples of ion-exchange resin, a decrease in the exchange capacity of ion exchangers to 5% was revealed. Unfortunately, the authors did not specify what kind of exchange capacity of the ion exchanger they are talking about.

Starting from the second half of the 20th century, membrane technologies have been actively used for water treatment at thermal power plants in Russia. During operation, membrane installations are exposed to biological contamination, which accounts for more than 45% of all types of membrane contamination [39, 40].

In their studies, the authors of [41] identified bacteria found in biofilms of reverse osmosis membranes and concluded that these bacteria belong to such species as *Mycobacterium*, *Flavobacterium*, *Pseudomonas*, *Corynebacterium*, *Bacillus*, *Arthrobacter*, *Acinetobacter*, *Cytophaga*, *Moraxella*, *Micrococcus*, *Serratia*, *Lactobacillus*, and *Aeromonas*.

The authors of [42] identified four mechanisms of biological contamination of ultrafiltration membranes: complete, partial, and internal blockage of pores and crust formation.

METHODS FOR COMBAT BIOLOGICAL POLLUTIONS

The following methods can be used to combat biological pollution: mechanical, physical, chemical, electrochemical, acoustic, and electromagnetic.

To remove biological deposits mechanically and prevent the formation of mineral deposits in the condenser tubes, some TPPs have a ball cleaning system (BCS). At present, high-performance domestic-made BCS equipment is successfully operated by more than 40 thermal power plants, including Astrakhan CHPP-2, Berezovskaya, Zainskaya, Kashirskaya, Konakovskaya, Perm, Ryazanskaya, Troitskaya and Cherepovetskaya GRES, Volzhskaya CHPP-2, Naberezhno-Chelninskava CHPP, Novosibirsk CHPP-5, Orlovskaya CHPP, Minsk CHPP-3, and Perm CHPP-9, as well as at most CHPPs of OAO Mosenergo and other power plants. In addition, TPPs use the cleaning of heat-exchange surfaces with a hydrodynamic jet. In this cleaning method, a high-pressure jet of liquid is directed onto the contaminated surface, while the suspension may contain abrasives to increase the efficiency of the process. The cavitation method, in which a vapor-gas emulsion and microwave radiation are directed to the surface to be cleaned under pressure, under the influence of which it is possible to destroy and remove sediments of biological origin, is also used to combat biological pollution.

One of the traditional methods of combating biological pollution is the chlorination of treated water, which can be done by dissolving chlorine gas or using a solution of sodium hypochlorite NaClO. The effectiveness of the use of chlorine to combat biological contamination depends on the pH value, but the disinfecting effect of chlorine deteriorates as the pH rises within its acceptable range of 6.5-9.5. With a decrease in the concentration of H⁺ ions (increase in pH), the equilibrium shifts towards the OCl⁻ ion, which, as a biocide, is significantly less effective than hypochlorous acid HOCl.

During the treatment of water with chlorine, organochlorine by-products are formed: trihalomethanes (THM) or haloform compounds (for example, chloroform, bromoform, dichlorobromomethane, dibromochloromethane, etc.), which can be toxic even at low concentrations in wastewater.

Chlorine dioxide ClO_2 can serve as an alternative to chlorination due to its high efficiency when used as a bactericidal agent to combat biological contamination of condenser tubes in thermal power plants. In addition, chlorine dioxide forms a small amount of organohalogen by-products.

Hydrogen peroxide H_2O_2 is a disinfectant. It is effective against a wide range of bacteria, including those that are resistant to chlorine. Hydrogen peroxide treatment is widely used in combination with other disinfection methods, such as ultraviolet (UV) irradiation and ozonation. In aqueous solutions, H_2O_2 is often present together with dissolved ozone [43]. This effect underlies the processes called advanced oxidation [44]. Hydrogen peroxide by itself is not a bactericide. It must be converted into radicals [e.g., hydroxyl radical (-OH)], which react with cellular components: nucleic acids, proteins, and lipids. Antimicrobial properties of H_2O_2 manifest themselves in the formation of hydroxyl radicals on the surface of the membrane as well as the oxidation of sulfhydryl groups of proteins and the creation of double bonds.

Ozonation leads to the oxidation of inorganic and organic materials. The main feature of ozone is that it is a stronger oxidizing agent than chlorine and can decompose high molecular weight organic substances, such as humic acids (to form low molecular weight compounds), aldehydes, and carboxylic acids. Thus, ozone is considered to be a highly effective biocide. Ozonation reduces the amount of total organic carbon in water, but there are three main limitations to its use. First, ozone is unstable in water; at pH = 8, its half-life is less than 1 h. Second, it reacts with natural organics to form low molecular weight oxidized by-products. Thirdly, it cannot be stored in enterprises.

Effective biocontamination control by dosing NaClO in combination with NaBr into freshwater systems can lead to a reduction in the required dose of NaClO since free bromine, unlike HOCl, does not completely dissociate at pH > 7. Bromamines, reaction products with ammonia naturally present in water, are more toxic than chloramines.

TPPs use anionic, cationic, and amphoteric surfactants. Anionic surfactants are only effective at pH < 3 and include aliphatic acids, such as sodium dodecyl sulfate. Cationic surfactants are quaternary ammonium compounds that have been studied to a sufficient extent and are widely used as a bactericidal agent in WTP systems. The best known of these is benzalkonium chloride, which is a group of compounds with various aliphatic chain lengths (C_8-C_{18}).

The following types of surfactants are used to combat biological pollution: MOLaktiv E30, Kenolux E-D, sodium alkylbenzene sulfonate (LAS), Sulfopon 1216 G, SULFOROKAnol N232P, Hostapur SAS 60 (secondary alkane sulfonate), Capstone FS-61, Chemal EO 20, ROKAnol NL3, etc.

Biodispersants are synthetic surfactants and promote the penetration of biocides into organic deposits, thereby contributing to the destruction of anaerobic bacteria. They limit the formation of biofilms on clean surfaces, reduce biocorrosive activity, and do not reduce the effectiveness of other biocides. The action of bio-surfactants is that they break up biological contaminants into smaller particles and keep them in suspension in the cooling water. This process prevents the formation of biological contaminants and allows them to be removed from the system by flushing.

The company Agua-mol GmbH (Germany) proposed to use a method called MOLClean to combat biological contamination of equipment [45]. The main feature of this method is the ability to eliminate the cause of biological contamination and remove that already existing. The basic principle of operation of this technology is that metal catalysts are introduced into the cooling water and the chemical reagent MOLaktiv E30 is dosed, which is a 30% solution of H_2O_2 . When interacting with the catalyst metal, H_2O_2 molecules, as a result of the transfer of electrons, are activated, and the surface itself acquires a positive charge. Due to the electrostatic forces of attraction. bacteria and microorganisms rush to the surface of the catalyst. The bacterial cells are then destroyed by the action of hydrogen peroxide molecules. As a result of these reactions, surfactants of biological origin (biosurfactants) are formed in water, which are called biotensides by the developers of the method.

Toxic coatings for pipelines and heat-transfer surfaces may contain such substances as tributyltin oxide, which are gradually released from the coating during leaching (hydrolysis, surface erosion). Among various toxic coatings, those containing tributyltin oxide $(Bu_3Sn)_2O$ are very effective against a wide range of microorganisms. However, it ceased to be used at thermal power plants at the end of the 20th century due to its extremely high toxicity [46].

Nontoxic coatings allow biological contamination of surfaces but facilitate its removal due to the weakening of the adhesive bond between the coating and the biofilm. Silicone-based coatings are a special group of coatings that are promising for circulating water supply systems. They are applied on perfectly clean and dry surfaces or on clean and almost dry (moisture content 5% or less) concrete. Consequently, it is more difficult to apply coatings on the surfaces of existing RCSs and they can be effectively used only in the construction of new ones. Coatings of this type are sensitive to damage and mechanical abrasion. The expected service life of commercially available silicone coatings is 4–5 years.

Acoustic methods may become quite effective in the future to prevent biological pollution. Acoustic pulse generators (sparkers) create pulsed acoustic waves of a wide frequency spectrum. The design of sparkers and the principle of their operation are described in detail in [47, 48]. Studies of sparkers were associated with the inhibition of biological contamination of pipelines at industrial enterprises [49, 50].

Heat treatment is a fairly effective way to deal with biological contaminants and is used in some power plants in Europe and North America. The cooling water is gradually heated to a temperature of approximately 40°C and then maintained at this level in the water circuit for 30 minutes to 2 h. As a result, microorganisms of some species die from heat shock. However, heat treatment is not effective for combating biological contaminants and for removing biofilms since their removal requires a temperature of more than 70°C. In the Netherlands, at Hoogovens, Ijmuiden, Eems and Delfzijl TPPs, sea water previously subjected to thermal treatment in order to eliminate biological pollution is used as cooling water [51].

Ultraviolet radiation treatment finds wide application in various fields of industry. The destruction of bacteria occurs when exposed to photons with a wavelength in the range from 200 to 280 nm. Highenergy photons are most efficient at a wavelength of 253.7 nm [52]. Under the influence of UV radiation, molecules of ribonucleic acid and deoxyribonucleic acids are destroyed.

Organic matter and dissolved salts absorb UV radiation, so the more solutes present in water, the lower the transmittance. For water treatment, it is recommended to use UV radiation with a transmittance of at least 85%. In order to determine the actual impact of a UV system, the total suspended solids content of the water must be evaluated along with the transmittance. In standard UV water disinfection systems, the lamp dose is approximately 40 mJ/cm². The main advantages of UV water treatment are the absence of chemicals, safety, relative ease of use, and low energy costs.

CONCLUSIONS

(1) Biological contamination of equipment is observed at almost all stages of the preparation of the coolant at TPPs. In an CCS, the efficiency of the condensing unit is reduced due to biological deposits on the tube surface of the condenser, which negatively affects the efficiency of the TPP as a whole. Biofilms formed by anaerobic bacteria are the cause of bioinduced corrosion. Due to the formation of biological deposits on the walls of storage tanks for chemically treated water at thermal power plants, an unacceptable decrease in the quality of the coolant occurs, which can lead to emergency situations at once-through boilers.

(2) Almost all technological elements of the WTP are subject to biological pollution, which is the reason for the decrease in the quality of the coolant at TPPs. On a WTP with ion-exchange filters, organic and inorganic deposits and biofilms are found, which can lead to the destruction of the structure and deterioration of the technological properties of ion-exchange resins, while on a baromembrane WTP, pore blocking occurs due to the formation of biofilms.

(3) The most effective methods of combating biological contamination of technological equipment at thermal power plants include chlorination; the use of chlorine dioxide, hydrogen peroxide; ozonation; bromination; the use of anionic, cationic, and amphoretic surfactants; thermal, acoustic methods; and ultraviolet radiation treatment. It should be noted that the choice of the optimal option should be based on the identification of specific populations of bacteria that lead to biological contamination on certain equipment as well as feasibility studies and an assessment of the applicability of various methods for specific water treatment plants.

(4) At most TPPs, attention should be paid to continuous monitoring and prevention of the possibility of biological contamination of power equipment or its minimization. To do this, it is necessary to maintain an optimal water-chemical regime at the stations, use modern biocides, and also fight biological pollution by nonchemical methods, for example, by additional UV treatment of the coolant at certain stages of the water treatment cycle.

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