

Microbiological studies of ion exchange and combined water treatment plants

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Abstract — Filter materials biofouling in baromembrane water treatment plants at thermal power plants is an urgent problem. Biofouling causes ion - exchange resins “aging”, membranes destruction and leads to an increase in the content of organic impurities in purified water. The article discusses the operating water treatment plant of the branch of JSC “Tatenergo” Kazan CHPP-2. The article presents the results of a microbiological study of water samples from all stages of a water treatment plant according to the method of Droycon Bioconcepts Inc. To determine the types and the amount of bacteria, special BART-tests were used - Hab-BART, Slim-BART and Srb-BART. The research results allow us to assess the biocorrosion and water treatment equipment contamination risks, which makes it possible to predict unscheduled biocidal treatment of microfiltration and reverse osmosis units. Continuous monitoring of microorganisms at the water treatment plant allows maintaining high quality water purification and ensuring reliable filters operation.

Keywords—*Thermal power plants, water treatment, membranes, reverse osmosis, microbiological studies.*

I. INTRODUCTION

Over the past decades, more than 100 combined cycle gas turbines (CCGT) have been commissioned at the thermal power plants (TPPs) in the Russian Federation with partial use of foreign equipment. Due to the introduction of CCGTs at the TPPs, the quality of the feed water of the waste heat boilers requires its more thorough preparation [1], [2]. Therefore, most of the power plants have changed the traditional scheme of chemical water treatment by applying pressure-membrane (or baromembrane) technologies (Kursk TPP-1, Orlovsk TPP, Norilsk TPP-1, Kazan CHPP-2, Krasnodar TPP, TPP-20 Mosenergo, etc.) [3]. The most common types of membrane process used in thermal power plants are microfiltration and reverse osmosis. These methods are considered environmentally friendly by reducing the amount of alkali and acid used to regenerate the filters. But for membrane processes, the preliminary preparation of water is important before it is fed to the membrane. It is worth considering the impossibility of purifying water from volatile organic substances and chlorine.

Water treatment technologies are susceptible to bacterial contamination [4], [5]. The problem of biological contamination of the water treatment plant is still quite relevant. In [4], studies of biological contamination of the water treatment plant stages, consisting of pre-treatment on clarifiers and mechanical filters, and a chemical desalination unit, supplemented by mixed-bed filters, were carried out. An increased biological contamination of ion-exchange water treatment plants was revealed before and after regeneration. It was found that after regeneration and a long operation period,

ion-exchange resins are destroyed, cracks appear. Ion-exchange resins become a place for microbial settlements that are resistant to regeneration using various biocides [6].

In [7], studies of bacterial contamination of ion-exchange resins at the Shoubra El-khiema and Damietta TPPs (Egypt) are described. A high level of biological contamination was revealed, which negatively affects the ion-exchange filters operation, the exchange capacity of ion exchangers decreases (up to 5%).

The amount and types of microorganisms present in water treatment plants can be very diverse. And in general, it depends on the source of water supply, seasonality, filtration technologies used, water-chemical regime [8]. The growth and reproduction of microorganisms occurs due to soluble substances adsorbed in the initial water, and is accompanied by the release of an intercellular polysaccharide. Polysaccharides allow cells to be fixed to the surface of the equipment. This stimulates microbial colonization and the formation of a sticky biofilm in the form of mucus. Biofilms form a biocenosis with a complete life cycle of microorganisms [9]. Biofilm is a protective shield for microorganisms from the effects of chemical washes, aggressive media, biocides and pH fluctuations [10].

The nature and rate of occurrence of biological contamination depends on a number of factors. The process of fixing microorganisms on the surface of membranes is determined by its properties, material, degree of roughness, hydrophobicity, and surface charge of the membrane. For water treatment plants based on baromembrane technologies, the influence of the source water quality, the percentage of permeate obtained, recirculation are the important factors in the formation of microorganisms colonies. When a reverse osmosis unit is operating at 50% recirculation, the concentration of impurities in the concentrate stream doubles compared to the concentration in the permeate. Obviously, the higher the percentage of recirculation in the water treatment unit, the higher the risk of deposit formation.

Controlling the number of bacteria comes down to determining the total organic carbon [11]. It should be noted that control of the organic impurities concentration in the liquid and vapor phases presents significant difficulties. Previously, this indicator was not even standardized, so the methods of analysis were practically not used. In the traditional chemical control system in power plants, organic impurities are controlled only at the stage of preliminary water treatment, that is, at the stage of coagulation and filtration. In this analysis, the color of water (organic humic acids are colored), permanganate oxidizability or chemical oxygen demand are determined. Today there are analyzers for total

and organic carbon, but they are very expensive for thermal power plants.

The problem of controlling organic substances is very acute, therefore foreign researchers have discovered a method for their determination in an aqueous medium using an oxidizing agent [11]. The method for determining organic matter is based on the photooxidation of organic matter with a photocatalyst with the formation of at least one by-product of the photocatalytic action. This method includes two steps: passing the solution through a vessel containing a photocatalyst applied to the surface of the vessel and detecting a by-product. Illumination of the photocatalyst with ultraviolet light should be done in such a way that the photocatalyst that coats the surface of the vessel is positioned between the ultraviolet light source and the solution. Placing the photocatalyst in close contact with the light source ensures complete oxidation with the formation of by-products. These methods are focused on determining the total amount of organic matter. At the same time, there are no available methods for determining the species of bacteria inhabiting the aquatic environment.

The recognition that the presence of organic impurities in the coolant reduces the reliability of thermal power equipment operation took place in 1985 at the International Water Conference, although this issue was actively discussed even earlier. At that time, the total organic carbon content of up to 8 mg / kg was allowed in the steam-water cycle of power plants. Emergency situations are known that have led to serious damage to heat and power equipment, caused by a high concentration of organic substances. During thermolysis and hydrolysis in boilers, organic impurities are destroyed and converted into "potentially hazardous substances". These include not only potentially acidic, but also potentially alkaline and neutral agents, as well as substances that break down to carbon and create deposits on heating surfaces.

The content of organic substances in natural water is many times higher than the content of inorganic substances. They are very diverse in their composition and properties. By the nature of the organic impurities that may be present in the samples under study, according to chemical analysis, humic substances and some other organic molecules predominate. Humic substances have good solubility in water; their slippage through ion-exchange filters and transport with some vapor fractions occurs due to their thermal stability.

Disinfection of water using biocides can only be effective if the biocides are able to split off and further prevent the development of biofilms [12]. The use of traditional biocides (chlorine, bromine, hypochlorite) mainly leads to the destruction of microorganisms in a certain period of time and does not solve the problem of purification from the formed biofilms [13]. Even the acid-base washes used do not allow the membrane to be completely cleaned. This is due to the complex composition of the deposits, including organic compounds, mineral salts, siliceous compounds and parts of microbiological deposits.

II. MATERIALS AND METHODS

In 2011, at the Kazan CHPP-2 branch of JSC "Tatenergo", a unique water treatment unit was built during the commissioning of a combined cycle gas turbine unit. Its design capacity is 600 m³ / h. The water treatment plant at Kazan CHPP-2 includes the following process units:

- a mesh filters block for purification of source water from coarse impurities AMIAD EBS with a filtration fineness of 200 microns;
- coagulation unit with aluminum oxide (Al₂(OH)₅Cl-10%) with a coagulant dose of 10-24 mg / dm³;
- microfiltration unit;
- reverse osmosis unit for partial desalination;
- calciner;
- ion exchange filter unit for deep water demineralization, pumping equipment and flushing units.

The unit carries out a two-stage desalination of water with preliminary liming and coagulation, its clarification on mechanical filters. After passing through mechanical filters, the water is traditionally purified on H-cation exchange filters of the first stage and OH-anion filters of the first stage. In connection with the introduction of CCGT at Kazan CHPP-2, as the third stage of water purification, mixed-bed filters with internal regeneration were additionally installed. The use of a rational water purification system at Kazan CHPP-2 made it possible to reduce the consumption of reagents for water purification and the amount of hazardous substances, which increased safety. The main chemical reagents used at Kazan CHPP-2 are sulfuric acid, alkali, aluminum oxychloride, sodium hypochlorite, hydrochloric acid and antiscalant.

The microfiltration unit consists of nine modules with 50 membrane elements each. The reverse osmosis unit includes six "Sharya P-7000" modules. The reverse osmosis module consists of 12 pressure bodies assembled in a two-row scheme: 8 bodies in the first row and 4 bodies in the second. Each body contains six rolled reverse osmosis elements manufactured by RM Nanotech (Membranium). The ion exchange unit consists of a group of countercurrent cation exchange filters of the "Granophil Ion-Pr2-2031" type with a loading with a strongly acidic cation exchanger in the H-form and anion exchange filters "Granophil Ion-Pr2-2032" with a loading with a strongly basic anion exchanger in the OH-form.

The technological scheme of the water treatment plant at Kazan CHPP-2 is shown in Fig. 1.

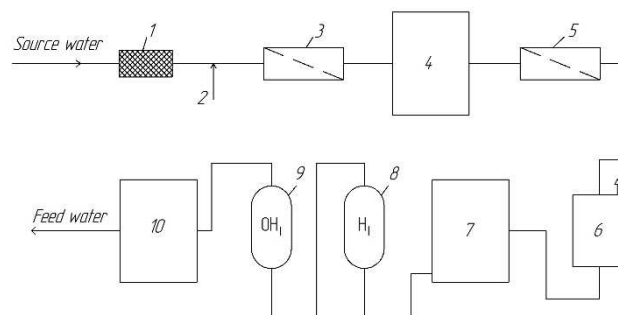


Fig. 1. The technological scheme of the water treatment plant at Kazan CHPP-2. 1 – mesh filter; 2 – the reagent dosing; 3 – microfiltration unit; 4 – clarified water tank; 5 – reverse osmosis unit; 6 – calciner; 7 – partially demineralized water tank; 8 – H-cation filter; 9 – OH-anion filter; 10 – demineralized water tank.

The source of water supply is the Kuibyshev reservoir of the Volga River. The water in the Volga River is characterized by increased oxidizability and a high concentration of suspended solids associated with the presence of humic substances, microalgae and waste products of aquatic microorganisms, as well as technogenic impurities [14].

The average values of physical and chemical indicators for the stages of the Kazan CHPP-2 water treatment plant are presented in Table 1.

TABLE I. PHYSICAL AND CHEMICAL INDICATORS OF WATER BY STAGES AT THE WATER TREATMENT PLANT OF KAZAN CHPP-2.

Indicator name	Unit of measurement	Source water	After clarifier	After microfiltration unit	After reverse osmosis unit	After ion exchange filters
General hardness	mg-eq/dm ³	5.5	5.5	Na-24.68	0.28	0.2 Na- 15
				Mg-5.47	0.03	
				Ca-60.12	0.32	
Alkalinity	mg-eq/dm ³	2.7	2.4	CO ₃ - 0.18	0	
				HCO ₃ 150.74	1.61	
Total iron	mg/dm	1.7	<0.5			1
Silicon	mg/dm	7.3	5	7.0	0.09	20
Chlorides	mg/dm	18.4	25	Cl ⁻ 24	0.11	
Specific electrical conductance	μS/cm			73.86	0.28	0.5
Sulphates	mg/dm	60.7				
Permanganate oxidizability	mg O/dm ³	10.3	5-6			
pH	units	8.1	7.0	7.2	5.32	
Nitrates	mg/dm	0.03				
Petroleum products	mg/dm ³	2.5	<1			
Suspended substances	mg/dm ³	15.3	<1			
Chromaticity	degree	30.5	1	0.01	0	0
TDS	mg/dm ³			340.05	2.72	<1

Periodic chemical acid-base washing is provided for microfiltration and reverse osmosis units. The daily chemical washing of microfiltration includes:

- alkaline washing with NaOH solution at pH = 12;
- disinfecting washing with NaOCl solution;
- acid washing with HCl solution at pH = 2.

In accordance with the recommendations of the reverse osmosis elements manufacturers, one comprehensive washing per month with 0.2% acidic HCl solution, alkaline NaOH solution with 0.1% Trilon B and disinfectant 1% HCOH solution is provided. To prevent the deposits appearance on the membrane surfaces, the antiscalant Aquarezalt-1030 is constantly fed into the source water before the unit, maintaining the concentration in the source water of 5 mg / dm³.

To reduce biofouling, in 2017, at the water treatment plant of Kazan CHPP-2, the company "Ecohimpribor" carried out pilot tests on water treatment using the aqua@LIK technology. The technology is based on the production of biological surfactants from microorganisms present in the process water. The resulting bio-surfactants do not affect the microorganisms themselves, but destroy the bonds by which the biofilms are

attached to the walls of the equipment. The main problem of biofouling is observed in the reverse osmosis unit. The use of this technology leads to a decrease in operating costs, stabilization of water quality in terms of microbiological indicators. The successful implementation of the technology allowed to reduce the amount of chemical reagents used, including the rejection of the use of chemically hazardous sodium hypochlorite, which increased the environmental friendliness of the power plant. The traditional method of using biocides for water disinfection is ineffective, since it does not solve the issue of biofilm formation.

As a result of the experiments carried out on the reverse osmosis unit No. 5, a high resistance along the path of the modules was revealed due to microbiological contamination in the form of mucus-forming biofilms. During the further operation of the water treatment system, the water quality stabilized in terms of microbiological indicators at the stages from the clarified water tanks to reverse osmosis units at the level of 0 CFU / ml with the initial microbiological load at the entrance to the chemical department at the level of 10³ CFU / ml, due to the absence of secondary growth of microorganisms in storage tanks and pipelines without the use of chemicals [15], [16].

III. RESULTS AND DISCUSSION

The analysis of biological activity in water samples from water treatment plants at Kazan CHPP-2 was carried out according to a certified method using biotestors BART-tests (Droycon Bioconcepts Inc., Canada). BART-tests are containers with a redox medium for detecting mucus-forming (Slime-BART), sulfate-reducing (Srb-BART), heterotrophic bacteria (Hab-BART), total aerobic and anaerobic bacteria, and fungi and yeast (dip slide).

Slime-forming bacteria (Slime-BART), which are capable of producing copious amounts of mucus, are more common where iron-reducing bacteria are presented. Iron-reducing bacteria can also form mucus. But according to the characteristics, the mucus is denser and textured due to the accumulation of various forms of insoluble iron. The optimal conditions for the growth of mucus-forming bacteria is the oxygen presence, so they often live under aerobic conditions. When these bacteria grow in the BART-test, turbidity should be observed or the structure may become gelatinous. Therefore, the presence of these bacteria can significantly change the taste and smell of water, as well as create excessive turbidity. The mucus-forming bacteria is a complex in which many bacteria are involved.

Sulfate-reducing bacteria (Srb-BART) are a group of anaerobic bacteria that produce hydrogen sulfide (H₂S). This type of bacteria has a unique property to live and increase its population by absorbing sulfate-containing components. Bacteria thrive in a wide range of environmental conditions. They most often occur in environments with extremely low or high pH, low or high temperatures.

These bacteria can significantly reduce the quality of water, from the presence of a "rotten egg" odor to blackening of equipment, mucus formation and initiation of corrosive processes. Sulfate-reducing bacteria are difficult to detect because they are anaerobic and tend to grow deep within biofilms (mucus) as part of the microbial community.

The peculiarity of heterotrophic bacteria (Hab-BART) is that as a result of the organic substances decomposition,

energy is obtained for the synthesis of new cells, as well as for respiration and movement. This type of bacteria can be divided into two groups, depending on their relationship to free oxygen. Aerobic bacteria can decompose organic matter to provide energy for their growth and reproduction, but only in the presence of free dissolved oxygen. The mechanism of aerobic bacteria action: organic matter + oxygen = carbon dioxide + water + energy.

Anaerobic bacteria oxidize organic matter in the complete absence of dissolved oxygen, using the oxygen contained in other compounds, such as nitrates or sulfates. The mechanism of anaerobic bacteria action: organic matter + nitrite-ion / sulfate-ion = carbon dioxide + nitrogen / hydrogen sulfide + energy.

In most cases, this test is used for a general determination of the number of bacteria (aerobes and anaerobes), without trying to identify specific groups of bacteria. The blue dye used in this test is methylene blue. When bacteria are presented, discoloration occurs either from the bottom or from the top, depending on the type of bacteria. In this case, methylene blue acts as an alternative to oxygen in the respiration of bacteria. That is, it shows the ability of bacteria to breathe during decomposition, when bacteria breathe, then methylene blue changes its color to colorless. Accordingly, the faster the discoloration of the dye occurs, the higher the respiration rate and, accordingly, the greater the number of bacteria. The presence of bacteria in water often causes problems associated with the formation of mucus, turbidity, odor and taste, and an increased rate of corrosion. Undoubtedly, this creates health risks and violates the hygienic standards of water quality.

According to the Droycon Bioconcepts Inc. method, the appearance of a reaction to the presence of bacteria is observed within 10 days, recorded and processed in the Bartsoft.v.6 software package. Depending on the time interval from sampling to the reaction appearance, this software package assesses the risks of biocorrosion and contamination of water treatment equipment [17] - [19].

Sampling points were determined according to the technological scheme: source water of the Volga River, water after the clarification unit, water after the microfiltration unit, concentrate at the outlet of the reverse osmosis unit and demineralized water after H-OH filters. Three water samples were taken from each point with an interval of 60 minutes.

In a sample of the source water from the Volga River, the reaction in Hab-BART tests appeared after 140 hours, the number of bacteria was 670 CFU / ml. In Slime-BART tests, after 72 hours, turbidity and the formation of layered light yellow films were revealed throughout the entire volume of the bioreactor, Fig. 2.

Slime-forming biofilms are a complex system in which a wide variety of bacteria are represented. Srb-BART test did not reveal the sulfate-reducing bacteria presence.

Hab-BART test showed that the amount of bacteria in water samples after the clarifier was 140 CFU / ml. Slime-BART test did not reveal the reaction. This proves the high efficiency of the $Al_2(OH)_5Cl$ coagulation process.

Hab-BART test in a water sample after the microfiltration unit on the first day showed a large presence of anaerobic bacteria – 4 720 000 CFU / ml. The presence of stagnant zones, the roughness and hydrophobicity of microfiltration

membranes could cause the bacteria growth and the biofilms formation. Planned acid-base washing and disinfection do not provide complete cleaning of microfiltration membranes from microbiological contaminants. Slime-BART and Srb-BART tests showed no reaction, as evidenced by the absence of mucus-forming, sulfate-reducing bacteria.



Fig. 2. Slime-BART bioreactor, the source water sample from the Volga River.

In a water sample taken at the outlet of the reverse osmosis unit, a reaction was detected after 32 hours. The reaction in the bioreactor indicated the presence of both anaerobic and aerobic bacteria. The amount of bacteria in the water sample taken at the outlet of the microfiltration unit was 564 000 CFU / ml. Slime-BART and Srb-BART tests were not carried out due to the lack of these types of bacteria in the previous stages of the water treatment plant.

In a water sample taken after H-OH filters, the reaction was not detected by any bioreactor. It is obvious that bacteria remain in the H-OH filters and are washed out during subsequent regeneration (Fig. 3).

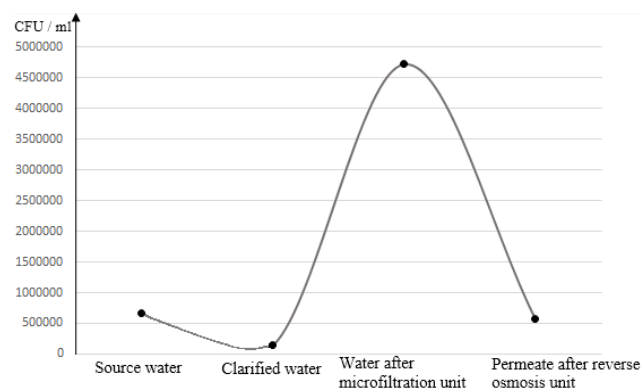


Fig. 3. The amount of aerobic and anaerobic bacteria according to Hab-BART tests.

Possible risks of equipment corrosion and contamination were calculated using the specialized software package “Bartsoft.v.6” (Droycon Bioconcepts Inc., Canada), as shown in Fig. 4. Water samples from Kazan CHPP-2 were also tested using Hab-BART tests to determine the total number of bacteria.

An assessment of the risks of equipment corrosion and contamination for water treatment plant at Kazan CHPP-2

indicates that the microfiltration unit and the reverse osmosis unit are susceptible to contamination and require chemical washing, as shown in Fig. 5. The operation of membranes in the “unscheduled treatment” zone reduces the efficiency and reliability of the operation of water treatment plants.

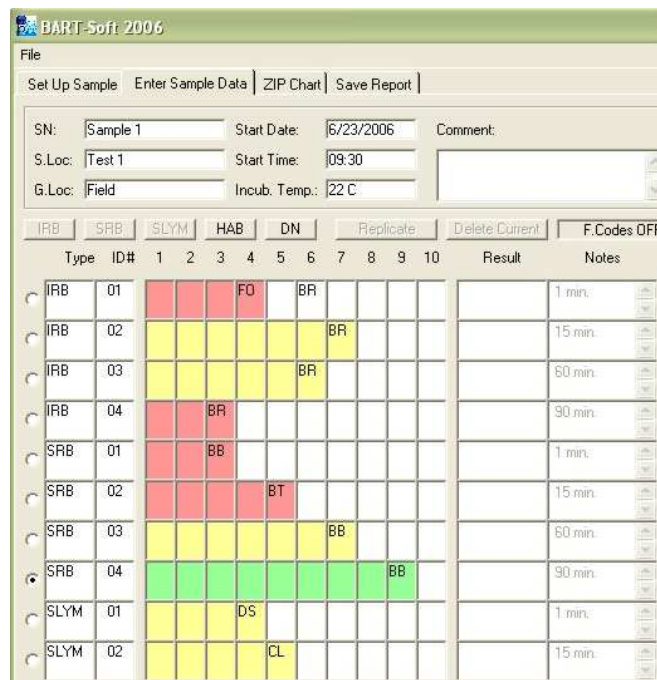


Fig. 4. "Bartsoft.v.6" interface (Droycon Bioconcepts Inc., Canada).

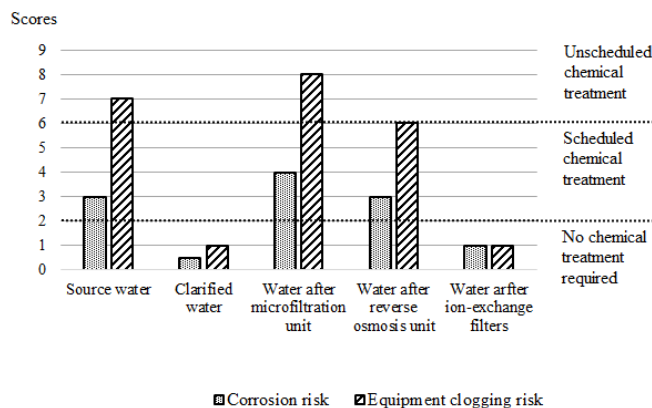


Fig. 5. Risk assessment of equipment at water treatment plants of Kazan CHPP-2 ("Bartsoft.v.6" software package).

The results obtained are consistent with the pilot industrial tests “Water treatment technology aqua@LIK” by Ecohimpribor, carried out at the reverse osmosis unit of Kazan CHPP-2 in 2017 [15], [16].

The assessment of water samples bacterial contamination at the water treatment plant of Kazan CHPP-2 is given. As a result of the research, the risks of corrosion and contamination of microfiltration and reverse osmosis units were identified. According to the results obtained in the Bartsoft.v.6 software package, the pollution level reached critical values from 4-8 points. Presumably, it can be noted that scheduled washing does not provide complete membranes cleaning. In the stagnant zones of the water treatment units, bacteria accumulate and multiply during the inter-washing period.

The amount of bacteria during the sampling period at the microfiltration and reverse osmosis units of water was $4720 \cdot 10^3 - 564 \cdot 10^3$ CFU / ml.

IV. CONCLUSION

As a result of microbial studies at the Kazan CHPP-2 water treatment plant, biological contamination was detected at some water treatment units. The corrosion and contamination risks of the microfiltration and reverse osmosis units were identified, the contamination level reached critical values (4- 8 points). The number of bacteria on the microfiltration and reverse osmosis units was $4720 \cdot 10^3 - 564 \cdot 10^3$ CFU / ml. Based on the results obtained, it was recommended for Kazan CHPP- 2 to strengthen the control and monitoring of water treatment plant biological contamination. It was also proposed to increase the concentration of the applied chemical reagents NaOCl, HCON in the summer period and to reduce the microfiltration and reverse osmosis units inter-washing period if more than $150 \cdot 10^3$ CFU / ml of bacteria are detected in the analyzed water samples.

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