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Development of quality monitoring devices for industrial water in heat supply systems

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Annotation. The article is devoted to the development of basic principles and the creation of prototypes of devices for monitoring the rigidity of industrial water in the heat supply systems of the power system. The proposed approaches are based on the electrochemical principle, according to which the industrial water is an electrolyte with a certain chemical composition and electrical conductivity. Based on this principle, new methods and measuring devices are being developed to determine the rigidity of industrial water in heat supply systems by continuously measuring the concentration of alkali and alkaline earth ions.

Relevance

At present, the development of effective methods and tools for the analysis of elements is one of the most important tasks the solution of which the development of many branches of the national economy depends on. The urgency of work in this direction is determined by fast-growing need of sophisticated science and technologies in clean and ultrapure materials, as well as monitoring of the environment and the World Ocean.

Among a wide variety of analytical methods, more and more attention is paid in our country and abroad to one of the most promising areas of electroanalysis - the method using membrane sensors based on ion-selective electrodes. Membrane sensors are devices that allow you to quickly and accurately determine the chemical composition of the environment in which the sensor is placed. It can be placed directly into the process solution, where it will acquire a potential, depending on the composition of the solution. Membrane technology is used in areas where traditional methods are inapplicable or ineffective. Convenience and simplicity of work with ion-selective electrodes promote their wide distribution and application in the most various areas.

Fields of application of membrane sensors are medicine, biology, soil science, oceanology, analysis of environmental pollution. They are used in the control of petroleum products, large chemical aggregates, nuclear reactors, technological solutions in many industries. At thermal power plants, the use of membrane sensors allows to automate the processes of water chemistry control, as well as automatically control the ionic composition of the industrial water at different stages of its processing. Such wide application of sensors is due to their ability to determine the concentration of the relevant components without disturbing the integrity of the object. The more selective the electrode is for a given ion, the wider its application in different media [1].

Advantages of membrane sensors are relative simplicity, compactness of hardware design, cheapness, speed, high sensitivity, selectivity, ecological purity, continuity of the measurement



process and the possibility of its automation. But with frequent and long-term use of an ion-selective membrane in the sensor (concentration measurement takes a long time), there is a rapid "poisoning" and clogging of the membrane with ions of other metals. As a consequence, the threshold of its sensitivity to the determined ions decreases, and its shelf life decreases. Elimination of these shortcomings by reducing the time of the measuring process and, consequently, increasing the accuracy of the measurement will make it possible to obtain more reliable data on the composition of the solution. In connection with this, the development of a fast-acting method for nondestructive testing of parameters of the natural environment, substances, materials and products using membrane sensors is an urgent task.

It is known that the rigidity of industrial water along with the level of free oxygen is one of the two most important factors that affect the efficiency of the heat transfer process of a water coolant and the service life of equipment in heat supply structures of various types (thermal power plants, thermal power stations, local systems). An increase in the level of stiffness associated with an increase in the concentration of Ca^{2+} and Mg^{2+} ions in the aqueous medium will promote the formation of a scale in the pipeline system of a closed heat exchange cycle and, thereby, reduce the efficiency of the heat transfer process. This can lead to significant energy losses in water heating systems as well as in case of violation of the high-speed regime of the water coolant. To avoid emerging problems, it is necessary to develop effective methods and devices for the continuous monitoring of the water-chemical balance of the aquatic environment. In this context, the proposed project is relevant and aimed at addressing specific energy conservation objectives.

To determine the concentration of ions of alkaline and alkaline earth metals, at present, the use of membrane sensors based on ion-selective electrodes is promising. They have a high sensitivity and an acceptable measurement speed. In connection with this, the development of such sensors is an urgent task.

Methodology of research

The membrane sensor is a galvanic half-cell consisting of an ion-selective membrane, an internal contacting solution and an internal reference electrode (Figure 1). For practical convenience, they are all located in the same housing. Another half-cell is formed by an external reference electrode immersed in a standard electrolyte. The membrane is an elastic transparent film with a thickness of 0.1-1 mm made of a plasticized polymer (matrix) with an ionophore embedded in it. Ionophore is a structure that passes ions from the solution into an internal solution. Crown ethers, calixarenes, and podands are used as ionophores. The polymer matrix is made of polyvinyl chloride and plasticizers [2].

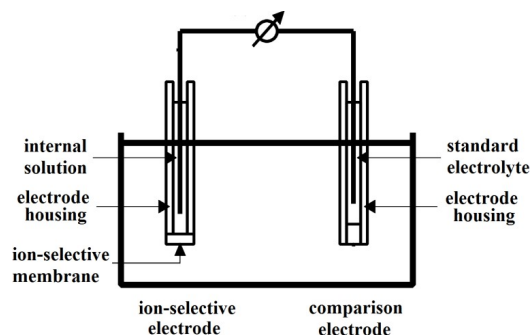


Fig.1. Membrane sensor circuit

The use of such sensors is based on the measurement of membrane potentials. The membrane sensor is an ion-selective electrode consisting of an internal semi-reference element immersed in an internal solution, a membrane and a reference electrode consisting of a comparison semi-element

immersed in a standard electrolyte. Both electrodes are placed in the test solution. The principle of the sensor is based on the fact that the membrane transmits ions of only one metal, preventing the penetration of other ions. Consequently, a potential difference appears at the boundaries of the membrane, which corresponds to the measured concentration [3].

The ion-selective membrane transmits ions of only one metal, preventing the penetration of ions of other metals. With the appropriate composition and structure of the membrane, its potential depends only on the concentration of this ion on both sides of the membrane. No other process that takes place in the membrane affects the membrane potential. Consequently, a potential difference appears at the boundaries of the membrane, which corresponds to the measured concentration. If the ion-selective membrane passes only the detectable ions, then at a constant temperature the electrode potential can be expressed by the Nernst equation.

The membrane is a film with a thickness of 0,3-0,5 mm made of a plasticized polymer (matrix) with an ionophore embedded in it. Crown ethers, calixarenes, and podands are used as ionophores. In the sensor being developed, the polymer membrane is made of polyvinyl chloride and plasticizers.

An equivalent scheme of the membrane sensor is proposed (Figure 2). It consists of a circuit R_iC and an ideal voltage source U_c . R_i is the output resistance of the sensor. Thus, the sensor is a capacitor that, when immersed in a solution, is charged through R_i to E , and when it is removed from the solution it is discharged.

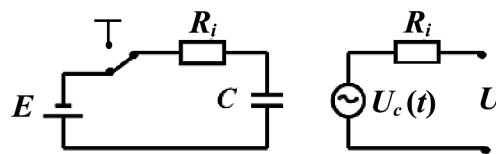


Fig.2. Equivalent Circuit of Membrane Sensor

Description

Observance of the water-chemical regime is an essential component of the normal operation of a thermal or nuclear power plant, as well as any local heat and water supply system. Under conditions of elevated temperature and pressure, strict limitations on the ionic composition of the water coolant must be carried out to reduce the formation of deposits and its corrosive properties in order to extend the life of the equipment used. This requires careful water treatment and, consequently, continuous monitoring of the chemical composition of the aqueous solution entering the cycles of power plants or water supply and heating systems.

To determine the ionic composition of an aqueous solution, membrane sensors based on ion-selective electrodes with replaceable membranes are widely used, which make it possible to determine the concentration of ions of various types with a high degree of accuracy. For example, the limit for measuring impurity concentrations with ion-selective electrodes for industrial water is $10^{-6} \div 10^{-8}$ mol/l, while for feed water of steam generators, about 10^{-5} mol/l.

It is known that the membrane sensor is a first-order measuring system with a transient operating mode. Therefore, a standard measuring method in laboratory conditions involves the selection of water samples from the pipeline with a certain periodicity, the possible preparation of the sample and the measurement itself after the sensor has reached a stationary operating mode in a minute time interval.

This method is well tested and will be very effective when the ionic composition of the water coolant flowing in the pipeline deviates markedly from the allowable on spatial scales, which are determined by the speed of the water flow and the total time including the period of the measuring process and the duration of the individual measurement. If the scale of deviations is much less than the specified value, there is always a danger that one can not "see" a noticeable violation of the water-chemical regime that will take place in the interval between adjacent measurements. To avoid such a situation, it is necessary to make the measuring process continuous. To do this, the membrane sensor should be placed in a bypass line with possible preparation of the water flow (filtration of solid

particles, establishment of the required pH-factor and ionic strength of the solution, masking of interfering ions) and then transmit the digitized signal for remote processing in the appropriate information measuring environment.

With this approach, ion concentration monitoring of the water flow will be conducted at time scales determined by the signal-to-noise ratio of the analog signal of the membrane sensor and the sampling rate of the analog-to-digital converter, for example, a microcontroller or National Instruments interface board. If the change in the ionic composition of the aquatic environment occurs at times significantly exceeding the time constant of the sensor, which is a few seconds, then it manages to enter the stationary mode of operation. Otherwise, it is necessary to take into account the peculiarities of the transient mode of operation of the membrane sensor during the measuring process.

In determining the variable concentration of ions in the liquid that is washing the sensor, the lag effects associated with the time over which the concentration of ions of a given type on the surface of the ion-selective membrane will correlate with the value in the flow will influence the measurement process. This time depends on the thickness of the fixed diffusion layer near the surface of the membrane sensor (Nernst layer), which is determined by the flow regime of the water flow in the flow system. Thus, with continuous electrochemical analysis of the water flow, a number of features of the measurement process that require preliminary consideration arise in order to determine the optimal measurement regimes and design an appropriate information and measurement system.

The advantage of the developed information-measuring system based on the membrane sensor is a wide range of detectable concentrations. It has been experimentally established that the system can be used to determine the concentrations of alkali and alkaline earth ions in the range from 1 to 10^{-6} mol/l.

Results

Continuous monitoring of the hardness of industrial water based on the measurement of the concentration of ions Ca^{2+} , Mg^{2+} and other metals is carried out using an information-measuring system based on a membrane sensor. To determine the ionic composition of an aqueous solution, membrane sensors based on ion-selective electrodes with replaceable membranes are widely used, which make it possible to determine the concentration of ions of various types with a high degree of accuracy.

With the help of the proposed high-speed method for determining ion concentration in an aqueous medium on the basis of ion-selective electrodes, it is possible to continuously monitor its chemical composition. The accuracy of continuous measurements is comparable to the accuracy of traditional discrete measurements, which are carried out in the stationary mode of operation of the membrane sensor. This will make reliable information about the ionic composition of water reliable and will allow monitoring its correct changes in real time. Note that the corresponding information-measuring system is sufficiently simple in its design and does not require significant monetary costs in the implementation.

The innovative component of the project is determined by the desire to create inexpensive and competitive devices for the continuous monitoring of the water and chemical balance of the coolant in heat supply systems, so that the costs of creating, operating and maintaining these monitoring devices are significantly less than the economic losses caused by energy overexposure.

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