MATHEMATICAL MODELLING OF PROCESSES AND SYSTEMS

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THEORETICAL BASES FOR THE DEVELOPMENT OF CHEMOSENSITIVE DETECTING SURFACE IN TECHNICAL DEVICES FOR ENVIRONMENT PROTECTION

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Abstract*—In modern industrialized world with technogenic catastrophes, there is a need to detect harmful chemicals in areas with industrial pollution, appeared due to the destruction of objects causing chemical pollution, in the regions of Chernobyl accident, and etc. As a result, the development of devices and systems (robots, drones, other systems) with detectors registering chemical pollution of the environment become important. The required detector subsystem of such devices contains sensory elements, in which the chemo-sensitive membranes, specific coatings and layers of substances were proposed; that, being in contact with certain chemicals, demonstrate chemo-sensitivity and/or the ability to perform initial identification of these substances. Studies focused on the creation of devices for the detection of various environmental pollutants; they are based on a detailed study of membrane systems simulating the basic physical and chemical properties of artificial and natural membranes, including their selectivity to ions. The publication considers the theoretical basis for the development of such sensors with chemo-sensitive surface. The purpose of the work is to form the theoretical basis for the development of device models for the detection of chemical pollutants of environment, especially those released during fires and other emergencies, in particular, at chemical enterprises, enterprises of oil and gas cycle, etc.*

Index Terms—mathematical model; detector; sensor device; chemical substances; chemical pollution of environment.

I. INTRODUCTION

Contemporary reality is characterized by antropogenic disasters that happened from time-to-time with the release of harmful chemicals, and it is necessary to detect them in the environment in order to save the Nature, to save the life and health of the people and other living organisms. The greatest necessity to do this is in industrial regions of Ukraine due to the technogenic pollution, to the fires and destruction of the objects that cause chemical pollution, in the regions affected by the Chernobyl accident, and etc. So, the development of devices – robots, drones – with detectors registering chemical pollution of environment as elements of large-scaling information system, for example, based on the previously developed fire extinguishing system are also necessary [1], [2]. Consequently, the necessary subsystem of detectors for such devices can include such sensory elements, like chemosensitive membranes (artificial and/or of natural origin), specific coatings and layers of substances, and etc. They, when coming into contact with certain environmental chemicals, have to demonstrate chemosensitivity and/or ability to perform these substances initial identification [3].

II. PROBLEM STATEMENT

The analyzing unit, developed by the authors earlier [1], [2], allows to estimate objectively the scale of ignition basing on the sensor data. The system called ASCOP was created as large-scaling information fire extinguishing system. According to the information from an automatic control system for an object or a process (ASCOP) it was done for the estimation of the real degree of fire danger in the area where the fire occurred. Respectively, it has to define the development of the fire and to activate the necessary number of devices incorporated in the control algorithm.

The efficiency of the system is largely determined by the flexibility of its control – the ease and speed of transition from one algorithm of the executive system to another and the adjustment of algorithms depending on changes in the reserve of executive devices and

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modules as they operate, as well as the current parameters of the protected object. The main rule to make a decision on the choice of algorithms is to achieve the most rapid and effective extinguishing with the smallest violations of the mode of operation of the object – and ASCOP realizes these functions.

The present studies aimed on the creation of devices for detecting various environmental pollutants emanated at fire, during disasters, due to other environmental pollution; they have to be based, from our point of view, on detectors included chemosensitive membrane systems. But the successful development and use of such systems need a good theoretical background. There are necessary detailed studies of membrane systems that simulate the main physicochemical properties of artificial and natural membranes, including their selectivity to ions; and such studies are becoming increasingly important [3], [4]. In present publication the theoretical bases for the elaboration of such sensors with detector surface are supposed.

The aim of the work performed is formation of theoretical background for the development of models of devices for detecting chemical environmental pollutants, especially those that are released during fires and other emergencies, in particular, at chemical plants and oil and gas cycle enterprises.

III. Problem Solution

A. Development of the technical systems with analytical possibilities and detecting of chemicals in environment

The fire extinguishing programs of ASCOP were designed in such a way that, depending on the place of occurrence of a fire, a real fire extinguishing tactic is developed at a given facility, the choice of which is guided by the actual speed of the fire spread, determined by the sensor system readings, and by the possibility of increasing the speed determined , loading it with explosive substances, finding people in it, etc. Sure, for the complete analyses of all this information volume, for finding of the optimal mode and for making of the command for its implementation can only the modern enough powerful computer or processor is the 2nd or 3rd generation. Reliability, speed of the executive system and reduction of the probability of false signals can be achieved at the same time in the following ways: by increasing the resistance of sensors to interference due to the spatial structure of the sensor network, their duplication or the introduction of additional units for detecting false signals and noises from the fire, using sensors that operate on logic circuits confirming the reliability of the fire signal, the use of a centralized information collection on changes in state of object parameters and environment. These systems extinguish equally effectively regardless of the options for the occurrence of fires and fire development schemes, if the fire is insignificant, it develops quickly and can go on to a great fire, regardless of the degree of fire danger of the protected area or facility, which is constantly changing in the conditions of emergency situation in contemporary life.

In present work we would like to develop chemosensitive detector subsystem, primarily for above described information system ASCOP that would be possible to modify further for other technical systems with sensor groups like robots, drones, and etc.

B. Theoretical base for some chemosensitive detectors functioning

Inventing of chemosensitive detectors for above described information system ASCOP we decided that a scientific basis for such developments can be a set of works on the selective chemically sensitive surfaces of various types of glass, various samples of which have specific chemical sensitivity either by themselves or acting as a substrate – the basis for covering them with layers of other specific substances.

One of the most interesting features of electrode glasses is the ability to obtain different values of cationic selectivity coefficients by varying their composition. The systems of aluminosilicate glasses (Na_2O (or K_2O)–$A1_2O_3$–SiO_2) and alumino-borosilicate (Na_2O (or K_2O)–$A1_2O_3$–B_2O_3–SiO_2) glasses have been studied the most fully in this regard [4]. For the first system, there are isotherms, which characterizes the dependence of K_{ii} constants on the for the alkali metal cations on the fraction of oxides in the glass. The numbers of such diagrams characterizing the dependence of KKNa on the composition of sodium aluminosilicate glasses have been obtained in experimental conditions. Systematic studies relating to this and a number of other electrode glass systems, carried out by Eisenman, showed that the K_{Ki} values and the sequence of alkali metal cations arranged in the lines – sequences according to the increase of these coefficients which consequently linked with the function of glass composition. Concerning the last, out of a total of 120 possible rearrangements, only 11 different sequences were experimentally detected [4].

During the study of membranes of electrode glasses of various compositions, it was found that the values of their specificity for alkali metal cations can be unambiguously predicted if the value of one of constants of cation specificity, in particular K_{KNa},

is known. Also there were found shows the dependences of the changes in Gibbs free energy (ΔF_{ij}) for the ion exchange reaction for all alkali metal cations and H^+ ions on the magnitude of the change in free energy of the K^+ and Na^+ ion exchange reaction (ΔF_{KNa}). The equilibrium constant of ion exchange reactions were assumed to be equal to the constants of cation specificity, established by potentiometric determinations, for example, when measuring the values of bi-ionic potentials [4].

$$\Delta F_{ij} = F\varphi_{ij} = -RT \ln K_{ij}. \quad (1)$$

Eisenman [4] developed a general theory of ion specificity, applicable both to explain the specificity of ion-exchange materials such as electrode glasses, and the specificity found in the case of liquid ion-exchange membranes and membranes containing cyclic complexing agents. This theory is based on consideration of atomic models of places that hold cations in the membrane or as a result of Coulomb attraction (in the presence of negative charge), or due to ion-dipole interactions (in the case of a neutral group with the dipole moment).

Changes in the free energy during the full exchange reaction between the glass material and the solution (ΔF_{ij}) can be determined if the differences in the internal hydration energies of the ions participating in the exchange process $(U_i - U_j)$, and the differences internal ion energies in the membrane $(\overline{U}_i - \overline{U}_j)$ [4]:

$$\Delta F_{ij} = -RT \ln \overline{K}_{ij} = (U_i - U_j) - (\overline{U}_i - \overline{U}_j). \quad (2)$$

The first of the internal energy differences in control [4] can be found on the basis of the tabular data. The difference between the internal energies of cations in an ion-exchange material, such as glass, can be approximated if there is a certain conditional value *r*, in addition to the crystal radius of the cation, determined by the distance of the closest approach of the cation to the electric center of gravity of the anionic place in the glass. This quantity, which characterizes the strength of the anionic field of ion-exchange sites, according to the considered theory determines the ionic selectivity of the membrane.

In the case when the strength of the anionic field of the site that binds the cation in the membrane is small (i.e., the *r* value is high), of the two cations participating in the exchange process, one that has a greater crystalline radius; because in this case, the difference is less in comparison with the difference, and the latter will determine the preference of the ion transition into the membrane matrix. In this case, the sequence of alkali metal cations arranged in decreasing order of membrane specificity will correspond to the sequence of decreasing crystalline radii [4]:

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ > H^+.$$

At sufficiently small values of *r*, i.e. a large force of the anion field, of the two above-mentioned differences of the values of internal energies determining the transition of ions into the matrix of the membrane will be the difference of the internal energies of cations in the membrane. In this case, the preference is given to the ions with smaller crystalline radii, which leads to the distortion of the cation sequence just given. There were obtained the isotherms characterizing the specificity of ion exchange with a change in the value of *r*, and zones corresponding to the already mentioned 11 sequences of alkali metal cations, which are predicted by theory, are indicated [4]. Note that with a gradual increase in the value of *r*, i.e., with a gradual decrease in the strength of the anion field, the first violation of the sequence is determined by the rearrangement of ions Li + and Na +, which leads to the series $Na^+ > > Li^+ > K^+ > Rb^+ > Cs^+$ (series X). The following rearrangement with a further decrease in the strength of the anion field leads to the fact that the Li^+ ions are already in third place: $Na^+ > K^+ > Li^+ > Rb^+ > Cs^+$ (series IX) [4].

With the opposite direction of changes in the strength of the anion field from its smallest values, i.e. with a gradual decrease in the value of *r*, the first rearrangement is linked with Cs^+ и Rb^+, concerns the Cs^+ and Rb^+ ions, which gives the $Rb^+ > Cs^+ > K^+ > Na^+ > Li^+$ series (series II). The second rearrangement moves the Cs^+ ions to third place: $Rb^+ > K^+ > Cs^+ > Na^+ > Li^+$ (series III) [4]. It should be noted that the change of series II, III and IV occurs in a very narrow range of changes in the value of r^- that is, the characteristic "biological" series of permeability of alkali metal cations $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$ (series IV) with a very small decrease in the field strength is replaced by serie III, in which the first place are the Rb^+ ions [4].

The strength of the anionic field of ion exchange sites in glass is determined by the chemical structure of ion exchange sites and even more – by the state of oxygen atoms. It was demonstrated in numerical publications of Nikolsky et. al., Eisenman, Belyustin and Schultz, Nikolsky and Schultz, Schulz et al. [4]. If into the crystal lattice of the main glass former (in particular, SiO_2) the elements that violate this lattice are introduced; and they prevent the polymerization (for example, Na^+, Li^+, etc.), this leads to the appearance of SiO^- groups with high anionic strength and detecting a greater affinity to cations with small crystalline radius. These glasses include

the usual H^+-specific samples used to prepare hydrogen glass electrodes. Anionic sites with high ionic strength as a result of hydrolysis can appear on the surface of pure quartz according to Eisenman [4].

When oxides of the type B_2O_3, Al_2O_3 or Ga_2O_3 are inserted into the glass, strong acid groups are formed in these glasses. The binding strength of H^+ ions decreases in this case, the hydrogen electrode function decreases accordingly, and metallic electrode functions are registered. Eisenman, who investigated in detail, as already mentioned, the system of sodium-aluminosilicate glasses, considers that the introduction of Al_2O_3 into the glass composition leads to the appearance of places like $(AlOSi)^-$ – and characterized by relatively low anionic strength. For glasses of the ternary system (for example, sodium-aluminosilicate), an increase in the proportion of oxide Al_2O_3 should lead not only to the appearance of a pronounced metallic function, but also to a gradual transition from lithium-sodium specificity to preferred potassium-cesium specificity. It was registered that the ratio of Na_2O/Al_2O_3 mole fractions started to determine the cation specificity of the glasses.

If we assume that anions F^-, Cl^-, Br^- and I^-, differing in the values of crystalline radii, can to some extent simulate anionic sites in the glass matrix, then it is possible to compare the values at the points corresponding to the crystalline radii of these anions on the isotherms obtained according to Eisenman's theory, with tabular data on the heats and magnitudes of free energies, the formation of halides of various alkali metals in their diatomic gaseous state. Such comparisons, which showed an extremely good agreement between the experimental and calculated values of the energy differences (according to Eisenman), is a strong argument in favor of this theory [4]

IV. Conclusion

In present work the chemosensitive systems with glass detecting surfaces that can selectively interact with with various chemicals were suggested. Studies were focused on the creation of devices for the detection of various environmental pollutants; they are based on a detailed study of membrane systems simulating the basic physical and chemical properties of artificial and natural membranes, including their selectivity to ions. The required detector subsystem of such devices contains sensory elements, in which the chemo-sensitive membranes, specific coatings and layers of substances were proposed; that, being in contact with certain chemicals, demonstrate chemo-sensitivity and/or the ability to perform initial identification of these substances. The study is important for the understanding of physicochemical nature of ion selectivity and specificity in the broad sense of the term, since the approximation of such non-isomorphic systems is important in the development of sensory groups for detecting of harmful chemicals in the environment.

The publication considers the theoretical basis for the development of such sensors with chemo-sensitive surface. The series with different ionic selectivity were proposed on the base of glass surfaces studies. The theoretical bases for the development of device models for the detection of chemical pollutants of environment, especially those released during fires and other emergencies [5], [6], in particular, at chemical enterprises, enterprises of oil and gas cycle, etc. were suggested.

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В. М. Шутко, В. Д. Захматов, О. О. Колганова, А. М. Миколушко. Теоретичні основи розробки хемочутливої детектуючої поверхні в технічних пристроях для захисту навколишнього середовища

У сучасному індустріалізованому світі з техногенними катастрофами виникає необхідність виявляти шкідливі хімічні речовини у районах з промисловим забрудненням, внаслідок руйнування об'єктів, що викликають хімічне забруднення, в регіонах, постраждалих від аварії на ЧАЕС, і т. ін. Внаслідок цього важливим стає розробка пристроїв та систем (роботів, дронів, ін. систем) з детекторами, що реєструють хімічне забруднення навколишнього середовища. Необхідна підсистема детекторів для таких пристроїв містить сенсорні елементи, у якості яких запропоновано хемочутливі мембрани, специфічні покриття та шари речовин, які при вступі в контакт з певними хімічними речовинами демонструють хемочутливість та/або здатність виконувати початкову ідентифікацію цих речовин. Дослідження, орієнтовані на створення пристроїв для виявлення різних забруднювачів навколишнього середовища, базуються на детальному вивченні мембранних систем, що імітують основні фізико-хімічні властивості штучних і природних мембран, включаючи їх селективність до іонів. В публікації розглянуто теоретичні основи для розробки таких датчиків з хемочутливою поверхнею. Метою роботи є формування теоретичного підґрунтя для розробки моделей пристроїв для виявлення хімічних забруднювачів навколишнього середовища, особливо тих, які виділяються під час пожеж та інших надзвичайних ситуацій, зокрема, на хімічних підприємствах, підприємствах нафтогазового циклу тощо.
Ключові слова: математична модель; детектор; сенсорний пристрій; хімічні речовини; хімічне забруднення довкілля.

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В. Н. Шутко, В. Д. Захматов, Е. О. Колганова, А. Н. Миколушко. Теоретические основы разработки хемочувствительной детектирующей поверхности в технических устройствах для защиты окружающей среды

В современном индустриализованном мире с техногенными катастрофами возникает необходимость выявлять вредные химические вещества в районах с промышленным загрязнением, вследствие разрушения объектов, вызывающих химическое загрязнение, в регионах, пострадавших от аварии на ЧАЭС, и т. д. В результате большое значение приобретает разработка устройств и систем (роботов, беспилотников, др. систем) с детекторами, регистрирующими химическое загрязнение окружающей среды. Необходимая подсистема детекторов для таких устройств содержит сенсорные элементы, в качестве которых предложено хемочувствительные мембраны, специфические покрытия и слои веществ, которые, вступая в контакт с определенными химическими веществами, демонстрируют хемочувствительность и/или способность выполнять начальную идентификацию этих веществ. Исследования, ориентированные на создание устройств для обнаружения различных загрязнителей окружающей среды, основаны на детальном изучении мембранных систем, имитирующих основные физико-химические свойства искусственных и естественных мембран, включая их селективность к ионам. В публикации рассмотрены теоретические основы для разработки таких датчиков с хемочувствительной поверхностью. Целью работы является формирование теоретического базиса для разработки моделей устрой Теоретические основы разработки хемочувствительной детектирующей поверхности в технических устройствах для защиты окружающей среды. устройств для обнаружения химических загрязнителей окружающей среды, особенно тех, которые выделяются во время пожаров и других чрезвычайных ситуаций, в частности, на химических предприятиях, предприятиях нефтегазового цикла и им подобных.
Ключевые слова: математическая модель; детектор; сенсорное устройство; химические вещества; химическое загрязнение окружающей среды.

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