Development of Optimum Mixture for Multicomponent Inhibiting Composition by Methods of Mathematical Modeling of Experiment

A I Gabitov

1Ufa State Petroleum Technological University, Mendeleeva St. 195, 450000, Ufa, Russia

E-mail: gabitov.azat@mail.ru

Abstract. Great loss of metals, numerous economic losses take place due to accidents in pipelines, industrial chemical and technological installations, etc. because of acceleration of corrosion processes. Therefore, actually all the developed countries of the world pay much attention to protection against corrosion in all manifestations thereof. Highly efficient multicomponent inhibiting composition to be obtained by modification of 4,4-dimethyl-1,3-dioxane wastes is developed and proposed to be industrially implemented by methods of mathematical design of experiment. Component mixture of each composition to be tested was optimized by maximum protective efficiency. Concentration of components in the mixture analyzed was considered as the major factor. Regression equation analysis enabled to find best component ratio. Synthesis of inhibitor obtained under 4,4-dimethyl-1,3-dioxane wastes enables to solve the problem of rational utilization thereof.

1. Introduction

Nowadays many branches of present-day industrial production, agriculture and housing and utility complex use metals as the main material. The majority of industrial facilities of chemical, petrochemical, oil-production enterprises and refineries are complicated large-scale metal-intensive groups [1, 2]. Protection of metals against corrosion over the last years has become global and international challenge [3].

Great loss of metals, numerous economic losses take place due to accidents in pipelines and industrial chemical and technological installations, etc. because of acceleration of corrosion processes. Therefore, actually all the developed countries of the world pay much attention to protection against corrosion in all manifestations thereof, because metal corrosion damage exceeds 5% of the national product [4].

Now there are several directions of protection against corrosion [5, 6, 7]. Engineering, manufacturing and application of corrosion-resistant materials for making pipelines, structures, manufacturing equipment, etc. are considered to be the most promising ones. Taking into account high value of new corrosion-resistant materials the researching engineers are engaged in selection of the most durable and efficient materials to be applied under certain conditions.

Papers devoted to making corrosion-resistant coatings, and to methods and technologies for treating surfaces of materials exposed to aggressive action (application of special compositions both to inner and outer surface of pipelines exposed to chemically aggressive media) are well numerous.
Electrochemical methods to protect engineering equipment and pipelines are widely applied. However, such methods do not result in metal loss decrease, although they greatly increase reliability of systems. In this respect the primary focus of a majority of scientists is on formation of new design for anode beds, determination of effective range thereof, optimization of number of cathodic protection stations and anode beds to decrease both energy and metal loss [8].

Thorough analysis of accidents with pipelines and engineering equipment has revealed that it is the so-called “metal stress” sections that are greatly affected by the corrosion. Extra stress appears in bends, curves, buckles, welding spots, insulation defects, etc. Corrosion intensification because of mechanical loading and hereditary-type technological deformation - mechanochemical corrosion [9] is stipulated by mechanochemical effect mainly caused by changes within the dislocation structure of metal occurring in the course of deformation. This kind of corrosion gave rise to a new direction in metal protection consisting of set of measures for making, engineering, manufacturing and operation of pipelines, structures and engineering equipment preventing metal stress.

Application of corrosion inhibitors combining high efficiency and optimum producibility of the process implementation is economically quite reasonable [7, 10, 11].

There are no universal corrosion inhibitors, therefore new kinds thereof are to be actually made for each certain system. Intermediate products and different industrial wastes are often used nowadays for making inhibitors. Application of petrochemicals, including intermediate products and petrochemical wastes is promising for making new highly efficient and quite cheap corrosion inhibitors. Due to indicated reasons the range of corrosion inhibitors to be developed and made is vast [12, 13, 14].

2. Materials and methods
As inhibitors have complex composition and, as a rule, they are not individual chemical substances further analysis has been done with application of separate compounds that are basic components in the proposed inhibiting compositions.

The research has been done with samples made from St 3 construction steel, 20 quality carbon steel and 17G1S construction low-alloy steel widely applied in oil and gas industries.

NACE (US National Association of Corrosion Engineers) blank medium saturated with hydrogen sulfide has been used as the working solution [15, 16]. Generally accepted corrosion testing procedure was used [3].

3. Research
Intermediate products and various industrial wastes are more often applied for making inhibitors nowadays. Due to this fact application of petrochemicals, including intermediate products and petrochemical wastes is promising for making new highly efficient and quite cheap corrosion inhibitors [1, 2].

Individual acetal and heteroanalogs thereof possess extremely high protective effect, aftereffect time and excellent technological properties (low density, solidifying point, etc.). However, cost thereof is much higher than that of industrially applied inhibitors. Therefore, researching of corrosion inhibitors with the use of acetals was made in two directions:

a) making corrosion inhibitors with increased protection properties and improved processing quality by blending with other substances;

b) tailor-made synthesis of corrosion inhibitors of acetal type using cheap and available petrochemical stock [3, 14].

4. Theoretical
Currently methods of mathematical modeling of experiment significantly improving efficiency of research have become widely applied in scientific and applied research, stipulated by their versatility and applicability in most of researching areas, chemistry, medicine, biology, etc. [17, 18].

English mathematician, Ronald Fisher, was the first who in 20s of the last century demonstrated the advisability in simultaneous variation with all factors instead of widely applied one-factor experiment.
In early 50s of the twentieth century there appeared a new direction in experiment modeling related to the process optimization, i.e. extreme experiment modeling. One of the first papers in this field was published by Box and Wilson in 1951. According to Box-Wilson method a researcher is recommended to make small sets of experiments where all the factors are simultaneously varying by certain rules. These sets are organized so that conditions for making (i.e. planning) the next set are selected after mathematical treatment of the previous set. So, step by step optimum conditions may be achieved [17].

Mathematical methods of experiment modeling were applied in the Soviet Union in 50-60s of the last century when making experiments in metallurgy, and further developed by V.V.Nalimov – the prominent scholar, Professor of Mathematics [19, 20].

Upgrading of mathematical tools may be said to be largely related to expanding such research areas as multicomponent and multiphase systems, catalytic processes, and chemical solid-phase reactions. Theory of nonstationary and nonequilibrium reactions supported by powerful range of computational mathematics tools is getting more progress. Partial equation theory and theory of groups, mathematical statistics and theory of chance, computational mathematics methods stipulated by computerization in solving applied mathematical problems are applied in chemistry [21].

Many problems of chemical technology were being solved largely empirically in the beginning of XX century due to low power of chemical reactors at that time. Empirical approach to researching and engineering of chemical technology processes involved experiments to be made in full-size installations. Description of processes by physical and chemical reactions is likely to reduce both economic expenditures of chemical production and environmental risk, pertaining thereto [22].

Mathematical planning of experiment to be one of mathematical modeling section is considered to be a promising direction of modern chemistry [22, 23].

Currently actually all the objects to be studied refer to complex system class characterized by a significant majority of interrelating parameters. Researchers are to find relationship between input data, i.e. factors and output data, i.e. quality indicators for the system functioning, and to fix levels of factors enhancing output data of the system. Problems of identification and optimization, i.e. finding optimum conditions for the process running or optimum composition for multicomponent systems are solved by experimental statistics because of incomplete knowledge of the phenomena mechanism. Under experimental statistics analysis of the object the relations between input and output data of the system are described by polynomial. Statistical materials characterizing the system in its functioning is required for assessing the polynomial coefficients approximating true relationship (response function) [16].

The objective of similar complex multicomponent systems is to define relationship between properties and composition and to find optimum composition of the system (i.e. multicomponent inhibiting composition, in our case). Analysis of such systems may be solved by two ways.

Following the fact that only $q$-1 composite variable may be varied, one composite variable is excluded from consideration, and approximating polynomial is plotted for other independent $q$-1 composite variables and $k$-$q$ operation factors (variables process). The $q$-th component therewith affecting the property under analysis will be somehow distributed by polynomial coefficients.

In cases when it is desirable to have relationship between properties and composition in wide range of changing of all $q$ composite variables (range of definition of composite variables is regular simplex with peaks in $(q-1)$-dimensional space) and $k$-$q$ operation factors, other models plotted under condition $\sum_{1 \leq i \leq q} x_i = 1$ ($i = 1 \ldots q, x_i > 0$) should be applied. Optimum plans in the range of definition of all $k$ variables (polyhedron to be defined in $k$-dimensional factor space by limitations in $k$-$q$ variables and conditions $\sum_{1 \leq i \leq q} x_i = 1$ ($i = 1 \ldots q, x_i > 0$), will be regarded as the range of definition of all $k$ variables analyzed are to be plotted for evaluation of such polynomial coefficients.

It should be noted that among other problems and methods of mathematical planning of experiment and mathematical modeling a new researching area called “machine design in chemistry” is appearing. This direction includes planning of composition and structure of compounds with presdesigned properties, and search of optimum ways for synthesizing complex organic compounds as well. The challenges of the new direction in mathematical chemistry relate to higher order of complexity [24].
5. Practical, research results

Our fractional analysis of each composition to be tested was optimized by maximum protective efficiency. Concentrations of fractions in the composition under review were considered to be significant factors. Analysis of regression equation enabled to find optimum ratio and in the long run efficiency. Concentration of additives may be found when using wastes, petrochemical by-products and end products as well as ways to raise efficiency thereof [25, 26, 27, 28].

6. Results

Petrochemical heterocyclic acetal-based compounds and analogues thereof are found to be efficient corrosion inhibitors. Main directions in search for new inhibiting compositions may be found when using wastes, petrochemical by-products and end products as well as ways to raise efficiency thereof.

7. References

[1] Keshe G 1984 Metal corrosion Physical-chemical principles and current challenges (M.: Metallurgy) 400
[2] Kuznetsov Yu I 2015 Scientific advance in corrosion inhibitors Corrosion: materials, protection 3 12-23
[3] Rakhamankulov D L, Bugai D E, Gabitov A I et al 2007 Corrosion inhibitors Theory and practice of oilfield equipment and pipeline protection against corrosion (M.: Chemistry) vol 4 300
[4] Kuznetsov Yu I 2004 Physical-chemical aspects of corrosion inhibition in water solutions Success of Chemistry vol 73 1 79-93
[5] Kolotyrkin Ya M 1985 Metal and corrosion (M.: Metallurgy) 88
[6] Ulig G G, Revi R U 1989 Corrosion and corrosion control. Introduction to corrosion S&T: Translated from English Edited by A M Sukhotin (L.: Chemistry) Transl. from USA 456
[7] Rozenfeld I L 1977 Corrosion inhibitors (M.: Chemistry) 350
[8] Rakhamankulov D L, Kuznetsov M V, Gabitov A I et al 1999 Current systems of protection against electrochemical corrosion affecting underground facilities (Ufa: Reactive) 232
[9] Gutman E M 1981 Mechanical chemistry of metals and corrosion protection (M.: Metallurgy) 271
[10] Kuznetsov Yu I 2015 Scientific advance in corrosion inhibitors Corrosion: materials, protection 3 12-23
[11] Kuznetsov Yu I 2016 Organic corrosion inhibitors. Where are we now? Adsorption Review Corrosion: materials, protection 3 25-40
[12] Ivanov Ye S 1986 Corrosion inhibitors for steel in acidic media (M. Metallurgy) 175
[13] Reshetnikov S M 1986 Inhibitors against acid metal corrosion (L.: Chemistry) 144
[14] Gabitov A I 1998 Results and outlook in theory and practice in corrosion prevention (Ufa: "Reactive") 122
[15] Vigdorovich V I, Strelnikova K O 2012 Some aspects of methodology in studying hydrogen-sulfide corrosion of steel Corrosion: materials, protection 4 23-27
[16] Kovalyuk E N, Gorevaya M A 2015 Kinetics of alloy-steel hydrogen sulfide corrosion Bulletin of Angarsk State Technological University 9 20-23
[17] Adler Yu P, Markova Ye V, Granovsky Yu P 1976 Modeling of experiment when finding optimum conditions (M.: Science) 280
[18] Grachyov Yu P, Plaksin Yu M 2005 Mathematical methods in experiment planning (M.: DeL imprint) 296
[19] Nalimov V V 1971 Theory of experiment (M.: Science) 208
[20] Nalimov V V, Golikova T T 1981 Analytical underpinnings for experiment modeling 2nd ed. revised (M.: Metallurgy) 152
[21] Blekhman I I, Myshkis A D, Panovko Ya G 1976 Applied mathematics: subject, logics, approaches (Kyiv: Naukova Dumka) 269
[22] Batuner L M, Pozin M Ye 1989 Mathematical methods in chemical equipment (M.: Chemistry) 295
[23] Gabitov A I, Rolnik L Z 2009 Development of optimum mixture for multicomponent inhibiting composition by methods of mathematical modeling of experiment Bash.Chem.J. vol 16 3 113-115
[24] Clarke T 1990 Computer chemistry: practical guide to calculation of molecule structure and energy (M.: Mir) 381
[25] Rakhmankulov D L, Bugai D E, Gabitov A I et al 2005 Corrosion inhibitors Principles of technology for making domestic corrosion inhibitors (M.: Inter) vol 3 346
[26] Rolnik L Z, Bugai D E, Gabitov A I, Khabibullin I R, Zlotsky S S, Rakhmankulov D L Patent of invention RUS 1531429 25.01.1988
[27] Bugai D E, Gabitov A I, Zlotsky S S, Rakhmankulov D L 1989 Complex mechanoelectrochemical approach to making stress metal corrosion inhibitors Abstracts of the USSR Academy of Sciences 305 4 887-889
[28] Bugai D E, Gabitov A I, Bresler I G, Rakhmankulov D L, Paushkin Ya M 1990 Applications of quantum chemical protection indices of corrosion inhibitors under explanation of protection mechanism Abstracts of the USSR Academy of Sciences 314 2 384-386