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Development and Implementation of Methods of Cybernetics in Technologies of Chemical Reagents and High Purity Substances

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One of the clusters of the scientific school of the academician Viktor Kafarov is the direction created by us – cybernetics of chemical and technological processes in the industry of chemical reagents and high purity substances. For 40 years this direction was developed in the Institute of chemical reagents and high purity substances, and in recent years in the Science centre "Low-tonnage chemistry".
Works were conducted in the following 4 directions: modelling and optimization of processes for production of chemical reagents and high purity substances (HPS); system analysis in technology of HPS and synthesis of the optimal individual and flexible multi-assortment manufacturing; creation of automated systems of scientific researches and technological processes control systems; development of automated databases, expert systems of the artificial intelligence and computer systems for making of the decisions.
In the 2000-s, we have taken the leading positions in the chemical complex of Russia for development and implementation of information CALS-technologies - ISO 10303 STEP (Klemeš, 2010). Based on them there were developed the automated systems of design documentation in the technology of high purity substances, biotechnology (Bessarabov et al., 2010); plasma-cryogenic technology for obtaining of nanodispersed powders etc. (Bessarabov et al., 2013) CALS systems of computer quality management for the technology of high purity substances and nanomaterials were developed (Bessarabov et al., 2011b).
In recent years, during the development of strategy of development of the chemical industry information technologies for the system analysis and rating estimation of innovative potential of 83 leading joint-stock and state ownership R&D organizations were developed for the Ministry of industry of Russian Federation. Also the system analysis of the innovation resources of 165 leading industrial enterprises of chemical and petrochemical complex was carried out.

1. Modelling and system analysis in the technology of chemical reagents and high purity substances

The main researches in the area of cybernetics of chemical technological processes in the industry of chemical reagents and high purity substances were conducted in the following directions:
1. Modelling and optimization of technological processes of chemical reagents and high purity substances (CR and HPS).
2. System analysis in technology of CR and HPS and the synthesis of optimal individual and multi-assortment industries.
3. Creation of the automated systems of scientific researches (ASSR) and automated systems for control of technological processes (ASCTP)
4. Development of automated data banks, expert systems of artificial intelligence and computer systems of decision making.
Modelling issues in technology of high-purity substances are considered on the example of complete mathematical model of production of high-purity solid products (HPSP) which represents a hierarchical 4-level structure.

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On the 1st level of modelling there are models describing the individual processes of synthesis, purification, separation and thermal treatment. At this level two main tasks are solving: identification of the model parameters and checking of its adequacy.

On the 2nd level of the hierarchy closed subsystems are modelled included in production of high-purity production. Processes which are included in these subsystems are interconnected and optimized by general technological or economic criteria. The problem of the optimization of technological regimes and hardware design is solved at this level.

Closed modelling subsystems on the 3rd level are included in the complete mathematical model of production of HPSP. These productions can be calculated both for individual HPSP, and to be flexible CTS, producing a wide range of final products. The optimal values of the criteria for the functioning of production of HPSP are additive function of optimal values of the criteria for each closed modelling subsystem of the 2nd level (Lainez et al., 2009).

4th level of the hierarchy includes simulation systems of the 3rd level, developed for various enterprises and joint by the certain class of HPSP. At this level we solve the problem of the optimal placement of the required items of HPSP while minimizing transport, energy, labour and raw material costs (Bessarabov et al., 2011a).

Mathematical models of deep purification of crystallization, ion-exchange, adsorption, extraction and chemical methods were developed and applied to a wide class of industrial processes on the 1st level of modelling. For chemical processes, ion-exchange extraction and purification on the basis of formation and analysis of thermodynamic hypotheses about the likely mechanisms of reaction there were developed mathematical methods of analysis of the reaction mechanism and chemical forms of impurity. Identification of the reaction mechanism and form of the limiting impurity was carried out for the chemical cleaning processes for $Al(2\text{-}OC_4H_9)_3$, ion-exchange purification $Ti(OC_4H_9)_4$ and H_3PO_4, extraction cleaning of $Si(OC_2H_5)_4$ and $AsCl_3$.

Mathematical approaches for describing of the kinetics of treatment with taking into consideration changes in the mechanism of chemical transformations during the transition from the area of the macro- to the area of microconcentrations on impurities were developed. Modelling of kinetics of chemical cleaning for drying of ethanol and 2-butanol by the relevant alkoxides of Al was performed. Kinetic parameters were identified. The analysis of the kinetic dependence of the activation energy and the degree of association of plastic molds allows you to select macro- and microconcentration intervals where a qualitative leap of parameter appears, associated with the change of the proportion of dimer and trimer forms of aluminum butoxide and the change in the average degree of association of aluminum ethoxide.

Simulation of drying process for tetraethoxysilane (TEOS) was made. A significant change in the activation energy (12.9 to 7.2 kJ/mol) at concentrations of TEOS less than 0.082 mol/l allows to suppose the change of the reaction mechanism in the field of microconcentrations of water, where the process of substitution of the second ethoxygroup and formation of spatial polymers by condensation begins.

Complex of the competing mathematical models of processes of deep extraction cleaning allowing to describe the hydrodynamic conditions in the vehicles, the kinetics of transition of impurities and stratification, and calculate the technological regimes and instrumentation was created (Ryabenko et al., 2003). Kinetic parameters of the periodic process of extraction cleaning for $AsCl_3$ were defined from the experimental data. the immutability of forms of transition impurities in the extraction system "$AsCl_3$ - HCl" was mathematically proved. Calculation of the industrial periodic process of extraction cleaning of $AsCl_3$ in the production of high-purity arsenic oxide was made according to the mathematical model. The simulation of a semi-continuous process of extraction cleaning for $B(OC_2H_5)_3$ was carried out. The new approach to the description of the interfacial equilibrium "liquid-liquid" in systems not forming the binary mixture was developed. Model of the "pseudobinary" equilibrium in order to describe the two-phase system "$B(OC_2H_5)_3$ - $H(OC_2H_5)$ - HCl" was proposed.

Complex of the mathematical models of processes of adsorption and co-precipitation in deep cleaning of substances in order to describe the dynamics, kinetics, equilibrium and dynamics of processes was created. The simulation of the kinetics of transition of impurities when cleaning of alkoxytitanates on different types of sorbents was carried out. Model of co-precipitation of impurities was proposed taking into account the formation of the phase of manifold. The simulation of the co-precipitation of impurity of iron from the sodium and potassium nitrates solutions on freshly prepared aluminium hydroxide was carried out. The simulation of treatment of the lead nitrate solution on different types of manifolds. Availability of this refinement eliminating transition metals impurities, and also Bi, V, and P on freshly precipitated basic lead nitrate was showed.

Simulation of process of clearing of the TEOS ion-exchange resins was made. Technological modes and construction features of industrial vessels were calculated. Mathematical methods by which identification of the most probable mechanisms of processes and forms of transferring impurities in ion-exchange

purification of tetraethoxysilane and phosphoric acid, extraction and sorption cleaning of the TEOS and the co-deposition of impurities on the manifolds of the solution of $Pb(NO_3)_2$ were developed.
The model of process of distillation clean was made. A method is proposed that allows the total combined model to describe the vapour-liquid equilibrium in the field of micro- and macroconcentration of impurity component. According to the experimental data the parameters of the mathematical model and calculation of industrial processes of distillation clean of As, B, and Al ethers were made.
In the production of high-purity Pb and Zr oxides basic reference reagents are $Pb(NO_3)_2$ and Zr oxychloride. The best method of their clearing - isothermal crystallization (salting out). Description of equilibrium at salting out in the triple system is carried out with account of the complex formation. For the system "$Pb(NO_3)_2$ - HNO_3 - H_2O" thermodynamic parameters of the model were calculated.
On the basis of experimental research using the method of radioactive isotopes (Fe59, Co57, Mn54) mathematical model of the salting out process, in which, along with differential equations of material and heat balance and kinetics on macrocomponent, there were included kinetic equation to account occlusion and sorption inclusion of impurities (Ryabenko, 1996). The optimal speed of tide for salting out agent providing maximum depth cleaning of $Pb(NO_3)_2$ solution and Zr oxychloride were calculated by means of the model.
For the analysis of complex productions of CR and HPS there were created the theoretical bases of the system analysis and decomposition of technologies on the basis of a hierarchical approach on the apparatus-technological characteristics, and also classification of micro-impurities, reagents and target products was held.
On the basis of a system of generalizations, and also on the basis of developed automated information bank there was created a targeted subsystem of analysis and selection of patterns of chemical technology of production of high purity materials.
In FSUE "IREA" works on automation of specific processes for CR and HPS were carried out. The automated control systems synthesis of multicomponent materials for fiber optics, the synthesis and distillation clean Ge and B alkoxides, hydrofluoric acid etc. were designed and developed.
Two problems of stabilization processes of distillation clean (Klemeš and Huisingh, 2008) were set and solved. The former assumes a known amount of optimal flow and allowed interval of its oscillations. For the latter criterion for stability is the minimum of mean-square deviations from optimal of the observed flow. When solving these tasks is to improve the accuracy of management takes into account numerous random factors affecting the cleaning process. This has resulted in optimal laws of discrete control, taking into account physical and chemical properties of products, as well as technological and structural characteristics.
In technology of CR and HPS the great attention is paid to technical re-equipment of enterprises, together with a more intensive use of the existing industrial potential. Optimal reconstruction can only be achieved with the application of modern methods of cybernetics, modelling and automation.
By means of elements of flexibility and system analysis there were developed a general framework within which works for the optimal reconstruction of existing productions of titanates of metals, manganese-zinc ferrite powders (MZFP), as well as nitrates and lead oxides reactive qualification were carried out.
For each of the existing chemical-technological systems (CTS) three stages of preliminary analysis: classification of CTS, definition of optimum technological routes and optimal scheduling are examining. The analysis determined the rate-limiting step: for titanates of metals - calcination, MZFP - deposition of pasta, nitrates and lead oxides - crystallization clearing. Optimization of "bottlenecks" of production without attracting additional volumes of equipment is carried out at the expense of optimization and stabilization processes implemented on this CTS. For example, the reconstruction of existing production of lead compounds only at the expense of optimization of structure of flows and technological mode improved performance by 70 %.
Expansion of the assortment of products at optimal reconstruction was carried out in stages within hierarchical systems: technological flexibility, structural flexibility and organizational flexibility of first and second level. Reconstruction of existing CTS on the basis of flexible production systems allows to expand assortment, to increase productivity and improve product quality at the same production area.

2. Introduction of information technologies in the area of chemical reagents and high purity substances

On the basis of the earlier created large databases (DB) "Reagent" and "Construction materials" there were carried out work on the development of expert systems (ES) for the analysis of the deficit of registered reagents and analysis of structural materials, in the creation of equipment and containers for

high purity substances, reactors of chemical apparatuses, for the development of microelectronics products and medical equipment.

Information about the interaction of structural materials with different environments (up to 50 applications), and other information was included to the ES “Constructional materials”. Solution of the problem of the choice of construction materials and products of them is based on the empirical rules for determining the relationship between material properties and the area where it will be applied products from it.

Multilevel systematization of published data and expert assessments on the methods of cleaning was conducted. It has allowed to create an expert system for choice of the cleaning method and analysis of the apparatus-technological design processes for the automation of the procedure of the analysis of deep purification processes.

Knowledge in the ES are represented as objects and rules linked them. In the result of the analysis there were selected the following objects: “substance”, “impurity”, “physical-chemical properties”, “the method of purification”, “equipment”, “material”, “operation”, “control mode”. The rules of the knowledge base (KB) apply to the procedure described in KB objects during the consultation. Part of ES is the editor of the rules for automatic replenishment of the knowledge base by defining new concepts and new rules. This ability makes users of ES independent from developers with replenishment of KB. An important feature of ES is “openness”, the relative ease with additions and modifications of its rule base on the phase of operation.

The developed system allows to choose the method and instrumentation of processes of deep clearing with respect to physical-chemical properties and content of trace contaminants in the original substance and the target product. The system is designed for getting individual helps of recommendations and technological and instrumental study of the totality of the issues of high purity substances.

The institute has developed an automated system for analysis, receipt and use of funds for the development of science and technology in the chemical and petrochemical industry. The program was created within the database management system FoxPro (Puigjaner and Heyen, 2006). To realize the assigned tasks there were developed structures of necessary databases: database of chemical and petrochemical industry branches, the database on receipt of means from enterprises, database of using of extra-budgetary fund. Peculiarities of the system operation were taken into account which suggested hierarchical approach to the data structure. For example, connection database "factories" and "payments" is the ratio of 1:M. The same approach applied to relation of database "institutions" and "application".

There was conducted a systematic analysis of the problem of financing of the new technological development. The evaluation criteria was proposed. On the basis of hierarchy analysis method there was developed mathematical apparatus for evaluation of promising projects. Universal computer shell of the system of support of making decisions (De Benedetto and Klemeš, 2009) on two criteria-based levels was developed. Major economic and hardware technological systems were developed necessary for optimum decisions at all levels of management: Ministry, sub-branch of CR and HPS, organization, technology project. The analysis of projects on the example of three technologies for the production of high purity lead nitrate was made. Ratings of projects for economic and hardware technological factors were calculated.

3. Criterial analysis of leading scientific organizations of chemical complex of Russia

The development of an integrated criterion for assessing the rankings of research institutes in the chemical complex relied on the use of the most informative static and dynamic indicators of innovation capacity. A static analysis of the scientific and economic potential was conducted for the last year of the period of study (2012). This is due to the fact that today’s indicators had a maximum weight in the comprehensive assessment on the innovation potential of the industrial chemical research sector.

Based on the results of the static and dynamic analysis, the following model of the integrated ranking assessment on the innovative capacity of the research institutions in the chemical and petrochemical industries (RN) was suggested:

$$RN = l_1 \cdot S_1 + \sum_{i=2}^{n} l_i \cdot D_i = l_1 \cdot S_1 + l_2 \cdot D_2;$$
$$l_i = (n - \alpha_i + 1) / (\sum_{j=1}^{n} \alpha_j);\ n = 2;\ \alpha_1 = 1;\ \alpha_2 = 2; \quad (1)$$

where l is a weighting factor calculated by the lexicographic principle, S1 is the R&D output reduced to the average of 2012, and D2 is a powered dynamic index of intellectual potential (reduced to the average ratio of the average number of employees for 1990 and 2012).

As a result of the ranking assessment, all scientific organizations were divided into three groups by their innovation attractiveness as follows: the upper cluster (R1) had a ranking score higher than 1.25, the average cluster (R2) had a ranking score of 0.75-1.25, and the lowest cluster (R3) had a ranking score

below 0.75. The distribution density of public research organizations was analyzed by the ranking assessment for 1990-2012, which shows that the upper, average, and lowest clusters included less than 33, 39, and 28 % of state unitary enterprises. This analysis clearly highlighted the development prospects of the R2 (let alone the R1) cluster and detected the problems associated with an urgent need of restructuring the R3 cluster.

The developed mathematical model (1) and the subsystem created on its basis allowed the selected research institutes to be ranked in accordance with their assigned ranks and the results to be exported into the required format (in the system, the results are imported in Excel format). The strictly formalized approach to developing ranking assessments allows one to evaluate the economic efficiency of high technology projects implemented based on a particular organization with an alternative choice. Furthermore, the assigned ranks represent a complex criterion for assessing the innovative development of organizations, and the changes in this indicator can be a measure for a development pathway chosen by a scientific organization. In addition, the ranking of research organizations in the chemical sector by the applied assessment criterion allows one to properly define the status of every R&D institute in the sector's innovative potential (Bessarabov et al., 2012).

4. Computer analysis of innovative development of the leading chemical and petrochemical enterprises of Russia

For the purposes of computerized analysis of innovation development in the leading chemical and petrochemical companies, we developed the Innov-Chem 1.0 analytical information system. This system is a multicomponent structure consisting of several units. Such a software designing principle enables the addition and deletion of any functions to increase the system flexibility and scalability.

Our comparison of the data resulting from the analysis of the basic parameters of corporate innovation activities in the chemical industry from 1995 to 2012 showed higher corporate costs of innovation activities and the simultaneous reduction of all the resulting parameters. Thus, the resource consumption of innovation products per company increased by 2.68 times, while the manufacture of innovation products decreased by 4.5 times for these seventeen years (Bessarabov et al., 2009).

Despite of the general decrease in the level of innovation activities (costs of innovation activities), the share of innovation products, introductions, and other characterizing parameters for five years, the volume of production increased. This fact can be accounted for by a significant reserve of scientific and technical developments and inventions, launching new technological lines in full capacity, and sufficient available corporate funds for the implementation of industrial, administrative, and organizational changes that finally enabled the achievement of such results.

The results of this computerized analysis showed that the effect of the scientific and technical component in the corporate innovation resources for the studied period (1995 to 2012) remained insufficient because the innovation processes of the recent years were not practically targeted to the improvement and enhancement of the competitiveness of the manufactured products (main parameters of development in innovation sphere fluctuated at a rather low level). Therefore, the enhancement of production volumes for the years of growth was accounted for by the reproduction of old models, rather than by updating the range of products and developing an issue of new commodities.

Despite of all the aforementioned negative factors, in 2003 chemical industries became leading with respect to the dynamics of growing investments: the volume of investments to fixed assets of large and middle companies in these industries increased by almost a third for a year and achieved 53.1 billion rubles. According to the results of 2012, foreign investment amounted to 1.7 billion dollars. At the same time, borrowed foreign funds exceeded by 1.8 times the level of the preceding year. After a long period of industrial recession, the chemical industry showed an expansion. For the period of 2000 to 2012, the industrial production volume increased by 1.5 times.

In conclusion, note that such a significant growth of chemical manufacture was of an extensive nature and realized primarily by loading the created capacities. The development of innovation activities by chemical companies in Russia is still complicated by the maladjustment of the former system to the new conditions of business.

5. Conclusions

In the result of conducted scientific researches in the cybernetics of high purity substances:

- there were developed theoretical bases of the system analysis in HPS technology allowed to decompose of complex chemical-technological systems by the apparatus-technological characteristics, and also classification of micro-impurities, reagents and target products;

- subject to system generalizations, and also on the basis of the automated factual data banks program-target system analysis and selection of patterns of chemical-technological manufacturings of HPS was established;
- a theory of multilevel system analysis and synthesis of flexible multi-assortment manufacturing of HPS was developed;
- mathematical models of the individual and combined processes of deep purification of key input reagents by the crystallization, ion exchange, adsorption, extraction, chemical and distillation methods were based on the change of the mechanism of process of transition from the area of the macro- to the microconcentrations area of the impurities;
- to regulate and forecast dispersion of the obtained HPS mathematical models of processes of extraction at low temperature granulation, plasma-chemical synthesis, chemical deposition, high-intensive drying in the high-frequency field, rotor-film and spray devices.

The developed criterion for integrated assessment of scientific organizations and conducted rating analysis branch research institutes of the chemical complex. In the rating analysis all scientific organizations were divided into three clusters (R1 - R3) by innovation attraction. The analysis clearly shows the potential for development research institute cluster R2 (and especially R1) and the problems associated with the need for urgent reorganization in the cluster R3.

For computerized analysis of innovative development of the leading chemical and petrochemical enterprises there was developed the informational-analytical system “Innov-Chem 1.0”. The analysis shows that the contribution of the scientific and technical component of the innovation resources of the enterprises in the period 1995-2012 was insufficient, as the innovation processes of recent years have not been directed to the improvement and competitiveness of manufactured products. Expansion of production volumes during the years of growth was not due to updating of assortment of production and mastering the production of new goods, but due to replication of old samples.

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