CHEMICAL ENGINEERING TRANSACTIONS

VOL. 43, 2015

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-34-1; **ISSN** 2283-9216

DOI: 10.3303/CET1543171

Rectification Purification of Inorganic Acids

Arkadiy Bessarabov*, Vasiliy Trokhin, Alexander Kazakov, Galina Zaremba, Andrey Vendilo

R&D Centre "Fine Chemicals", Krasnobogatyrskaya st. 42, Moscow 107564, Russian Federation
bessarabov@nc-mtc.ru

Among inorganic acids of the extra purity, an important role belongs to fluoric and hydrochloric acids used in atomic power engineering, microelectronics, fiber optics etc. The quality of an extra pure acid is determined by the content of limited microimpurities in it. When choosing purification methods those are preferred which limit possible additional contamination. For fine cleaning such processes as rectification (distillation), absorption, crystallization, ion exchange etc. are mainly used. In these processes, the extra pure acids are cleaned up to 10^{-6}-10^{-8} % of separate impurities of the weight (Blyum et al., 2008).
To get the specified acids we have developed the fine purification process with periodic rectification and absorption based on the international information standard ISO 10303. At the developing stage special attention paid to the possibility to use the same unit for cleaning both hydrochloric and fluoric acid. The main criterion for the implementation of this possibility is similarity of the processing conditions (Bessarabov, 2014).
The developed technology is based on the standard apparatus modules where the distillation (rectification) and absorption modules are the main ones. The distillation (rectification) module is designed to be used at the final stage of producing the specified acids with qualification “extra purity”. In this module the base products are cleaned from impurities which are effectively separated with this method (mainly cations of metals).

1. Analysis of constructional materials

For the most aggressive fluoric acid the analysis of constructional materials was carried out. The designs applied in the general chemical technology from high-alloyed steels and the devices gummed by rubber are suitable in production of fluoric acid only at stages of receiving and storage of a technical product.
Long time as the main material for receiving of special purity fluoric acid was platinum but after it was revealed that at the limited level ($1 \cdot 10^{-5}$% by weight) it is also dissolved in fluoric acid, its application was limited to receiving acid of reagent purity ("pure", "pure for the analysis", "chemically pure").
Researches on selection of materials for use them in technology of fluoric acid of special purity showed that the best are fluoroplast-4 and its modifications, and also polypropylene and polyethylene.
Use of the graphite impregnated with phenol formaldehyde resin is limited to its rather small firmness, especially in the concentrated boiling acid. Experience of industrial operation of graphite cubes at plants of chemical reactants in rectifying installations for receiving fluoric acid showed that the term of their working capacity makes some months.
Polypropylene can be used for creation of the equipment working only up to the temperatures about of 363 K. This material, as a rule, serves for internal facing of the equipment which isn't exposed to thermal loadings.
Use of polyethylene is limited because of the low temperature of its melting and other negative properties. As a rule, in production of especially pure substances it is recommended to use polyethylene only of a high pressure. This is due to the fact that polyethylene of low pressure contains inclusions of many heavy and alkaline metals getting to material from the catalysts. The ash-content in such polyethylene reaches 2%.
Polyethylene of a high pressure got broad application at production of container for packing of especially pure products, but it is also applied at those technological stages where there are no increased temperatures.
However, recently it was established that from polyethylene of a high pressure in fluoric acid organic impurities are washed away because of the high concentration of the dissolved fluoric hydrogen.

Please cite this article as: Bessarabov A., Trokhin V., Kazakov A., Zaremba G., Vendilo A., 2015, Rectification purification of inorganic acids, Chemical Engineering Transactions, 43, 1021-1026 DOI: 10.3303/CET1543171

From all known polymeric materials fluoroplast-4 is the best in technology of fluoric acid. It possesses the greatest mechanical firmness at the increased temperatures (up to 523 K) in the most various environments, including fluoric acid. Pipes, plates, films, capacities and other products from fluoroplast-4 are issued in the industrial way.

Fluoroplast-4 has a number of serious disadvantages as cold fluidity, bad heat conductivity and also lack of ability to welding and pasting.

Considering indispensability of fluoroplast in production of high-pure fluoric acid washing away of the alien impurity which got in ftoroplast-4 at its production and storage was studied. Researches of kinetics of process were conducted on the example of the manganese impurity which was artificially entered in fluoroplast. It was shown by authors that the speed of pollution of fluoric hydrogen is limited by diffusion in pores which are formed at washing away of superficial impregnations of impurity and doesn't depend on intensity of hashing.

Special difficulties are caused by creation of the heat exchange equipment from fluoroplast. At thermal loadings to 15000 kcal/sq.m • h and temperatures of the reactionary environment 390K fluoroplast devices with external heating are used. For creation of the thermal loadings reaching 35000 kcal/sq.m • h, the tubular electric heaters covered with a thin layer of fluoroplast and placed in devices are used. Efficiency of such heat exchange devices comes nearer to efficiency of metal heat exchange devices. For condensation of vapors, cooling or heating of high-aggressive liquids, in particular, of fluoric acid, heat exchangers of lamellar type were developed. For dispensing and hashing of especially pure liquids bellows-sealed dosing pumps at which the working part is completely executed from fluoroplast-4 are offered. Bellows-sealed pumps have no rubbing details and gland packings in flowing part that causes their high tightness.

Operating experience of the heat exchange equipment made of fluoroplast-4 in laboratory installations showed that the cooling water following from condensers had the increased acidity. For determination of permeability of fluoric hydrogen through fluoroplast the corresponding researches were conducted. Results of these researches showed that permeability of fluoric hydrogen through fluoroplast is really quite great: in 1 hour its concentration in the water cooling a wall 0,4 mm thick and of 1 sq.m, reached 0,1 mol/litre, and led to increase in acidity of external water. This effect needs to be considered as similar acidity of the reverse (cooling) water causes corrosion of pipelines and leads to other unpleasant consequences causing the necessity of introduction of additional converters. The same belongs to condensate pipelines when using steam for heating of the specified system.

The conducted researches showed that the practical exception of permeability requires a wall not less than 1 mm thick. Such thickness of a wall provides the contents fluoride ion in external water (condensate) at the level of maximum concentration limit equal to $5 \cdot 10^{-4}$ mg/l. Thus, for hardware registration of processes of receiving of the high-pure fluoric acid the main constructional material is fluoroplast-4. Also the thickness of the walls of the equipment relating to the main technological stages has to be about 4-5 mm. Similar thickness of a wall provides a sufficient stability of shape of products at thermal loadings and small influence of hostile environment owing to permeability of material.

2. The modular design technology

The process-flow diagram is constructed of standardized equipment modules, in which come from the purification processes of a certain group of impurities, flow separation and isolation of the major product.

Selection of the modules and their sequence, and the organization and formulation of process flows are determined by the level of quality required, and selection of the feedstock (Grinberg et al., 2008).

The process that we have developed for the production of inorganic acids of extra purity (Figure 1) is based on five standard equipment modules: chemical treatment, periodic rectification, correcting the composition, ad-, de- and absorption. The module for correcting the composition are output modules, i.e., the appropriate finished product is discharged from it. The sorption, chemical treatment and rectification modules are not output modules. Internal process flows from which there is no recovery of a product are placed between these modules and the distillation modules. They are connected of the technological streams (so-called internal) from which gathering of product isn't made.

The equipment modules were developed within the framework of the most modern and promising computerized support system – the CALS-technology (Continuous Acquisition and Life-Cycle Support – a continuous information support of the product life-cycle) (Saaksvuori, Immonen, 2010). The CALS concept is based on complex of the unitized information modules and standardization of method of access to information and its correct interpretation.

Among other things, the CALS technology is an ISO 10303 STEP standard - a means of solving the problem of electronic representation of designer and builder information using a standardized integrated description of an article. Design data in the STEP format (Standard for the Exchange of Product Model Data) can be used for technical preparation and production control, layout of requirements, etc.

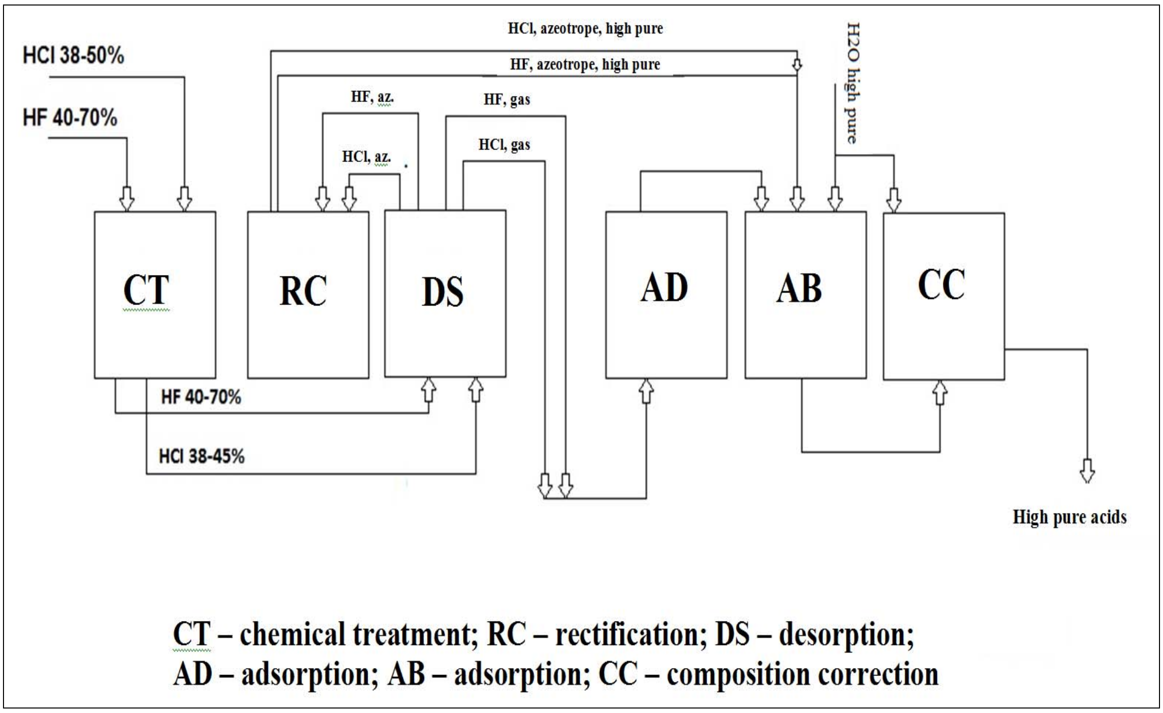

Figure 1: Modular scheme of technology of receiving inorganic acids.

The ISO 10303 standard is constructed in a manner such that in addition to the basic components (integrated resources), so-called applied protocols defining the specific structure of the information model. It is suitable for various objective branches (for example, the chemical industry) enter into this standard as component parts. All applied protocols (applied information models) are based on standardized integrated resources. When a new applied protocol is developed, therefore, continuity with solutions already in existence is assured.
We have examined in detail the basic steps for computerized description of the life cycle (LC) of equipment modules in the CALS concept (Vinodh, 2011). In examining the LC steps (marketing, design, production, implementation and operation), we focused major attention on design. In conformity with the ISO 10303 STEP standard, the builder's electronic description contains the structure of the categories, documents, statuses, and groups of articles with their versions, properties, classifications, etc.
A standard scheme (user protocol) for a continuous production schedule was created for development of equipment modules based on the informational CALS standard ISO 10303 STEP. The basic information structure is the Position Pertaining to Production Schedules at Chemical-Complex Establishments issued on May 6, 2000.

3. Stage of rectification purification

The main element of the rectification module is the packed rectifying column presented by a 1000mm high shell with a diameter of 100 mm and made of fluoroplastic-4 flanging. The shell is filled with the packing i.e. the rings made of fluoroplastic-4 (Rashig rings) manufactured of a tube. The accessories of the module include head tank, totes, remote boiler, overflow devices, heat-exchanger and condenser, heat-exchanger and distillation tube. These elements and others are made of corrosion-resistant material fluoroplastic-4.
To evaluate the efficiency and possibility of obtaining of the high-purity hydrofluoric acid of the nearly azeotropic composition, the “liquid-vapor” equilibrium was investigated. The studies were conducted using the Bushmakin apparatus. The partition coefficients (the partition coefficient is a feature that defines for a given substance and under given conditions the maximum degree of the purification at a unit with the single-stage separation by distillation) were determined as the ratio of the impurity concentration in the liquid phase to that in the vapor phase.
The analysis of samples in the liquid and vapor phases was carried out using standard techniques and ICP-MS method (Bessarabov, Zhdanovich, 2007). Table 1 lists the partition coefficients for the specified impurities in hydrofluoric acid. It can be concluded from the table 1 that distillation techniques can be effectively used for obtaining high-purity hydrofluoric acid of the nearly azeotropic composition.

Table 1: The partition coefficients for the specified impurities in hydrofluoric acid of the nearly azeotropic composition.

Impurity	Concentration in the liquid phase, % by weight	Concentration in the vapor phase, % by weight	Partition coefficient
Aluminum (Al)	$1 \cdot 10^{-5}$	$5 \cdot 10^{-7}$	20
Barium (Ba)	$8 \cdot 10^{-6}$	$2 \cdot 10^{-7}$	40
Boron (B)	$1 \cdot 10^{-6}$	$1 \cdot 10^{-7}$	10
Iron (Fe)	$5 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	50
Potassium (K)	$1 \cdot 10^{-4}$	$2 \cdot 10^{-5}$	5
Calcium (Ca)	$2 \cdot 10^{-4}$	$1 \cdot 10^{-5}$	20
Cobalt (Co)	$1 \cdot 10^{-5}$	$1 \cdot 10^{-7}$	100
Magnesium (Mg)	$1 \cdot 10^{-4}$	$1 \cdot 10^{-5}$	10
Manganese (Mn)	$2 \cdot 10^{-5}$	$2 \cdot 10^{-7}$	100
Sodium (Na)	$5 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	10
Lead (Pb)	$2 \cdot 10^{-5}$	$5 \cdot 10^{-7}$	40
Zinc (Zn)	$6 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	60
Chlorides (Cl)	$5 \cdot 10^{-4}$	$8 \cdot 10^{-5}$	6.25

The fractioning efficiency was governed not only by statistical characteristics, but also by hydrodynamic and mass-exchange parameters including the operational load of the column (L). Table 2 lists the results of calculations of L using Zhavoronkov equation as well as the experimental data.

Table 2: The load values for the column during fractional distillation of hydrofluoric acid of the nearly azeotropic composition and 20% hydrochloric acid.

Acid	$L^*_{calc.} \frac{kg}{h}$	$L^*_{\mathrm{exp.}} \frac{kg}{h}$	$L^* \frac{kg}{h}$
HF	42.3	37.2	33.9
HCl	32.3	30.1	26.9

The main application of the absorption module is removing gas and other difficult to separate impurities from gaseous raw material (hydrogen chloride and hydrogen fluoride). This can be done due to redistribution these impurities between liquid and gaseous phases proportionally to their fractional pressure with receiving strong acids and their further desorption. Absorbent is the relevant acid of azeotrope composition.

The main element of the absorption module is the packed absorption column which is similarly to the rectifying column is presented by the shell made of fluoroplastic-4. The packing for the absorption is presented by Rashig rings. The accessories of the module include container for absorbing liquid, overflow devices, filter for gas and finished product, sanitary heat-exchanger, and heat-exchanger and cooler. These elements are made of fluoroplastic-4.

The absorption purification module as well as the distillation module is assembled of devices and units which are used for construction of the other modules on the basis of general principals and construction techniques. Besides, it is possible to assembly main and additional devices and units (distillation and absorption columns, overflow devices, dephlegmators, condensers and all switching cells) using common techniques.

To develop instrumentation modules on the basis of informational CALS-standard ISO 10303 STEP, the typical diagram (application protocol) was established for permanent technical regulations. Information structure (Figure 2) is based on the “Provision on production technical regulations at the enterprises of chemical industry” (Trokhin et al., 2012).

Typical diagram of the CALS-project for technical regulations of instrumentation modules contains the following 14 main categories of the upper level: general description of production facilities; description of manufactured products; characterization of feed stock, materials, semi-products and energy resources; description of engineering process and process flow diagram; mass balance; consumption rates for the main types of stock, materials and energy resources; waste generation rates; production and process control; troubleshooting; environmental protection; safe operation; list of mandatory instructions; flow chart drawing; specification for the main process equipment.

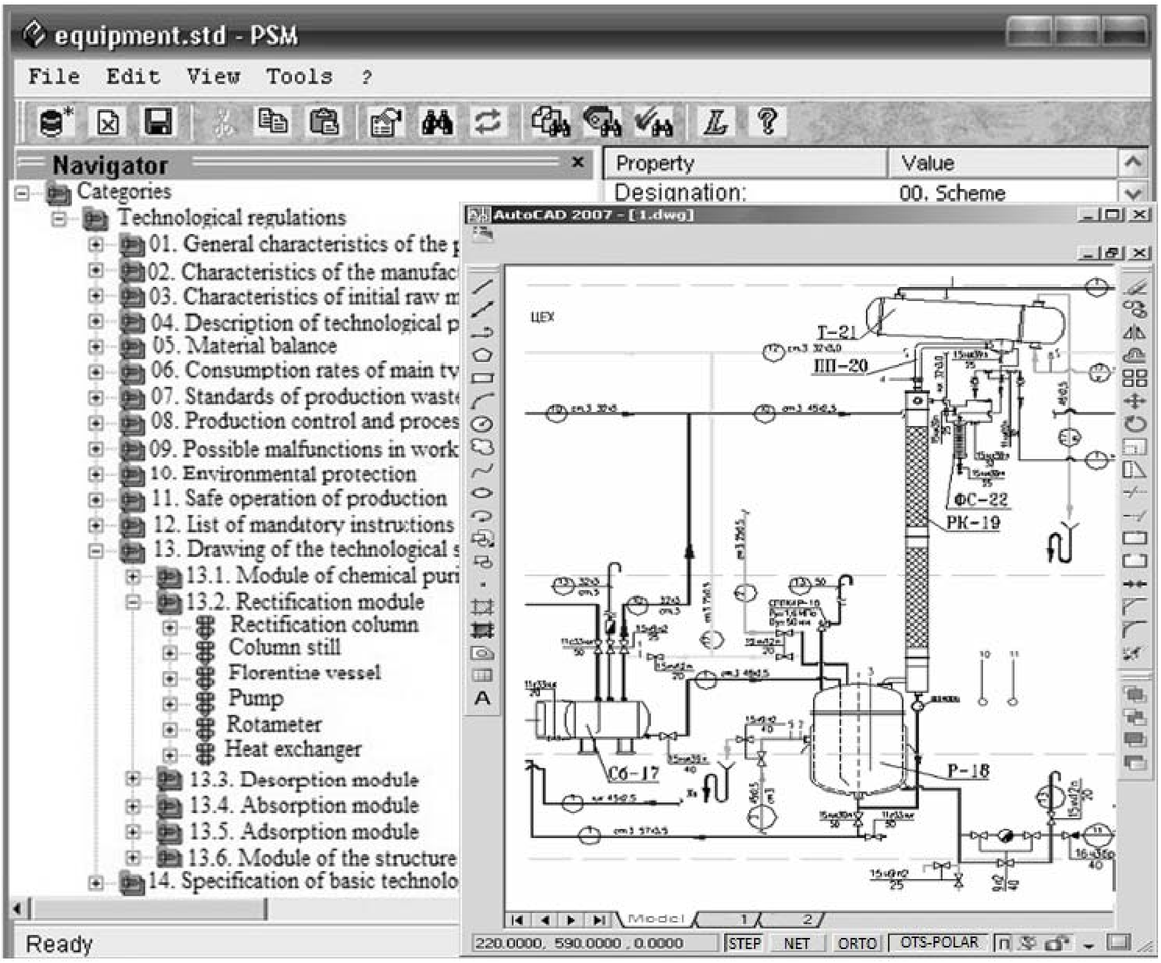

Figure 2: The element of the CALS-project for the rectification module.

The separate units and components of the rectification module are shown as an example in Figure 3 within the engineering CALS-project.

When designing the rectification module, efforts were made to ensure process efficiency and, where possible, to fulfill the requirements on manufacturability for components, units and the whole installation. To meet this requirement, one needs easy formation of the flow chart and maintainability of its constituents, fast replacement of out-of-operation components by means of their manufacturing using standard process technologies (welding, turning and milling operations). To do this, the apparatuses and the units (absorption column, heat exchangers, containers, pumps), unitized with the analogous components of other modules, were used as much as possible when developing flow chart of the absorption and distillation module.

Application of CALS-technologies for developing of instrumentation possesses the unchallengeable advantages. At present, manufacturing of competitive products should be accompanied with the informational support on the basis of computer-aided CALS-technologies, i.e. using common standardized information space at all stages of life cycle of products, from design to operation. Implementation of informational CALS-technologies during development of the instrumentation modules for production of necessary substances allows to increase quality of R&D. Also it ensures the full-scale computer-aided support including electronic copies of the whole necessary documentation.

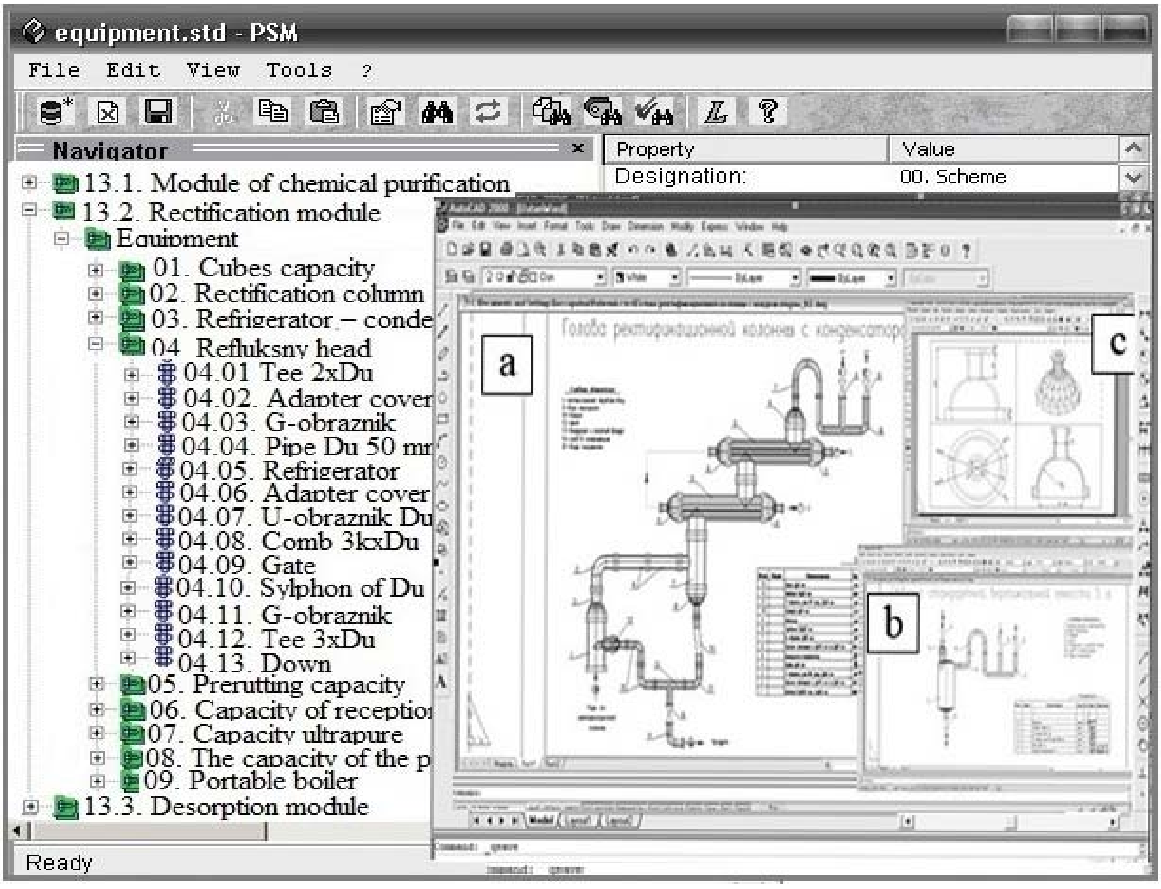

Figure 3: The element of the CALS-project. Subcategory „Equipment". The units and components of the flow chart: a – the head of the rectification column; b – tubing of standard vertical container; c – cover-reducer.

4. Conclusions

As a result of this work was developed the universal modular system for high pure inorganic acid (hydrofluoric and hydrochloric acid), which has the design flexibility. The load on the column for the given parameters of the distillation process has been established. The partition coefficients for the specified impurities in hydrofluoric acid of the nearly azeotropic composition were defined. For modules rectification and absorption were created CALS-projects in accordance with ISO 10303 STEP.

References

Bessarabov A., 2014, Development and implementation of methods of cybernetics in technologies of chemical reagents and high purity substances, Chemical Engineering Transactions, 39, 1003-1008, DOI:10.3303/CET1439168

Bessarabov A.M., Zhdanovich O.A., 2007, Development of an analytical quality control system of high-purity chemical substances on the CALS concept basis, Oxidation Communications, 30(1), 206–214.

Blyum G.Z., Ryabenko E.A., Yaroshenko A.M., Polosin V.M., Sobolev S.B., Bolshakov D.A., 2004, Modular technology of hydrofluoric acid, Inorganic Materials, 40(4), 437-440.

Grinberg E.E., Sudarikova E.Yu., Syrychko V.V., Strel'nikova I.E., Potelov V.V., Baranov K.V., 2008, Technological aspects of preparation of high-purity compounds for sol-gel and pyrolytic synthesis methods, Glass Physics and Chemistry, 34(4), 515-518.

Saaksvuori A., Immonen A., 2010, Product Lifecycle Management. 3rd ed. Springer, New York, USA

Trokhin V.E., Vendilo A.G., Bessarabov A.M., Kazakov A.A., Stepanova T.I., 2012, Use of the CALS concept for development of equipment modules producing reagent-quality aliphatic hydrocarbons, Chemical and Petroleum Engineering, 48(5-6), 271-277, DOI: 10.1007/s10556-012-9609-0

Vinodh S., 2011, Environmental conscious product design using CAD and CAE, Clean Technologies and Environmental Policy, 13(2), 359-367.