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HIGH PURITY KRYPTON AND XENON PRODUCTION

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Abstract

Air separation products (ASPs) are an important component of many technological processes. The main industrial source of rare gases is atmospheric air. Inert gases are extracted in the form of lean concentrates during the operation of high-performance air separation plants. The presented work examines the features of rectification and adsorption-distillation technologies for the production of krypton and xenon. Currently, in the air of industrial cities there is a whole "bouquet" of harmful compounds present in significant quantities, formed as by-products as a result of the implementation of various technological processes. In the process of producing high-purity inert gases, along with Kr and Xe, air components similar in properties to them are enriched. Methods for purifying intermediate products and pure inert gases from three groups of substances: hydrocarbons; oxides of nitrogen and carbon; fluorinated gases. Purification of the krypton-xenon mixture from flammable impurities, as a rule, is carried out at all stages of the technological sequence. Hydrocarbons are separated by chemical methods, nitrogen and carbon oxides are separated by sorption. Condensation and chemical methods are promising methods for purifying krypton and xenon mixtures from fluorine-containing impurities. They provide the specified quality of gas products and a high degree of recovery.

Keywords: Krypton and high purity xenon; Burning out. Catalyst. Rectification. Adsorption. Purification of fluorine-containing air components.

ОТРИМАННЯ КРИПТОНУ І КСЕНОНУ ВИСОКОЇ ЧИСТОТИ

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Анотація

Продукти поділу повітря (ППП) є важливою складовою багатьох технологічних процесів. Основним промисловим джерелом рідкісних газів є повітря. Інертні гази злобуваються у вигляді бідних концентратів під час роботи установок поділу повітря високої продуктивності. У поданій роботі розглянуто особливості ректифікаційної та адсорбційно-ректифікаційної технологій отримання криптону та ксенону. В даний час в повітрі промислових міст у відчутних кількостях присутні шкідливі сполуки, що утворюються як побічні продукти як результат реалізації різноманітних технологічних процесів. У процесі отримання інертних газів високої чистоти разом із Kr і Xe відбувається збагачення близьких до них за властивостями компонентів повітря. Досліджено способи очищення проміжних продуктів та чистих інертних газів від трьох груп речовин: вуглеводородів; окислів азоту і углероду; фторвмісних газів. Очистка криптоноксенонової суміші від горючих домішок, як правило, здійснюється на всіх етапах технологічної послідовності. Відділення вуглеводнів виробляється хімічними методами, оксидів азоту та вуглецю – сорбцією. Перспективними методами очищення криптонових та ксенонових сумішей від фторвмісних домішок є конденсаційний та хімічний. Вони забезпечують задану якість газової продукції та високий ступінь вилучення.

Ключові слова: Криптон та ксенон високої чистоти; випалювання; каталізатор; ректифікація; адсорбція; очищення від компонентів повітря, що містять фтор.

Introduction

Despite the events of recent years and the associated decline in industrial production, inert gases remain in demand. Air separation products (ASPs) are an important component of many technological processes. They are consumed in large volumes in metallurgy, chemistry and petrochemistry, and cessation or interruptions in supplies make it impossible to produce a number of industrial products [1-4]. The main consumers of highly pure gas products are countries with developed economies: USA, Germany, Japan, France, China, Korea [4].

One of the rapidly developing areas of use of krypton and xenon is medicine [3, 4]. Xenon is an ideal anesthetic and therapeutic agent with a wide range of pharmacological properties [2]. Experimental studies have shown that Xe can be used as an antiviral agent, and the bright light of xenon lamps can be used to destroy bacteria.

Xenon-oxygen mixture is used for therapeutic operations: treatment of stress of various etiologies, headaches, sleep disorders, chronic fatigue syndrome, depressive disorders, rehabilitation and recovery of the body after illness. It can be used to improve performance, in the treatment of drug addiction, and to restore the body after alcohol intoxication [2].

Significant volumes of Xe are consumed by the rapidly developing electronics industry [2]. In the process of producing microchips by ultraviolet lithography, xenon plasma is used, and the source of radiation is electrical excitation by a xenon laser. The introduction of such technologies makes it possible to reduce the chip size to 7 nm.

Compared to xenon, krypton is a gas product that is several orders of magnitude less in demand. The main areas of use of krypton: production of double-glazed windows with increased heat and sound insulation; as a working fluid for high-power lasers; rocket fuel oxidizer.

Review of known krypton and xenon production technologies

Raw materials for the krypton and xenon production. The Earth's atmosphere is the main industrial source of inert gases: neon, krypton and xenon [1–6]. Inert gases are extracted in the form of lean concentrates during the operation of high-performance air separation plants.

Below we list the main promising sources of xenon production, the use of which until recently was unprofitable [2, 7–13].

Involvement in the sphere of industrial production of medium and low productivity air separation plants, not equipped with units for the primary enrichment of technical gases [6].

For reasons of explosion safety, "dirty" oxygen is removed at the "tail" of the technological scheme of such installations, which, in addition to hydrocarbons, contains quite acceptable amounts of Kr and Xe [5–9]. Their volumetric content is an order of magnitude lower than in the primary concentrate, so in this case it is economically feasible to produce only one of the heavy inert gases – xenon.

According to preliminary estimates, equipping medium-capacity air separation plants with adsorption units for primary xenon enrichment will increase its production volume by approximately 10 %.

Use of membrane technologies for direct extraction of xenon concentrate from air [2]. In most cases, membrane separators are able to operate effectively at ambient temperature levels. However, the recovery rate of target components using membrane methods is significantly lower than for commonly used cryogenic installations.

The chemical industry uses a number of technologies in which oxygen, which is part of the air, is an oxidizing agent:

– roasting of sulfide ores of non-ferrous metals to produce sulfur dioxide in sulfuric acid and pulp and paper production;

– incomplete oxidation of hydrocarbons in the production of alcohols, aldehydes, acids, etc.

Air nitrogen is a raw material in the production of synthetic ammonia and other nitrogen-containing substances.

When implementing technological processes for which atmospheric air is the raw material, waste streams are formed in which inert components accumulate [2; 6]. In the process of complex processing of these mixtures, it is rational to simultaneously extract concentrates of inert gases. For example, in works [2, 9] the process of extracting hydrogen-based helium concentrate and methane-based krypton-xenon concentrate during processing of stripping streams from ammonia production is considered. A preliminary assessment showed that the introduction of this technology

only for Ukraine will increase the annual volume of xenon produced by ≈ 10 % [6; 9].

Gaseous waste generated during nuclear fuel regeneration [2]. During the reprocessing of spent nuclear fuel, noble gases are released at the stage of fuel pre-treatment (cutting, dissolution). When chopping fuel assemblies, only a small proportion of the noble gases present in the irradiated fuel are released. The main amount of these gases is released during the subsequent dissolution of the fuel in nitric acid. A vapor-gas phase is formed in the solvent apparatus, which contains a large amount of volatile xenon compounds formed as a result of the interaction.

Gas emissions from nuclear fuel regeneration plants can become an additional raw material source for producing xenon approximately 400,000 times richer than air. For example, at one radiochemical plant processing 5 tons/day of nuclear fuel, it is possible to obtain up to 1 million dm^3/year of stable xenon, the market value of which is estimated at 8.0 US dollars per 1 dm^3 [2].

The development of non-traditional sources of raw materials requires capital investments in the creation of new technologies. This is a rather lengthy and costly process. The most cost-effective process in current conditions is the process of rational use of already produced xenon. For example, recycling xenon in medicine can save up to 80% of its consumption. The development and implementation of technologies for collecting waste xenon fractions will make the problem of xenon deficiency less acute.

Sources of impurities in the production of Kr and Xe from air. Currently, in the air of industrial cities there is a whole "bouquet" of harmful compounds present in significant quantities, formed as by-products as a result of the implementation of various technological processes. An increase in the content of individual gases leads to the so-called greenhouse effect – an increase in average air temperature due to insufficient transparency of the atmosphere for infrared rays. The main gaseous components responsible for the greenhouse effect are water vapor, carbon dioxide, ozone, methane, nitrogen oxides, chlorine and fluorine-containing compounds. Chlorofluorocarbons, widely used in various sectors of the national economy, when released into the stratosphere, lead to the destruction of the planet's ozone layer. The total emissions of gases polluting the atmosphere in 2000 already amounted to about 42 billion tons of CO_2 equivalent [7].

Producers of krypton and xenon encounter a number of substances synthesized on the basis of hydrocarbons (Table 1) at all stages of the technological sequence for obtaining pure products [4; 7].

Table 1

Basic properties of individual substances included in krypton and xenon concentrates [4, 15]

Component	Chemical formula	ISO classification name 817–74	Molecular weight, kg/kmol	T_{boil}, K	Density (at P = 0,101325 МПа and T = 293 K), kg/m³	Lifetime in the atmosphere, years
Noble gases						
Krypton	Kr	R784	83.8	119.7	3.491	**
Xenon	Xe	R831	131.3	165.1	5.489	**
Major impurities						
Carbon dioxide	CO_2	R744	44.0	194.7*	1.839	50…200
Nitrous oxide	N_2O	R744a	44.0	184.7	1.840	130…170
Hydrocarbons						
Methane	CH_4	R50	16.0	111.7	0.6682	12
Ethane	C_2H_6	R170	30.1	184.6	1.260	0.21
Ethylene	C_2H_4	R1150	28.1	169.4	1.173	0.2***
Propane	C_3H_8	R290	44.1	231.04	1.865	0.1***
Fluorinated gases						
Tetrafluoromethane	CF_4	R14	88.0	145.1	3.67	50 000
Hexafluoroethane	C_2F_6	R116	138.0	195.1	5.80	10 000
Sulfur hexafluoride	SF_6	R846	146.1	204.9*	6.15	3 200

* – sublimation temperature; ** – not listed in reference literature; *** – estimated value

Purification of inert gases from certain impurities requires the development of special separation methods and subsequent certification of finished products [4; 14]. In the production of krypton, it is tetrafluoro-methane, for xenon it is carbon dioxide, hydrocarbons, nitrous oxide, sulfur hexafluoride and hexafluoroethane.

2022 saw one of the deepest declines in global steel production in recent history. According to Worldsteel, global production in 2022 amounted to 1878.5 million tons (Fig. 1), which is 4.2 % less than in the record year 2021 and 0.1 % less than in the "Covid" year 2020 [16].

Until the beginning of the 21st century, large enterprises consuming airborne substances, as a rule, had their own air separation shops. Currently, the global practice is to transfer the production of technical gases to third-party specialized enterprises, i.e. to outsourcing [4; 7]. This allows you to significantly reduce energy costs for non-core activities and concentrate your efforts on developing your core business.

Fig. 1. The world's largest steel producers in 2022 [16]

Typically, gas enterprises produce excess volumes of technical gases and are interested in the fullest use of raw materials. Due to the steady increase in demand for inert gases, this area of the gas business is currently one of the most promising [7].

Technological steps for the Kr and Xe production. The production of pure products is concentrated in industrialized regions of the world. Only five countries have the technology to produce xenon and krypton on an industrial scale [4]. At the moment, there are no more than 20 installations in the world for the production of final products - pure Kr and Xe. Despite the similar cleaning technologies used in these plants, the quality of the final products can vary greatly.

Currently, two technologies for the production of krypton and xenon have been developed and implemented: rectification and adsorption-distillation (Fig. 2) [4; 9]. Regardless of the type of technology, at the first stage of the technological sequence, primary krypton concentrate (PKC), which contains up to 0.5 % (Kr + Xe), is extracted directly in the krypton column of the air separation unit (Fig. 2, point 1). Along with heavy inert substances, explosive hydrocarbon impurities accumulate in the mixture, the content of which, for safety reasons, should not exceed specified limits [1–6].

Next, the primary krypton-xenon concentrate is sent for processing to a specialized installation. In accordance with rectification technology, this is done in separately located installations for the concentration of raw krypton (USK-1, USK-1M or USK-0.45, Fig. 2, item 2) [1; 5; 12; 13].

Due to a number of disadvantages, the main one being the low recovery factor (about 0.75), installations of the USK type are almost universally replaced by more modern ones of the "Chrome-3" type (Fig. 3, paragraph 2), the main advantages of which are [1; 5; 12; 13]:

- absence of an oxygen compression unit, due to which specific energy consumption in the

production of krypton-xenon mixture (KKS) is reduced;

- the extraction coefficient of krypton and xenon reaches a value of 0.99;

- the installation scheme uses internal compression, the devices have low hydraulic resistance values, there are no oxygen pipelines operating under high pressure.

At the final stage of rectification technology, the krypton-xenon mixture is purified from microimpurities of oxygen, nitrogen, hydrocarbons and its division (Fig. 2, point 3) into high-purity krypton and xenon [4; 5; 7].

In adsorption technology, krypton and xenon are obtained in the form of semi-finished products –

krypton-nitrogen and xenon-nitrogen mixtures [1; 2; 7]. The krypton fraction is separated from the xenon fraction at the stage of PCC enrichment by the adsorption method. During the regeneration of the adsorber, oxygen, which is the main component of the PCC, is replaced with nitrogen, resulting in increased explosion safety. Further processing of krypton-nitrogen and xenon-nitrogen mixtures is carried out using phase separation methods in a distillation unit to obtain pure products.

The main advantage of adsorption technology is the possibility of using ASUs as raw materials for xenon, in which there is no unit for concentrating heavy inert gases [6; 7].
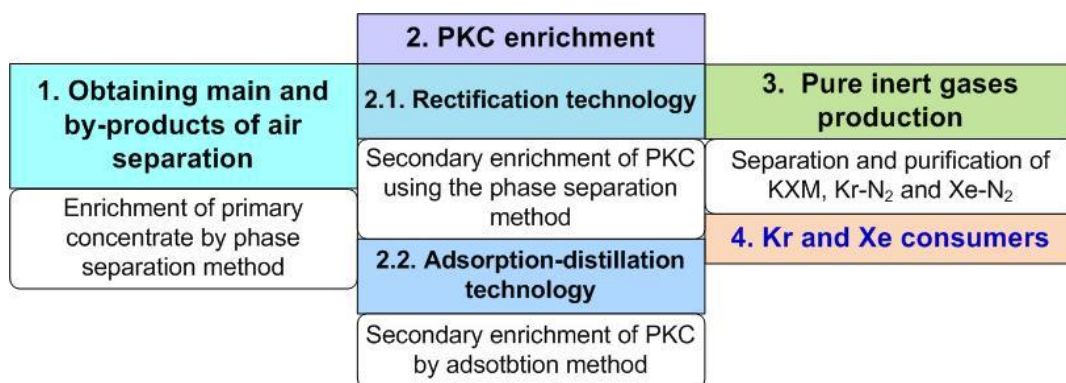

Fig. 2. Technological sequence of obtaining and using krypton and xenon

Experimental methods

Table 2 shows the typical compositions of krypton- and xenon-containing gas mixtures obtained in the process of implementing both rectification and adsorption-distillation

technologies [2; 5; 6]. As a result of 2–4 stages of enrichment of these mixtures, the content of the main component (oxygen or nitrogen) is significantly reduced. At the same time, together with krypton and xenon, the mixtures are enriched with high-boiling components [1].

Table 2

Typical compositions of krypton and xenon concentrates, % [5–7]

Component	Chemical formula	Primary Kr-Xe concentrate from ASU	Rectification technology Krypton-xenon mixture after USK or "Chrome-3"	Adsorption-distillation technology	
				Krypton-nitrogen mixture after krypton adsorbers	Xenon-nitrogen mixture after xenon adsorbers
Krypton	Kr	0.2	≥98	5.0…20	0.1…7.0
Xenon	Xe	0.015		–	0…45
Nitrogen	N_2	1.7	≤0.5	60…95	45…98
Oxygen	O_2	≈98	≤1.0		
Methane	CH_4	0.2…0.4	≤0.1	1.0…20	0.01…5.0
Tetrafluoromethane	CF_4	–	≤0.08	–	–
Carbon dioxide	CO_2	0.001	≤0.1	–	–
Ethane	C_2H_6	0.01	–	–	0.1…5.0
Hexafluoroethane	C_2F_6	–	≤0.002	–	–
Sulfur hexafluoride	SF_6	–	≤0.006	–	–
Water vapor	H_2O	–	≤0.01	–	–

The choice of a separation method for multicomponent mixtures begins with studying the features of their behavior in a wide range of temperatures and pressures. An additional source of information is the phase equilibrium diagrams of binary mixtures composed of the components of the source gas. Depending on the type of curves, mixtures are divided into non-azeotropic [17] and azeotropic [18].

Non-azeotropic mixtures (Kr-Xe, Kr-CF4, Xe-SF6, etc.) can be successfully separated by condensation methods. The use of these methods for the separation of azeotropic mixtures makes it possible to obtain only one of the components of a binary mixture with a low degree of extraction. To increase it, it is necessary to develop special rectification schemes [19] or use fundamentally different methods of removing impurities, for example, sorption, separation on membranes, chemical methods, etc. [1; 2].

In accordance with the classification established in the technology for producing heavy inert gases, we will consider the known methods of purification from three groups of substances:
- hydrocarbons;
- oxides of nitrogen and carbon;
- fluorinated gases.

Hydrocarbon removal. Despite the increase in overall costs, the recovery of krypton-xenon concentrate in air separation shops leads to an improvement in the quality of the oxygen produced. In this case, hydrocarbons, whose boiling point is significantly higher than oxygen, are enriched along with heavy inert gases. The content of hydrocarbon impurities in the concentrate is regulated by explosion safety: their concentration should not exceed 0.5 % [7; 20].

Purification of the krypton-xenon mixture from flammable impurities, as a rule, is carried out at all stages of the technological sequence from the enrichment of the initial concentrates obtained in the ASU to the production of high-purity products [1; 2; 5, 20]. Since hydrocarbons do not form azeotropic mixtures with inert gases, their separation can be carried out by both physical and chemical methods. The main disadvantages of physical methods are high specific energy consumption (Table 3) for cleaning and the danger of the formation of explosive concentrations of hydrocarbons in oxygen in certain areas of heat and mass exchange apparatuses.

Table 3

Characteristics of pilot plants for purifying krypton-xenon mixtures from methane [21]

| Cleaning method | Working temperature, °C | Pressure, MPa | Flow, m^3/h | Content of CH$_4$, % | | Specific energy consumption, kW·h/m^3 |
				In the original mixture	Result of purification	
Condensation (rectification)	−130	0.5	1…2	2	0.1	1.5…2.0
Chemical (burning)	600	1.5	20…25	≤0.5	0.1 ppm	0.2

The most common method of hydrocarbon removal implemented in industry is catalytic oxidation according to the reactions [1; 7; 22]:

$$CH_4 + 2O_2 = CO_2 + 2H_2O,$$
$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O,$$
$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O. \quad (1)$$
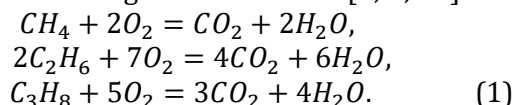
Reaction products (1) are absorbed in zeolite adsorbers at ambient temperature.

The operating temperature in furnaces depends on the type of catalyst used [22]. When using Al$_2$O$_3$ on a NaX zeolite substrate, the operating temperature is 600 °C (Table 4) [5]. By selecting the filler, it is possible to reduce the temperature in the reactor by 100…200 °C [7]. The choice of the most effective catalyst for burning hydrocarbons from a krypton-xenon mixture largely depends on its economic indicators.

Table 4

Test results of a new catalyst for the purification of a primary krypton-xenon mixture containing 0.01…1.5% Kr-Xe from hydrocarbons [4, 7]

| Catalyst Content in % wt. | Working temperature, °C | Volumetric flow rate of the mixture, hour^{-1} | Hydrocarbon content | |
			Before the burning block, %	Cleaning result, ppm
Zeolite NaX – 50%, Al$_2$O$_3$ – 50%	600	1000	0.6	6
MnO$_2$ – 5%, ZrO$_2$ – 95%	380	1000	0.6	≤3
MnO$_2$ – 10%, ZrO$_2$ – 90%	420	5000	0.6	≤3
MnO$_2$ – 20%, ZrO$_2$ – 80%	470	15 000	0.6	≤3

Since the content of hydrocarbons in the primary krypton-xenon mixture reaches values corresponding to the concentration of Kr-Xe, combustion units are included in the Hydrocarbon removal unit, which is an integral part of the installation for the production of final products - high-purity krypton and xenon. This allows us to ensure high quality products in accordance with customer requirements [4; 7; 14].

Methods for separating carbon dioxide and nitrous oxide. Currently, the carbon dioxide content in the atmosphere exceeds 380 ppm. During the air separation process, almost all CO_2 is absorbed in a zeolite purification unit installed at the inlet of the ASU [7]. Nitrous oxide is practically not absorbed by zeolite. Residual CO_2 and N_2O penetrate into low-temperature equipment and are enriched simultaneously with krypton and xenon, accumulating in the primary krypton-xenon concentrate to a content of 100...150 ppm [6, 7, 23].

Experiments on the enrichment and purification of xenon concentrate from CO_2 and N_2O using phase separation methods showed that carbon dioxide, like N_2O, forms azeotropic mixtures with it [7]. In this case, CO_2 is partially removed by periodic rectification of the rich ($\approx$ 98 % Xe) xenon concentrate, but the recovery rate of the pure product is only about 20 %.

In the process of implementing rectification technology during the secondary enrichment of the krypton-xenon mixture, carbon dioxide is absorbed in the adsorbers of the hydrocarbon combustion unit along with their oxidation products. Since a 5 Å molecular sieve is used, virtually no nitrous oxide is absorbed.

The results of experiments on the purification of liquid oxygen from N_2O by cryogenic adsorption on VSM-Sh brand silica gel at a temperature of 90 K are interesting (Table 5) [7; 23]. Studies have shown that the content of dissolved nitrous oxide in liquid O_2 does not exceed 11 ppm. Under these conditions, the task of purifying production oxygen is handled by a small-volume adsorber (no more than 1 liter of silica gel when purifying several tons of O_2).

The use of xenon adsorption on silica gel at temperatures lower than the ambient temperature is irrational, because leads to increased losses of valuable product due to the high adsorption capacity of xenon.

Nitrogen oxides, like hydrocarbons, can be separated chemically. It turned out that the decomposition of nitrogen oxides can be carried out together with the burning of hydrocarbons. Removing nitrous oxide from krypton- and xenon-containing mixtures is rational in a hydrocarbon removal unit using a more active catalyst, for example, based on palladium. Despite the increase in capital costs associated with the high cost of Pd, this will result not only in improving the quality of gas products, but also in reducing operating costs by reducing the combustion temperature of hydrocarbons.

Table 5.

Results of purification of liquid oxygen from nitrous oxide on silica gel [7, 23]

Sorbent volume, cm^3	N_2O content, ppm	Volume flow, l/s	Mass of purified O_2 before "breakthrough" (0.003 ppm)	Adsorption capacity for N_2O, dm^3/kg
14.78	2.2	2.16	310	0.058
14.78	9.9	1.48	560	0.469
6.16	4.1	1.23	220	0.183

Perfluoride removal. The search for simple and fairly cheap methods for purifying heavy inert gases from CF_4, C_2F_6 and SF_6 is currently becoming an increasingly urgent task. Growing air pollution [5–7] and a simultaneous increase in requirements for production gases leads to strict regulation of the content of these microimpurities [4; 7; 14].

Adsorption cleaning method. The methods proposed in the literature for purification from fluorine-containing compounds are divided into two directions: low-temperature methods using sorption or phase separation and chemical methods, which are implemented at elevated temperatures.

Research was carried out on adsorption-distillation technology for the production of krypton and xenon, in particular, the purification of the resulting products from fluorocarbons. Based on the statement that the adsorption capacity of components with higher volatility exceeds that of components with lower volatility [24; 25], the authors of these works calculated the adsorption curves of CF_4 on activated carbon AG-2 based on data for Kr and C_2F_6 based on data for Xe.

During the research, mass transfer coefficients

and kinetic coefficients for these gases were calculated. The results obtained were used to plot the output curves for CF_4 and Kr, as well as C_2F_6 and Xe. By calculation, the proportion of krypton purified from tetrafluoroethane containing 1 % CF_4 was determined [24], which, when purified to a content of 1 ppm CF_4, was about 0.65 (Table 6).

Table 6

Comparison of perfluoride removal methods

Cleaning method	Product	Impurity	Options			Impurity content		Recovery factor
			Flow, m³/h	Pressure, MPa	Temperature, K	Original	Remaining accurate	
Adsorption	Kr	CF_4	*	0.2	135	1%	1ppm	0.65**
	Xe-N_2	C_2F_6	*	0.2	160	0,33%	1ppm	0.26**
Condensation	Kr-Xe	CF_4	24…26	0.25…0.15	125-185	800	0.1	0.998
		C_2F_6, SF_6				100	0.1	
Chemical	Kr-Xe	CF_4	422	0.25	853 (580°C)	133	0.1	0.999
		C_2F_6				23	0.1	

* – data not provided; ** – calculated value

Similar studies were carried out for a mixture of Xe-N_2 with an admixture of hexafluoroethane [25]. Research has shown that if the sorption method is implemented to purify a xenon-containing mixture from C_2F_6 from 0.33 % to 1 ppm, the calculated degree of xenon extraction will be 0.26 of the original amount (Table 5).

In addition to the low recovery coefficient, the disadvantages of the adsorption method are the cyclical operation of adsorbers, as well as the presence of additional losses of a valuable product during their regeneration. An increase in the recovery factor can be achieved by using other purification methods, in particular rectification [4; 7; 26–29].

Condensation cleaning method. In the process of separating a krypton-xenon mixture, three columns are usually used [4; 7; 26]. However, it is almost impossible to purify perfluorides in such an installation [7; 26]. This drawback was eliminated in a distillation unit (Fig. 3) designed to obtain highly pure products (99.9999 % Kr and Xe) from a krypton-xenon mixture [7; 29].

The installation works as follows. The krypton-xenon mixture in accordance with GOST 10218-77, previously purified from hydrocarbons and nitrous oxide, is sent for separation into the K1 distillation column to form two streams: a gaseous krypton fraction and a liquid xenon fraction. Next, the krypton fraction enters column C2 to form a stream of purified krypton fraction and a stream of intermediate impurities (actually tetrafluoromethane concentrate). The krypton fraction of column C2 is separated in column C3 to form production krypton and strip gases, which are further processed in column C6. In the C6 cube a krypton concentrate is obtained that needs to be reprocessed.

The xenon fraction stream from column C1 enters column C4, where it is separated to form a gas stream of purified xenon fraction and a dirty stream (concentrate of sulfur hexafluoride and hexafluoroethane). Next, the xenon fraction, purified from high-boiling impurities, is fed into column C5, in which production xenon and stripping gas (xenon with an admixture of krypton) are formed. The C5 column stripping is also recycled.

The main disadvantages of the phase separation method are high capital costs and significant operating costs, the complexity of the process flow diagram and the installation control system.

Chemical cleaning methods. Along with condensation methods, a number of industrial systems use chemical methods for purifying krypton and xenon from fluorine-containing microimpurities [4; 7; 29]. It should be noted that fluorocarbons are highly inert: CF_4 decomposes only under extremely harsh conditions, for example, upon contact with a tungsten filament heated to 1000 °C or molten sodium.

One of the purification options is the plasma-chemical decomposition of perfluorides on nickel followed by oxidation of the products with water vapor [7].
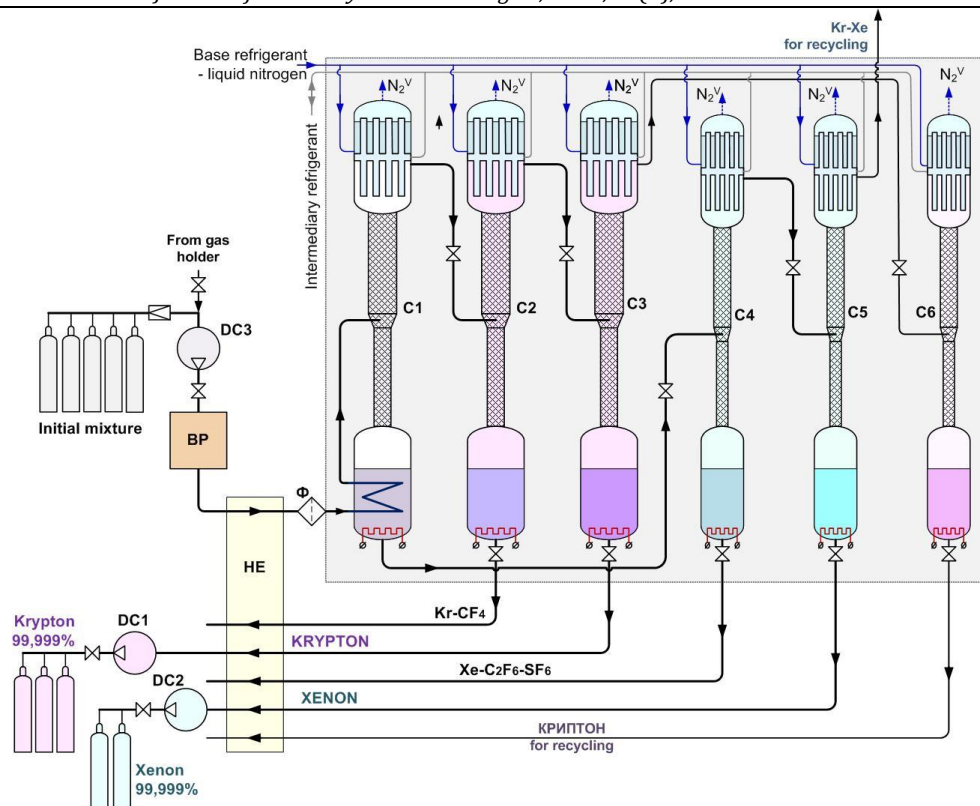
Fig. 3. Simplified installation diagram for obtaining extremely pure Kr and Xe from a krypton-xenon mixture by the rectification method. Designations: C1-C6 – packed distillation columns; AG-1-AG-3 – membrane compressors; BO – hydrocarbon and nitrous oxide removal unit; TO – heat exchanger-recuperator; F – filter

Conversion of tetrafluoromethane upon contact with a nickel surface begins at temperatures above 910 °C, and the specific energy consumption for implementing the proposed method is 5 kW h/kg CF_4. In addition to high energy consumption, additional impurities in the form of reaction products and water vapor will appear in the mixture, which, accordingly, will require the creation of additional purification steps.

Let us consider the results of experimental studies on the purification of a krypton-xenon mixture with active aluminum oxide grade F2 given in [26]. Parameters of catalyst granules: length – 4...25 mm, diameter – 4...6 mm, bulk density – 550...750 kg/m³.

The authors of [1; 2; 7; 26] propose using a cheaper combustion method using catalysts (active copper oxide, magnesium or aluminum oxide). This method allows you to significantly reduce the reaction temperature (up to 400...600 °C), accordingly reducing operating costs for cleaning.

A krypton-xenon mixture containing tetrafluoromethane 133 ppm and sulfur hexafluoride 23 ppm was subjected to purification. The interaction process is described by reactions:

$$3CF_4 + 2Al_2O_3 = 4AlF_3 + 3CO_2,$$
$$6SF_6 + 6Al_2O_3 = 2S_3O_8 + 12AlF_3 + O_2. \quad (2)$$
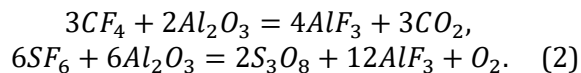
The volume of the catalyst was 40 dm³, the power of the heater located on the walls of the reactor was 3.5 kW. Gaseous reaction products were retained in a series adsorber.

One of the reaction products is solid aluminum trifluoride, which accumulates in the reactor during the purification process. The result was a reduction in impurity content to 0.1 ppm.

The advantages of the method of catalytic oxidation of perfluorides described above are simplicity, minimal loss of product and fairly low specific energy consumption while ensuring a given degree of purification. The main disadvantage: periodic replacement of the catalyst is required.

The Kr and Xe production system (Fig. 4) [7], implementing technology [27], is designed for the simultaneous production of high-purity products from Kr-Xe, Kr-N_2 and Xe-N_2 mixtures. Regarding [27], the installation is supplemented with units

for purification of fluorocarbons and hydrocarbons.

A special feature of the cooling system is the use of a cascade circuit based on liquid nitrogen supplied from a tank. The intermediary refrigerant is nitrogen.

Purification of the mixture from hydrocarbons (methane, ethane, etc.), fluorine-containing compounds (tetrafluoromethane, sulfur hexafluoride, hexafluoroethane) is carried out using a chemical (BOF and BVU, Fig. 4) method; from moisture and carbon dioxide - by adsorption. Separation of the pre-purified krypton-xenon mixture to produce krypton and xenon is carried out by low-temperature rectification.

Let us dwell on the results of experiments on obtaining xenon with a purity of more than 99.9995 % [4].

The installation can be operated in two modes: cyclic and continuous. The cyclic mode provides for the accumulation of xenon concentrate in the cube of the first column to a level of 85...90 % at a temperature of 172...176 K and, then, pressing the accumulated concentrate into the third column, and then its further conditioning at temperatures of 177... 180 K in the cube of the third column. At the same time, as practice has shown, the concentration of the main impurity, krypton, cannot be reduced below 0.5...1.0 ppm. This is due to the presence of dead-end spaces (all kinds of leads to level sensors, differential pressure, etc.), caused by the design features of distillation columns. Continuous operation improves the purity of xenon by gradually washing out impurities from dead-end pipelines.
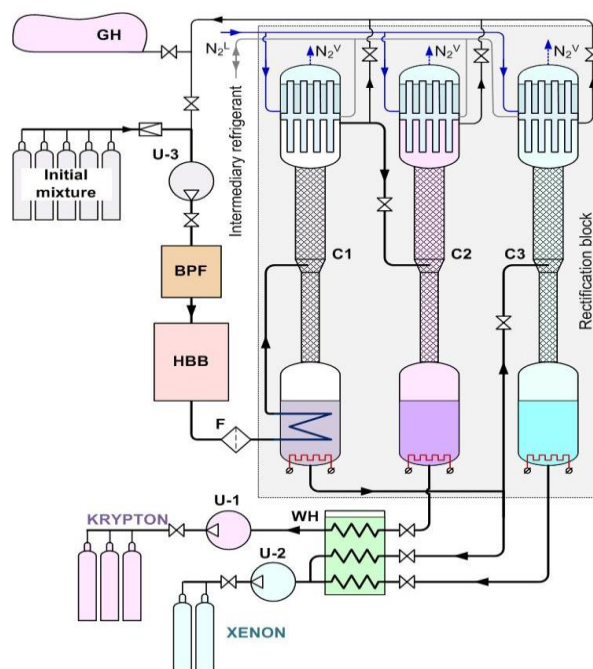

Fig. 4. Simplified diagram of the installation for the separation of mixtures containing krypton and xenon: C1, C2 and C3 – packed distillation columns; BOF – freon removal unit; BVU – unit for burning hydrocarbons and purifying combustion products; AG-1, AG-2 and AG-3 – membrane compressors; GM – soft gas holder; WH – water heater; F – filter

During operation, after a few hours the concentration of krypton in xenon drops to 0.1 ppm. It should be noted that for the operator, continuous operation is much more difficult than cyclic operation. He has to coordinate the work of three distillation columns with each other in terms of costs and at the same time maintain the specified modes in each column separately, which requires extraordinary skill.

The result of research on the first critical impurity (krypton) was the level of 10 ppb of krypton in xenon obtained in 2010; the experiment was repeated in 2011. A krypton content of 3 ppb was achieved. The maximum achievable concentration of krypton in xenon is 1 ppb.

As a result of the research, it was concluded that further improvement of xenon production quality requires significant modification of the existing xenon column design. In this case, all dead-end

spaces will need to be made flow-through, and to reduce losses, the waste lines will need to be led into a common freezer.

Studies on the removal of the second critical impurity – hexafluoroethane – have shown that C_2F_6 is not completely burned out in the freon removal unit (Fig. 3, Fig. 4, d) and in microconcentrations (less than 0.1 ppm) enters the separation unit, where it is enriched in the cube of the first and third columns to concentrations of 1...3 ppm. It has been established that the hexafluoroethane content in the product is directly proportional to the volume of the processed batch of krypton-xenon mixture.

Conducted studies [4] have shown that condensation and chemical methods are promising methods for purifying krypton and xenon mixtures from fluorine-containing impurities. They provide the specified quality of gas products and a high degree of recovery. The final choice of cleaning method is determined not only by technical, but also by economic indicators.

The complexity of purification from fluorides is caused not only by the peculiarities of the thermophysical properties of binary mixtures Kr-CF_4, Xe-C_2F_6 and Xe-SF_6, but also by the accepted sequence of operations in the technologies for producing krypton and xenon. As a rule, regardless of the type of technology being implemented, purification units for perfluorides and sulfur hexafluoride are included in the installations that complete the process of producing high-purity krypton and xenon.

Conclusion

The technology for producing inert gases is constantly being improved. The main criteria for evaluating devices included in the technological sequence for the production of krypton and xenon are the specific energy consumption for the production of products of a given quality. Research has shown that:

– in the process of obtaining clean gas products, manufacturers are faced with the problem of accumulation of microimpurities, the sources of which are atmospheric air;

– according to the complexity of purification, these impurities can be divided into three categories: hydrocarbons, carbon and nitrogen oxides, fluorine-containing components;

– hydrocarbons, as a rule, are removed by chemical methods, followed by sorption purification from carbon oxides and other reaction products;

– krypton – and xenon-containing gases can be simultaneously purified from CnHm and CO_2 from nitrogen oxides by catalytic decomposition using an appropriate catalyst;

– purification from fluorine-containing impurities is possible using absorption, condensation and chemical methods, however, only when implementing rectification and chemical methods the degree of extraction of inert gases exceeds 95 %;

– it is rational to include units for purification from hydrocarbons, carbon dioxide and nitrogen oxides in all installations included in the technological sequence for producing pure inert gases;

– regardless of the type of technology being implemented, purification from perfluorides and sulfur hexafluoride is organized at the final stage of obtaining high-purity krypton and xenon.

The results of the study of the patterns of purification of krypton- and xenon-containing mixtures from microimpurities presented in this work will allow us to correctly organize the purification process depending on the category of impurity, select the least expensive methods for obtaining gas products, and also take into account the above at the design stage of new installations.

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