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ANALYSIS OF ENVIRONMENTAL, LEGISLATIVE AND TECHNOLOGICAL ASPECTS OF THE CHOICE OF NON-AQUEOUS WORKING BODIES FOR POWER PLANTS

Представлено варіант вирішення завдання вибору робочого тіла з урахуванням обмежень Монреальського і Кіотського протоколів для теплосилового контуру енергетичних установок на наведених робочих речовинах з можливістю значного підвищення енергоефективності циклу і безпеки експлуатації установок. Для фторуглеродних робочих тіл і SF6 виявлено невідповідність на чотири порядки величини для критерію Lifetime, отриманого за даними IPCC-13, що дає підставу для їх застосування без обмежень, зазначених у Кіотському протоколі.

Ключові слова: *енергетична установка, робочі тіла енергетичних циклів, стабільність речовин, гексафторид сірки.*

1. Introduction

Working substances of synthetic and natural origin (including freons) have been used for more than half a century in power plants of small and medium power in small and distributed power systems. The range of the proposed substances is very diverse and wide: these are carbon dioxide, and aqueous solutions of ammonia, and hydrocarbons, and inert gases, and organofluorine compounds. Based on the results of recent research, the authors formulate a number of technical proposals for the introduction of organofluorine working substances into the heat-power circuit of fast neutron nuclear facilities with a liquid metal coolant.

A wide range of limiting national and international conditions for human and environmental safety, as well as requirements for energy efficiency, manufacturability and reliability of systems, in setting this multifactorial task made it expedient and justified to use a systematic approach to its successful solution. This means a priority for investigating the relationship between the arguments, while not rejecting the evaluation of the validity of the arguments themselves.

When solving the task of selecting working bodies today, in addition to sanitary, legislative and technological restrictions, the issues of validity of environmental restrictions also come to the fore. Therefore, the work will analyze the material balances of the presence of «greenhouse» substances in the Earth's atmosphere and take into account industrial and natural emissions during certain periods of time. It will also be shown that the provisions on which international agreements on the limitation of «greenhouse» substances, fixed in the Kyoto Protocol and the Paris Agreements, are groundless (and, therefore, invalid).

2. The object of research and its technological audit

The object of research is fluorocarbons and SF_6 gas (sulfur hexafluoride) as working bodies of power plants.

The working fluid selected for the power plant must have favorable chemical, physical and operational properties under the specified operating conditions, that is, be stable, non-flammable, explosion-proof, non-toxic, inert to construction materials. However, after the adoption of the restrictions of the Montreal and Kyoto protocols, the development of converters of thermal energy into electric power in the sphere of small-scale power engineering is now based on the use of hydrocarbons. It is clear that their main drawback is flammability, explosiveness and low thermal stability. Such facilities are limited by the temperatures of the recycled streams to 290 °C and have, in addition to the turbine, an additional circuit with a heat-resistant liquid (oil) and an intermediate heat exchanger, which affects the efficiency of the entire system. In the authors' opinion, the expansion of the temperature range of the use of non-aqueous working bodies, the increase in the energy efficiency of heat-power converters can be achieved through the use of precisely fluorocarbons and SF_6 gas. The high thermodynamic efficiency of the use of these substances for power plants with binary cycles was noted back in the 60s of the last century [1], since they possess physical, chemical and operational properties that are favorable for this purpose. In addition, these substances are stable, non-flammable, non-explosive, non-toxic substances, inert to construction materials. They can with good reason be attributed to relatively «young» and little-studied substances. Fluorocarbons were synthesized by J. Simons in the USA in the late 1930s, and SF_6 was synthesized by Moissan and Lebeau in France in 1900 [2]. The technology of industrial production and the profound study of the properties of these substances in the world began only after the World War II. A serious disadvantage of fluorocarbons and SF_6 gas is a relatively high price, since their molecule is 70–85 % composed of non-expensive fluorine. For this reason, in the 1980s, fluorocarbons were 5–10 times more expensive than chlorine-containing freons R-11 and R-12. SF_6 at that time was about three times more expensive than Freon-12.

Fluorocarbon substances, especially octafluoropropane (C_3F_8) and decafluorobutane (C_4F_{10}), are of particular interest from the standpoint of the possibility of using them as a working fluid (instead of water) in turbine cycles of conversion of thermal energy to electric for prospective nuclear power plants [3]. The schematic diagram of a heat-power circuit when introducing these substances as working substances in comparison with steam-water is much simpler (Fig. 1).

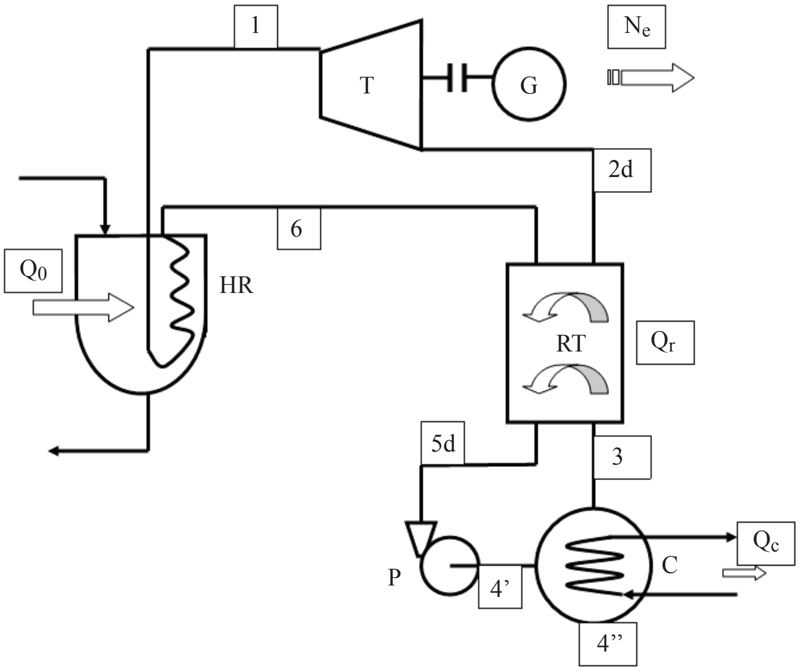

Fig. 1. Schematic diagram of a fast neutron reactor facility:
HR – heat exchanger of the reactor with thermal power Q_0; *T* – turbine; *G* – generator, generating electric power N_e; *RT* – regenerative heat exchanger with thermal power Q_r; *C* – condenser of thermal power Q_c; *P* – pump

Particular importance has the fact that, due to the particular configuration of the thermodynamic supercritical cycle on fluorocarbon working bodies (FWB), a high share of heat recovery is provided (in the likeness of gas-turbine cycles). In addition, the high average integral heat input temperature and high return temperature of the FWB are beneficial for the reactor unit (RU) with liquid-metal coolants (lead and sodium). At the same time, the compression process takes place in the liquid region and is realized by pumps, which is much more efficient in comparison with gas cycles and compressor compression. The problem of ensuring the temperature of feed water above the solidification temperature of lead (329 °C) is solved. It is also clear that the FWB introduction is promising for the RU with sodium coolant of the primary circuit (BN-600), since it guarantees the prevention of chemical interaction.

The configuration of the supercritical cycle on the FWB is shown in Fig. 2. The high average integral temperature of the heat input and the degree of regeneration are provided by the high temperature at the exhaust of the turbine (2d), by the low parameters of the critical point (K).

As calculations have shown, when using a FWB, the required level of thermodynamic efficiency is reached at a pressure of 6 to 10 MPa (for water up to 24 MPa), which positively affects the safety of the reactor plant without reducing the efficiency. In the indicated range of pressures and temperatures up to 550 °C there is an optimum pressure value at which the cycle efficiency is maximal and reaches 50 %. A small excess pressure in the condenser guarantees the absence of suction cups of the cooling medium and creates the prerequisites for the use of standard plate heat exchangers and the use of air fan cooling towers. The low freezing temperature of fluorocarbons allows one to design the condensation process also at negative temperatures.

Particular mention should be made of the thermal stability of fluorocarbons. When heated, their decomposition begins at temperatures of 400–600 °C [4] and higher, since the C–F bond has almost record dissociation energy of 485 kJ/mol [5]. Although an important condition for the stability of the molecule upon heating was and remains the influence of the catalysts upon heating.

Of the technological properties of fluorocarbons, it is also necessary to note the corrosive and fire-fighting properties. Metal fluorides formed on heating on their surfaces in contact with the products of destruction of fluorocarbons are firmly adhered to the surface of metals and are a kind of barrier for the development of deep corrosion.

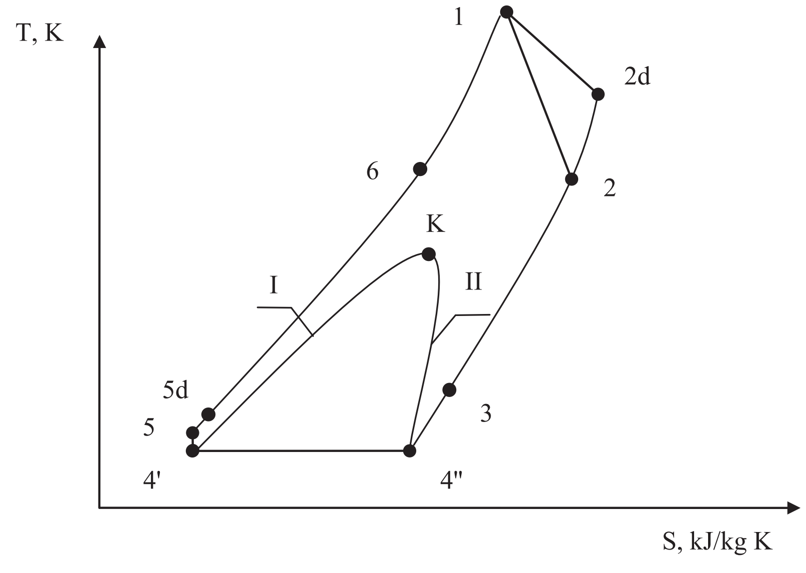

Fig. 2. The configuration of the supercritical cycle on the FWB:
I – the condensation line; II – the boiling line; K – a critical point; 1–2 and 1–2d – theoretical and actual expansion processes in the turbine; 2–3 – the process of FWB cooling in the regenerator; 4–5 and 4–5d – theoretical and actual compression processes in the pump; 5d–6 – the process of FWB heating in the regenerator; 6–1 – heating process in front of the turbine; 4′–4″ – condensation process

This effect is called passivation of the surface by fluorine. Exceptions are silicon and tungsten, which form gaseous compounds upon reaction with fluorine-ion. For this reason, steels containing silicon and tungsten in the ligature are not recommended for use in contact with fluorides during heating or in arc chambers of high-voltage apparatus with SF_6 gas [6].

The fire-retardant properties of fluorocarbons and SF_6 gas, more precisely – the properties of flame retardation, are also associated with the exceptional stability of the molecules of these substances during heating. The extinguishing concentration of the most known fluorocarbons R-218 (C_3F_8) is 8.6 % by volume, R-c318 (c-C_4F_8) – 7.5 % by volume. SF_6 has a 9 % vol. It is important to note that their upper and lower limits of cardiotoxicity (NOAEL and LOAEL) are 3–4 times higher than the extinguishing concentration. This is an important advantage for a person who finds himself in a fire extinguishing zone. For this reason, they are successfully used in automatic fire extinguishing systems for closed volumes [7].

With undoubted thermodynamic efficiency and zero ozone-depleting potential ($ODP=0$), fluorocarbons and SF_6 gas are classified by climatologists to so-called «greenhouse» gases. According to the International Panel of Independent Experts on Climate Change (IPCC) published in IPCC-94, fluorocarbons were given an extremely long life in the atmosphere (up to 50,000 years!), without presentation of the calculation methodology. The issue of the lifetime of these substances in the atmosphere has become today a key one, and the lifetime estimates for fluorocarbons given in the IPCC reports (IPCC-94, IPCC-2013) raise reasonable doubts about their reliability.

3. The aim and objectives of research

The aim of the research is an experimental study of the properties of fluorocarbons and SF_6 gas in order to obtain the missing data to perform a system analysis to determine the prospects, especially fluorocarbons, as working bodies of energy cycles.

At the same time it is necessary to solve the following applied tasks:

1. To determine the true values of the lifetime of fluorocarbons in the atmosphere on the basis of official data on the time variations in the concentrations of fluorocarbons in the Earth's atmosphere and known data on the emission of fluorocarbons.
2. To determine the limits of the temperature stability of fluorocarbons in contact with structural materials characteristic of a real turbine cycle.
3. To determine the stability of fluorocarbons to the radiation impact of different types of radiation, characteristic of the second circuit of the nuclear power plant.
4. To determine the most universal and reliable parameter for the onset of destruction of fluorocarbons in the case of thermal and radiation effects.

4. Research of existing solutions of the problem

The problem of choosing working bodies of energy cycles was considered earlier in [8, 9]. However, the studies were conducted in the «pre-Montreal era», and these works did not address the hypothesis of the causes of the death of stratospheric ozone and the emergence of global warming, as well as the limitations of the Paris Agreement. To date, it can be stated that there are statutory prohibitions on the use of chlorine-containing working bodies under the Montreal Protocol, and recommendatory in restricting the application in accordance with the provisions of the Kyoto Protocol for working bodies with a long life in the atmosphere. The Paris agreement is currently still a unifying document based on two hypotheses, and does not abolish the accepted restrictions.

It is also important to note the fact that in the absence of alternatives, the use of stable and long-lived fluorocarbons and SF_6 gas in the firefighting task became a completely permissible fact and did not cause condemnation of «fighters» with global warming, since it is a matter of directly protecting human life in extinguishing fire, i. e., on the constitutional priority of any country – a guarantee of the safety of human life.

In the general assessment, the problem of deciding on the choice of the working body of the energy cycles is extremely complex and ambiguous. When solving it, it is necessary to take into account the current legislative and medical restrictions of the national and international level. Thus it is necessary to consider four kinds of dangers for the person (toxic, fire, brisant and radiation), to take into account the costs of the consumer and the producer, and also to guarantee the reliability of energy systems and the availability of raw materials. In total, there may be at least 100 combinations of different connections that determine the possibility of using the proposed working bodies.

The most difficult in the forecast are the restrictions adopted at the international level, since they are of a political nature and vary according to the laws of world politics. These restrictions largely do not comply with the norms of Civil and Labor Rights. This was typical for the period 1990–2010 for the Montreal and Kyoto Protocols. However, the prohibitions and limitations of both protocols on the use of working bodies are not always unambiguous in comparing the early and late data in the reports of the IPCC (International Panel of Experts on Climate Change).

In the fifth IPCC-2013 report [6], data on the actual concentrations of working bodies in the Earth's atmosphere appeared. According to these data, it has now become possible to calculate the real lifetimes of working bodies in the atmosphere over a twenty-year period. On the basis of calculations, some of the substances can now be reasonably and effectively used in energy cycles in place of previously prohibited substances on the basis of ozone hazard. Banned, as is known, include chlorine and bromine-containing freons, some of which were used in turbine cycles in the 60–70s of the last century.

Having carried out a comparative analysis of the operating conditions of the working fluid in the turbine cycle, it is possible, based on the published conclusions of the authors [8, 9], to formulate the basic requirements for the working body of the turbine cycle. These requirements, in addition to thermodynamic perfection, will provide a number of other requirements that inevitably arise when using working bodies in different cycles.

The general necessary properties of any working bodies is a triad of safety for man, machine and environment, that is, the working medium must be stable, non-toxic, non-flammable, corrosion-passive and neutral in relation to the environment throughout the entire operational period. A consequence of these basic properties is the stability of the composition of the working fluid under the effects it experiences under the operating conditions of the turbine cycle, as well as the absence of the possibility of explosive and radiation-hazardous degradation products.

It is necessary to pay tribute to the requirements for the protection of the Earth's atmosphere, which arose on the basis of the 1985 Vienna Convention for the Protection of the Ozone layer. Despite the existence of twenty hypotheses on the death of stratospheric ozone [10], in addition to the current Molina-Rowland hypothesis [11], and the significant political background of these constraints, as well as the lack of accurate data for the reasons for the discussed effects, the interstate level of obligations under prohibitions on the use of chlorine and bromine-containing working bodies obliges them to be excluded from consideration as working bodies, at least until the true causes of the death of stratospheric ozone are clarified.

The second group of restrictions on the use of substances as working bodies arose after 1992 on the basis of the Framework Convention on Climate Change (FCCC) on the basis of the Fourier-Tyndall hypothesis, which arose more than a hundred and fifty years ago. The hypothesis has not been fully confirmed with regard to the global nature of its impact on the Earth's climate. The key parameter of the imposed restrictions is lifetime, i. e., the lifetime of the gas phase of this substance in the Earth's atmosphere. First, data on the lifetime of the main gaseous components of the earth's atmosphere were given in the IPCC-94 report in the form of estimated values, accompanied by the measured concentrations of these gases as of 1992 [12]. This was done because of the extreme complexity of the forecast of global atmospheric processes, and therefore the method of reliable calculation of this magnitude can't be performed in principle. The new data of IPCC-2013 on the concentration of industrial gases in the atmosphere for 2005 and 2011 [6], made it possible to accurately determine the Lifetime of technically important gases for which the emission values of these substances are known in the specified period.

The main condition for the precise definition of lifetime is the precise knowledge of the emission of anthropogenic, that is, man-made, greenhouse gases. These include gases such as SF_6, CF_4 and Freon R-22 (CF_2ClH). It should be noted that significant changes in the mass balances of atmospheric fluorine-containing gases are made by volcanoes, which emit them in significant amounts, both during periodic active eruptions, and constantly in the form of fumarolic gases near volcanoes. At the same time, the dynamics of volcanic emissions remains outside the forecast and introduces a significant error in the accuracy of the calculation of mass balances, on the basis of which it is already possible to determine the real lifetimes of «greenhouse» gases.

According to IPCC-94, the record-breaking «long-lived atmospheres» proved to be the safest for human and the environment, ozone-friendly, that is, containing no chlorine and bromine molecules in the homologous series of fluorocarbons C_nF_{2n+2} and sulfur hexafluoride (SF_6), which in Russia since 1938 years are called elegas, i. e., electrotechnical gas. These technical gases are exceptionally stable under heating conditions in the absence of a catalyst, which is silicon. But even in the presence of silicon, the thermal stability of CF_4 and its homologues C_nF_{2n+2} is 400 to 600 °C and higher [4].

For SF_6, thermal stability in the absence of moisture can also be estimated at 400 °C. In the presence of moisture, it decreases to 200–250 °C [13]. Apparently, the exceptional thermal stability of fluorocarbons and the exceptional recombination properties of SF_6 gas during arc extinguishing in electrical apparatuses, and served as the basis for assessing their longevity in the Earth's atmosphere according to IPCC-94.

However, the conditions of «life» of gases in the atmosphere are determined not so much by heating from solar radiation, as by the action of lightning discharges. On this topic in the Russian scientific press are known works [14, 15]. The main conclusion of these works was the conclusion about the role of lightning discharges as «atmosphere cleaners» from non-basic atmospheric gases, in particular hydrocarbons over the oil fields of Azerbaijan. The main gases in the Earth's atmosphere at that time were nitrogen, oxygen and argon. Non-basic – all the others, which today are called greenhouse. It should be noted that research on the effect of lightning discharges on atmospheric gases was published at the beginning of the last century. In 1906, the author of [16] proposed a two-stage scheme for the electrical effect of a lightning discharge in the atmosphere. Lightning refers to the spark discharge, which is preceded by the ionization of atmospheric gases in the area of the thunderstorm action. The ionization energy of almost all atmospheric gases lies in the range from 11.1 eV (for CCl_4) to 24.6 eV (for He). For Ar, N_2, CF_4, SF_6, CO_2 and CO, the ionization energy is in the range from 14 to 16 eV. For this reason, during the ionization period preceding the thunderstorm discharge, practically all atmospheric gases are ionized. In the theory of spark discharge, this stage is called the leader stage. The ionized and well-conducting gas channel has a radius of 2.5 m and the head current of the leader of the lightning 320 A [17]. Even with a small lead channel length of 1 km, even before the formation of the main lightning channel, at a thunderstorm ionizes about 25 tons of air.

The formation of the main lightning channel occurs in the second stage of exposure. The current increases to 40000 A and the discharge time is 50–100 microseconds. The impulse nature of the effect is observed with the formation of a plasma pinch, which is accompanied by the destruction of charged molecules with their subsequent recombination and the formation of new compounds other than the original ones. The molecules of gases that fall in the zone of action during a spark discharge are destroyed with the formation of radicals and fragments of destroyed molecules. Then they undergo recombination, as evidenced by the afterglow of a discharge gap of about 1000 μs duration. If there is only one gas in the spark discharge zone and there is no moisture and oxygen, a high degree of recombination is possible. For the conditions of the earth's atmosphere, such combination of circumstances is impossible, so the fragments of non-main gases combine with other radicals and assume new forms without returning to the previous form. This effect gave the author of the works [14, 15] the name of lightning discharges as «atmosphere cleaners». It should be taken into account that during the year at least 3 billion lightning discharges occur in the Earth's atmosphere. Let's note that almost complete recombination of the SF_6 dielectric gas is observed only in high-voltage switches filled exclusively with pure SF_6. It can be argued that for the main atmospheric gases (nitrogen and oxygen) the probability of recombination is much higher than for non-main, «greenhouse» gases, which have insignificant concentration.

Atmospheric air is also used as an oxidant in internal combustion engines, in boilers of thermal power plants and in aircraft engines. Thus, oxidizing hydrocarbons, the whole composition of atmospheric air undergoes short-term heating to a temperature above 1000 °C. Taking into account the mass of combustible hydrocarbon fuel in the world at the level of 6 billion tons per year, it is possible to estimate the amount of air that passed through the combustion chamber and the combustion chamber in 60 billion tons. This excess of air over the amount of fuel follows from the fact that oxygen in the air is only 20 %, and hydrocarbons are light, but there are also heavy, for example, diesel fuel and fuel oil. And they require large air consumption during combustion. At the same time, due to heating, practically all air impurities undergo changes, and the former «life» of gas molecules «changes beyond recognition», since air humidity and the presence of catalysts in the combustion zone play a big role in their destruction.

Rarely mentioned destroyer of the integrity of the molecules of the Earth's atmosphere is cosmic radiation and the «solar wind», which enters through the polar cusps and leaves its mark in the form of northern lights.

It is clear that such set of destructors of the integrity of the molecules of the non-main gases of the earth's atmosphere will not give an opportunity to estimate the true values of the lifetime of greenhouse gases. For this reason, the method of reliable determination of Lifetime never appeared.

Published IPCC-2013 data [6] put everything in its place. According to the IPCC-2013 table data for six years (from 2005 to 2011), a slight decrease in concentrations was noted only for chlorine-containing freons (CFCs). Hydrofluorocarbons (HFCs) increased their concentrations, as they took over the refrigerated park, which remained without R-11 and R-12 freons.

Freon-22 gave the largest increase (by 22 %, i. e., by 4.3 % per year), that is, in the absolute value for the year at least 7.3 ppt, which corresponds to the entry into the atmosphere of 105 thousand tons of freon-22. To release such quantity of freon-22 into the atmosphere for a year is rather difficult, even if it was used exclusively in semi-hermetic refrigerating units with a maximum leakage level of 15 % per year from the mass of fueling. In fact, the proportion of semi-hermetic machines with a leakage level of 15 % is negligible, compared to normally operated hermetic units with refrigerant leaks of 0.5–1 %. The reason for such high growth values of freon-22 concentrations in the atmosphere is volcanic activity. Moreover, the data on the concentration of freon-22 in the air above the Sea of Okhotsk at a level do not show 1000 ppm [18].

Given the fact of the constant volcanic activity of about 30 volcanoes in Kamchatka alone, it can be confidently asserted that the abnormal increase in the concentration of freon-22, noted in IPCC-2013, is largely due to volcanic activity.

The most interesting are the inconsistencies for the concentrations of CF_4 in the atmosphere indicated in IPCC-2013. The mass balances of this gas can be well monitored by the emissions of this gas in the production of aluminum, since there are practically no other sources, the feed of pure fluorine production. The reason is that since 1900, the world uses an unchanged fluorine technology of aluminum production. At the same time, for every ton of produced primary aluminum, 50 kg of CF_4 is emitted into the atmosphere, which is exclusively inert and not toxic, therefore, before the Kyoto Protocol was introduced, the task of capturing it was not. From the exhaust gases only toxic and dangerous gases were removed. But even later, with the advent of the problem of greenhouse gases, it is not possible to find a sorbent for the collection and disposal of CF_4. As a result, mass balances for CF_4 can be easily verified from the world's primary aluminum production.

The concentration of CF_4 in the atmosphere in 1992 according to IPCC-94 [12] is 70 ppt, i. e. $70 \cdot 10^{-12}$ volume fractions. The declared concentration of 70 ppm in the Earth's atmosphere is provided by 1 Mt of CF_4, which is formed when 20 Mt of aluminum is produced. Knowing its density in the gaseous state under normal conditions of 3.62 g/l, let's find that 1 Mt of CF_4 corresponds to $276 \cdot 10^6$ m^3 of the gas phase.

The weight of the earth's atmosphere is $5.085 \cdot 10^{15}$ tons. With an air density of 1.275 kg/m^3, let's obtain that the air volume of the Earth is $3.98 \cdot 10^{18}$ m^3. Let's divide the volume of 1 Mt of CF_4 by the volume of the Earth's air. Let's obtain $69.2 \cdot 10^{-12}$ vol., i. e. the declared IPCC-94 concentration of CF_4 as of 1992.

Since 1 Mt of CF_4 is produced in the production of 20 Mt of aluminum, let's conclude that when the life time in the atmosphere for CF_4 stated in IPCC-94 was 50,000 years, the concentration of 70 ppt was passed in 1960, when the total volume produced in the world of aluminum reached 20 Mt.

By 2010, the volume of aluminum produced in the world reached 900 Mt, which according to CF_4 emissions into the atmosphere was 43.5 Mt, and by concentration in the atmosphere of 3010 ppt, i. e., 3.01 ppb. However, this level could only be achieved if the atmospheric lifetime for CF_4 is at least 60 years. But in 2011, according to the IPCC-2013 data, CF_4 concentration in the atmosphere was 79 ppt, which determines the validity of life from 1 to 2 years.

Atmospheric electricity and lightning discharges, judging by the works of the last century, do not give a chance for a long «life» in the atmosphere for this inert connection.

For SF_6, mass balances also confirm the possible presence of a non-anthropogenic source. Although IPCC-2013 data on atmospheric concentration for SF_6 for 1962 are not specified, but its concentration in 2005 (5.64 ppt) and in 2011 (7.28 ppt) allow to make balance calculations.

In the mid-1990s, the annual emission of SF_6 gas with its leakage from high-voltage apparatus was estimated at 7 to 10 thousand tons. If follow these primary estimates, when 90 % of all SF_6 gas was in high-voltage switches and switchgear (GIS), then at a leakage level SF_6 gas from apparatuses 1–2 %/year, their refueling would average 660 thousand tons in operating vehicles, which is clearly overstated. This amount of SF_6 gas has not yet been filled in the apparatus. Although several large high-voltage substations with SF_6 have already been in operation.

For example, a very large SF_6 substation of the Oskol Electro-Metallurgical Combine (97 GIS cells of the SF_6

at 110–330 kV) had only 25 tons of SF_6 in the filling stations. This substation commutes an annual electricity volume of at least 2 billion kWh, or about 1/10,000 of the world's electricity production. Even if all the electricity produced in the world is switched by SF_6 circuit-breakers, the volume of refueling will be at the level of 250 thousand tons. It should be noted that since 2000, the SF_6 gas-insulated substations in the world have reduced the amount of SF_6 leakage from the apparatus to the atmosphere from 1–2 % 1 % per year. Since 2000, the total amount of SF_6 leaks per year has not exceeded 250–500 tons. This is the maximum amount of emissions that could be in the range of 1500–3000 tons for 6 years (2005–2011) or for gas $(2.37–4.74)\cdot10^5$ m^3. When referring to the volume of the Earth's atmosphere, let's obtain 0.06–0.11 ppt volume fractions, which is an order of magnitude smaller than the measured difference, by the 1.64 ppt wound specified in the IPCC. It should be noted that this difference in concentrations of 1.64 ppt, quite accurately corresponds to the emission of SF_6 in the volume of 7000 tons/year, declared in the mid-90's.

As in the previous case, mass balances do not coincide with the measured concentrations. Therefore, a more powerful source of non-anthropogenic SF_6 gas is quite possible. In volcanic gases, SF_6 is reliably detected and volcanoes undoubtedly contribute significantly to mass balances for this compound.

Real lifetime data derived from material balances are taken from fluorocarbons and other fluorine-containing volcanic gases, a greenhouse effect limitation that has existed since 1994 because of the IPCC-94 estimated Lifetime estimates for fluorocarbons and SF6 in the atmosphere. At the same time, the fact that CF_4, the most stable fluorocarbon, is overestimated in IPCC-94 is undoubtedly true. Based on calculations based on material balances, it lives in the atmosphere for no more than two years. A similar conclusion follows also from the data on the impurity CF_4 in xenon and krypton obtained on rectification columns in the production of oxygen from atmospheric air, which was reported back in 1995 [19].

The reason for such discrepancy between the results of calculations and material balances for measured concentrations can only be the methodology of the Lifetime assessment that was adopted in the 1990s, never published anywhere.

If from the physical model of the method of calculating the lifetime of a gas molecule in the atmosphere to exclude the effect of lightning discharges, leaving only thermal effects and ultraviolet radiation of the Sun, the gas molecules will live in the atmosphere only depending on the known dissociation energy. This does not take into account the impulse nature of the main source of impact – lightning discharges. It is possible that in the IPCC-94 forecast, only for this reason CF_4 became the record holder for life expectancy in the atmosphere, since it has a very high dissociation energy of 485 kJ/mol. Above only in HF (565 kJ/mol) [5].

When considering the influence of lightning discharges on the gas components of air, the picture changes significantly. As is known, a lightning discharge is a fairly powerful spark discharge having a steep front with duration of 1–10 μs, with a total discharge time of 50–100 μs. That is, the nature of the impact is of a pulsed nature and for the destruction of the molecule, enough energy is several orders of magnitude lower than under thermal action. Therefore, practically all gas molecules from the air composition that fall into the discharge zone are destroyed to the same degree and only a small part of them recombine to the former composition. The bulk of the destroyed molecules reacts with neighboring radicals and forms new compounds. Considering that thunderstorms on Earth are at least three billion a year, the rightly known statement that thunderstorms are «atmosphere cleaners» is true. This fundamentally changes the meaning of the limitations on the greenhouse effect on the basis of Lifetime, which existed since 1994 due to the estimated value of the lifetime of various gases in the atmosphere published in IPCC-94. The IPCC-2013 data is now sufficient to justify the life time correction for the gases mentioned above. The above calculations provide a basis for correcting the lifetime of fluorocarbons and SF_6 gas. At the same time, they open the way for serious studies of the technological properties of fluorocarbons and SF_6 gas, taking into account the possible prospects for their use as working bodies of energy cycles. There is no doubt that the effects of their use as working bodies are quite significant and for the industrial energy industry the prospect of using these substances has every reason.

5. Methods of research

Investigation of technological properties of fluorocarbon working bodies. By technological properties, among other properties, we mean the stability of the working fluid under various effects in a real thermodynamic cycle. In this case, the study of the properties of the working fluid is also carried out under conditions that are as close as possible to the real.

An important role in the choice of the object of research is played by the availability of data on its thermophysical properties. Fluorine-containing compounds have been studied in sufficient detail, however, data for long-term corrosion resistance at high temperatures and stability under the action of ionizing radiation are clearly not enough for them. For working bodies of TPPs and NPPs, these data are needed in a wide range of conditions for their application.

At the initial stage of the research, it is necessary to expand the range of knowledge on the corrosive effects on structural materials at an exposure of 1.5–2 h at temperatures of 400–600 °C, since the published data on the thermostability of fluorocarbons are given for 10 s exposure to Ni [4].

The study of the continuous thermal action is carried out in a steel sealed capsule with a volume of 200 cm^3, placed in a muffle furnace. Fig. 3 shows the scheme of connection of the capsule to the mass spectrometer and placement of thermocouples on the capsule body placed in the muffle furnace. Fig. 4 shows the arrangement of samples of structural materials inside the capsule. The heating temperature of the capsule body is controlled by three thermocouples. Samples of structural materials were placed inside the capsule. The capsule is filled with the test gas. After heating and holding for a predetermined time (about 2 hours), the capsule is cooled to ambient temperature and connects to a sample feeding system in a MI-1201b mass spectrometer (an isotope mass spectrometer was released in the USSR at the Sumy Electron Microscope

Plant in 1987). The gas sample is recorded in comparison with the recording of the sample of the substance before heating. Based on the results of the comparison, conclusions are drawn about the stability of the gas.

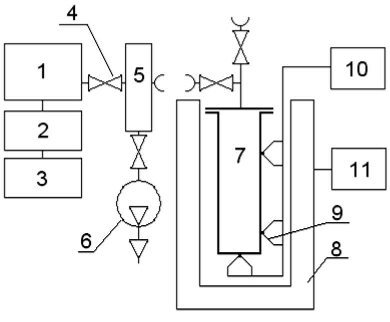

Fig. 3. Scheme of the experimental plant for constant heating: 1 – mass spectrometer; 2 – digital recorder; 3 – computer; 4 – inlet valve; 5 – filling system; 6 – fore vacuum pump; 7 – experimental capsule; 8 – muffle furnace; 9 – thermocouples; 10 – temperature registration unit; 11 – temperature control unit

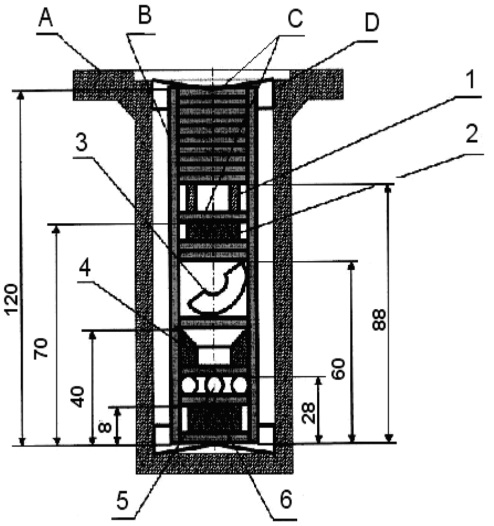

Fig. 4. Scheme of placement of samples in the capsule: A – working part of the experimental capsule (material – Х18Н10Т); B – a tube 30×5 from made of electrotechnical porcelain; C – pads made of porcelain; D – centering element (material – Х18Н10Т); 1 – sample: steel grade 10Х9НСМФБ-Ш; 2 – sample: titanium of grade ОТ2; 3 – sample: steel grade 10Х15Н9С3Б1-Ш; 4 – sample: nickel grade НП2; 5 – steel grade 95Х18-Ш; 6 – steel grade 09Г2С

After recording the samples on a mass spectrometer, the capsule is opened and a visual inspection of the samples of structural materials after contact with the heated fluorocarbon compound is carried out. The nature of the corrosive effect is determined from the color of the material surfaces. Stable materials have weak traces of exposure (in the form of patina). It is nickel НП-2, steel 95Х18, aluminum АД-0. Titanium sharply changes the color of the surface to bright blue, and the steel 09Г2С became blue-black.

The cyclic action is carried out according to the circuit of a closed loop with a circulation pump. Heating and cooling of the gas is carried out in a capillary with an internal diameter of 3 mm. Part of the capillary is placed inside the furnace, and a part in the water heat exchanger, as indicated in Fig. 5.

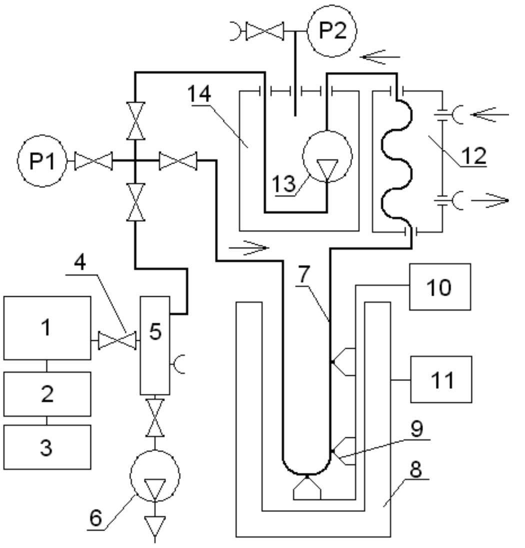

Fig. 5. Diagram of the experimental plant for cyclic heating: 1 – mass spectrometer; 2 – digital recorder; 3 – computer; 4 – inlet valve; 5 – filling system; 6 – fore vacuum pump; 7 – the capillary; 8 – muffle furnace; 9 – thermocouples; 10 – temperature registration unit; 11 – temperature control unit; 12 – heat exchange unit; 13 – circulating pump; 14 – buffer volume

The circulation circuit is connected directly with the mass spectrometer through the sample inlet system, as indicated in Fig. 5. The complete cycle of gas circulation in the loop is 3.5 s. For a day at the stand it is possible to get almost 25 thousand cycles of heating up to 500–600 °C and cooling to 18–20 °C.

In preliminary experiments, ion peak values for the substances studied are obtained and compared with tabulated values under identical ionization conditions. The results are shown in Table 1–4. Deviations are due to the design features of the instruments.

Table 1

The ion peak ratios for octafluoropropane (C_3F_8)

No.	M/e	Ion	Table value %	Experiment 1	Experiment 2	Experiment 3
1	12	C^+	2.40	0.07	0.10	0.09
2	19	F^+	1.00	0.05	0.05	0.07
3	24.5	CF_2^{++}	0.40	0	0	0
4	31	CF^+	28.80	8.34	7.95	8.78
5	36	STP	0.10	0.10	0.07	0.04
6	43	C_2F^+	0.60	0.14	0.15	0.15
7	50	CF_2^+	9.30	3.29	3.39	3.61
8	55	C_3F^+	0.10	0.05	0.07	0.07
9	62	$C_2F_2^+$	0.70	0.33	0.35	0.37
10	65.5	STP	0.10	0	0	0
11	69	CF_3^+	100	100	100	100
12	74	$C_3F_2^+$	0.20	0.10	0.10	0.11
13	75	STP	0.30	0.17	0.15	0.17
14	81	$C_2F_3^+$	0.70	0.50	0.54	0.59
15	93	$C_3F_3^+$	0.60	0.36	0.39	0.22
16	100	$C_2F_4^+$	6.60	6.15	6.20	6.54
17	112	$C_3F_4^+$	0.10	0.02	0.03	0.04
18	119	$C_2F_5^+$	9.00	8.13	8.47	8.32
19	131	$C_3F_5^+$	0.20	0.07	0.10	0.11
20	150	$C_3F_6^+$	0.10	0.02	0	0
21	169	$C_3F_7^+$	24.60	24.69	26.11	25.80

Table 2

The ion peak ratios for decafluorobutane (C_4F_{10})

No.	M/e	Ion	Table value %	Experiment 1	Experiment 2	Experiment 3
1	12	C^+	0.20	0	0.08	0.07
2	19	F^+	0.10	0	0.05	0.05
3	31	CF^+	12.20	5.88	6.05	5.91
4	43	C_2F^+	0.20	0.12	0.08	0.05
5	50	CF_2^+	4.20	2.15	2.15	2.18
6	55	C_3F^+	0.10	0.12	0.10	0.10
7	62	$C_2F_2^+$	0.50	0.39	0.36	0.37
8	69	CF_3^+	100	100	100	100
9	74	$C_3F_2^+$	0.30	0.24	0.23	0.25
10	81	$C_2F_3^+$	0.80	0.64	0.61	0.62
11	93	$C_3F_3^+$	1.20	1.25	1.22	1.22
12	100	$C_2F_4^+$	8.40	6.99	7.24	7.23
13	112	$C_3F_4^+$	0.20	0.24	0.20	0.20
14	119	$C_2F_5^+$	18.30	16.30	16.30	16.50
15	131	$C_3F_5^+$	8.40	13.87	13.74	13.77
16	150	$C_3F_6^+$	2.60	3.93	3.92	3.96
17	169	$C_3F_7^+$	2.10	1.60	1.68	1.68
18	181	$C_4F_7^+$	0.10	0	0.05	0.05
19	219	$C_4F_9^+$	2.60	7.42	7.58	7.73

Table 3

Qualitative change in the ionic composition of C_3F_8

t, °C	Type of heating	Catalyst	C^+	F^+	CF^+	C_2F^+	CF_2^+	C_3F^+	$C_3F_2^+$	SiF_3^+	$C_2F_5^+$	$C_3F_5^+$	$C_3F_6^+$	$C_3F_7^+$
			12	19	31	43	50	55	74	85	119	131	150	169
500	Cyclical	–	–	–	–	–	–	–	–	–	–	–	–	–
570	Cyclical	–	–	–	↑	–	↑	–	–	–	–	↑	–	–
600	Constant	+	–	–	↑	↓	–	↓	–	↑	–	↑	↑	–
620	Constant	+	↑	↑	↑	–	–	↑	–	↑	–	↑	–	↓
630	Cyclical	–	–	↑	↑	–	↑	–	–	–	–	–	–	–
670	Constant	–	↑	↑	↑	–	↑	–	↑	↑	↑	↑	↑	↓

Table 4

Qualitative change in the ionic composition of C_4F_{10}

t, °C	Type of heating	Catalyst	F^+	CF^+	C_2F^+	CF_2^+	C_3F^+		SiF_4^+	$C_3F_3^+$	$C_3F_4^+$	$C_2F_5^+$	$C_3F_5^+$	$C_3F_6^+$	$C_3F_7^+$	$C_4F_7^+$	$C_4F_9^+$
			19	31	43	50	55	75	85	93	112	119	131	150	169	181	219
500	Cyclical	–	–	–	–	–	↓	–	–	–	–	–	↑	–	–	–	–
600	Cyclical	–	–	–	↓	↑	↓	–	–	↑	–	↑	↑	↑	↑	↑	↑
610	Constant	–	–	↑	–	↑	–	–	↑	–	–	–	↓	↓	–	–	↓
640	Constant	+	–	↑	↑	↑	↑	↑	↑	–	–	↓	↓	↓	↑	↑	↓
650	Cyclical	–	↓	↑	–	↑	–	–	↑	↑	↑	↓	↓	↓	↑	↑	↑

Fig. 6 shows the characteristic mass spectrum of octofluoropropane under cyclic action, at a temperature of 600 °C.

The results of mass spectrometric analysis of the composition of impurities in fluorocarbons have revealed an important feature that when there are intense traces of corrosion, a reliable diagnosed SiF_3^+ peak with M/e appears in the spectra. The appearance in the spectrum of this peak indicates the reaction of the fluorine ion with silicon, contained in the structural materials of the capsule. The intensity of the peak indicates a quantitative picture of the reaction, depending on the temperature of the capsule heating.

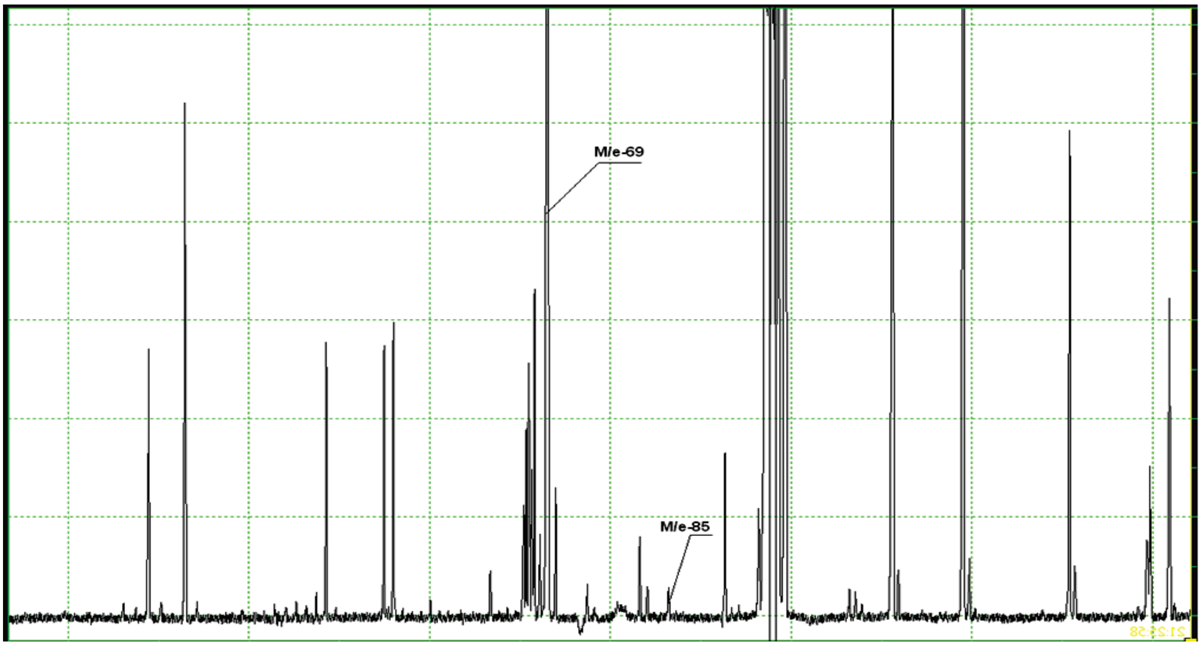

Fig. 6. Mass spectrum of octofluoropropane (C_3F_8)

6. Research results

6.1. Estimation of ionizing radiation for fluorocarbons and SF_6. *Description of the experiment on the evaluation of the effect of γ-irradiation on SF_6 and C_3F_8.* To assess the effect of irradiation, these substances are selected as the most probable for use as working bodies in the turbine cycle of an atomic reactor.

The methodological basis for the experimental determination of the effects of γ-radiation on a molecule of a fluorocarbon compound using mass spectrometry is the analysis of changes in the composition of ionic peaks in the mass spectrum before and after the action of γ-radiation on the gas molecule. For comparison, SF_6 is used in addition to C_3F_8 in the experiment.

During the study, a sample of gas is placed in a glass capsule made of laboratory glass. The capsules are sealed, then place in an assembly and lowers into the cassette space of the pool for holding the spent fuel assemblies of the reactor, stopped for a long exposure. The design of the assembled cassette with capsules is shown in Fig. 7.

Direct irradiation is performed at the experimental reactor ИРТ-2000 of the Engineering Physics Institute (Moscow, Russia).

The spectra are recorded on МИ-1201в mass spectrometer as samples arrived after their irradiation. The dose rate of gamma radiation was 15–20 R/s. The duration of exposure is 50 days, which according to the intensity of the collected radiation dose corresponded to 80±15 % Mrad. After collecting the calculated radiation dose, the experimental cassette is extracted from the pool, deactivated, and some of the capsules are removed for laboratory examination on a mass spectrometer, and the remaining capsules are continued to be irradiated in the reactor fuel pool of the reactor.

The extracted capsules are opened in the sampling system of the sample of the isotope mass spectrometer МИ-1201в. Then, at ionization energy of 70 eV, the mass spectrum of the investigated gas is recorded.

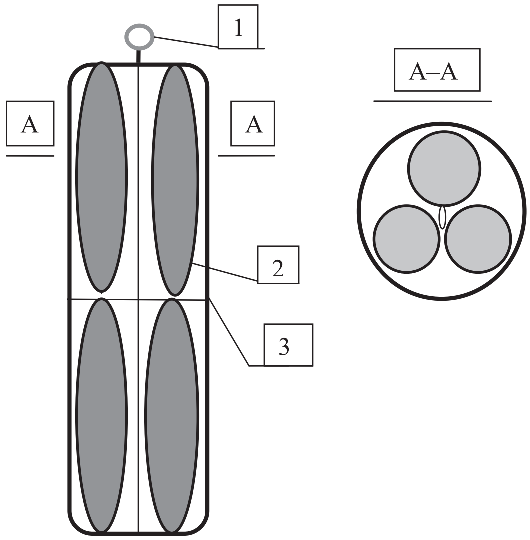

Fig. 7. Design of the assembled cassette:
1 – ring of the cassette fastening to a flexible cable; 2 – capsules with octafluoropropane and SF_6; 3 – cassette case

The recorded spectrum is compared to the spectrum of the non-irradiated sample. The effects of irradiation are determined on the basis of a comparison of ion peaks on the spectra, as well as the appearance of the ion peak of SiF_3^+, indicating the presence of a fluorine ion in the sample, which forms SiF_4 due to the reaction with glass.

The color of the glass capsules after irradiation became light brown, the intensity of the tone increases with increasing radiation dose.

Almost all spectra of irradiated gas observe a change in ion peaks. First of all, this applies to light and heavy ions. A significant increase in the intensity of the SiF_3^+ ion at M/e 85 is also observed, which indicates the generation of a fluorine ion upon irradiation. Table 5 shows the changes in ion peaks and impurity content found in the mass spectra of SF_6 gas immediately after irradiation and after 13 days. Judging by the changes, it can be concluded that the active fluorides, produced during the irradiation, after the end of irradiation gradually lose their activity due to reactions with the capsule walls and impurities from the gas composition. After 13 days, the intensity of the ion peaks is much closer to the initial values, but the impurity concentration increases.

Table 5

Changes in ionic peaks and impurity concentrations in SF_6

Ion peaks on the SF_6 mass spectrum	The source gas in the glass capsule	Gas immediately after γ-irradiation lasting 50 days	Gas after 13 days after cessation of irradiation
SF_5^+ M/e 127	100 %	100 %	100 %
SF_4^+ M/e 108	7.48 %	7.67 %	7.7 %
SF_3^+ M/e 89	17.26 %	19.22 %	17.23 %
SF_2^+ M/e 70	1.64 %	4.57 %	1.95 %
SF_4^{++} M/e 54	0.75 %	2.71 %	0.91 %
SF^+ M/e 51	0.64 %	4.11 %	1.23 %
S^+ M/e 32	0.21 %	1.76 %	1.2 %
Impurities, % vol.	–	–	–
SiF_4 M/e 85	0.161	0.495	0.989
SO_2F_2 M/e 83	0.528	1.259	1.97
SOF_4 M/e 105	0.104	0.011	0.172

Unlike SF_6, the changes in the spectra of C_3F_8 after γ-irradiation do not look as detailed (Table 6), as they are relatively poorly understood. However, the concentration of SiF_4 is quite noticeable and at an exposure of 50 days is in the range 1–2 % that is close to the values of irradiated SF_6. All the observed changes do not contradict the physics of the observed processes. The intensity of changes in ion peaks is close in magnitude to similar changes observed in the thermal testing of fluorocarbons in the temperature range 550–620 °C in the presence of catalysts.

Table 6

The results of C_3F_8 analysis after γ-irradiation

M/e	Ion	Source gas Peak M/e 69-100 %	After irradiation for 50 days and ageing for 8 days
31	CF^+	7.44	8.63
43	C_2F^+	0.15	0.37
50	CF_2^+	3.10	4.10
62	$C_2F_2^+$	0.32	0.40
69	CF_3^+	100	100
74	$C_3F_2^+$	0.10	0.13
81	$C_2F_3^+$	0.50	0.53
93	$C_3F_3^+$	0.38	0.44
100	$C_2F_4^+$	6.10	5.58
119	$C_2F_5^+$	8.16	8.71
131	$C_3F_5^+$	0.10	0.17
169	$C_3F_7^+$	25.35	16.95
85	Impurity SiF_4	0	2.30

The investigated levels of the effect of gamma radiation on the molecule C_3F_8 can be considered the initial stage of the destruction of the molecule with the formation of patina (but not deep corrosion) on the surface of structural materials in contact with the working body. This assumption must be checked in future experiments on samples of materials in contact with the irradiated working body.

If consider the use of C_3F_8 as the working fluid of the turbine cycle, it can be noted that this substance in the second circuit will be present in a significant amount with little, but always excessive, pressure. Since C_3F_8 has high thermal stability and fire-extinguishing properties, it is possible, with some reason, to predict the second application of this substance as a convenient and effective absorber of large energy flows in emergency situations that may arise during the operation of the nuclear reactor.

6.2. Evaluation of the effect of α- and β-radiation on octafluoropropane (C_3F_8). To obtain a more complete picture of the radiation effect on fluorocarbon compounds, an experiment is performed on α- and β-irradiation of samples of gaseous C_3F_8.

The experiment is carried out using steel sealed devices, inside which the radiation sources were located.

To test the effect of α-radiation on C_3F_8, a source with a power of $1.2 \cdot 10^7$ divisions per second is used. The source is placed inside a sealed capsule with a volume of 200 cm^3, filled with C_3F_8 at a pressure of 1.2 atm. Exposure time is 20 days.

To test the effect of β-radiation on C_3F_8, two sources with a power of $3.2 \cdot 10^7$ divisions per second ware used. They are placed opposite each other in the end parts of a cylindrical steel apparatus with an internal diameter of 80 mm and a distance between the ends of 200 mm. The apparatus is filled with C_3F_8 at a pressure of 1.2 atm. Exposure time is 20 days.

When analyzing the mass spectra recorded after irradiation, no traces of changes are found. This allows to conclude that, for a duration of 18 and 45 days, the combined effects of α- and β-radiation at 10^{13}–10^{14} divisions doesn't lead to appreciable changes in the mass spectrum of the studied C_3F_8.

7. SWOT analysis of research results

Strengths. The calculation of the real life time of fluorocarbons, as well as the lifetime estimation for SF_6 and R-22 based on the IPSS-2013 data, allow to more accurately determine their contribution to the global warming of the Earth's atmosphere. Thanks to this, it can be considered justified to remove them from the restriction on the basis of a «greenhouse hazard» for effective use in energy cycles. The use of fluorocarbons C_3F_8 or C_4F_{10} in the Brighton turbine cycle makes it possible to obtain an energy conversion efficiency of 49–51 %, provided that the working medium is relatively low (up to 100 atm.) and moderate temperatures (500–510 °C). This is significantly lower than the parameters of water vapor.

Materials science studies presented in this paper make it possible to draw a conclusion about the suitability and energy efficiency of fluorocarbons when used in the second circuit of nuclear power plants that have metallic coolants (lead or sodium) in the primary circuit.

The undoubted advantage of fluorocarbons and SF_6 gas is the combination of the three most important properties necessary for working bodies – safety for humans, machines and the environment, provided that energy efficiency in the energy cycles of Brighton or Rankine is higher than in steam.

Reference: Fluorocarbon C_3F_8 with a slight addition of SF_6 gas (halocarbone-510) is a universal and energy efficient working fluid for direct replacement of R-12 and R-22 refrigerants in refrigeration units operating in the reverse Rankine cycle.

Weaknesses. The weak side of fluorocarbons is the high price of the substance, in comparison with other working bodies.

This disadvantage can be significantly reduced by solving the problem of utilization and recycling of fluorocarbons, for which in the long term it is necessary to perform exploratory studies to accomplish this task.

Opportunities. The most significant positive effects of an economic nature when using fluorocarbons as working bodies are possible:

- in refrigeration technology, replacing R-22 and R-134a with halocarbone-510 due to the experimentally proven high energy efficiency, safety and stability of halocarbone-510, 95 % consisting of C_3F_8;
- in the industrial energy sector when water is replaced by C_3F_8 or C_4F_{10} in the turbine cycle when generating electricity at TPPs or NPPs, due to the possibility to increase the cycle efficiency by 8–10 % in comparison with the water cycle. This will ensure a reduction in the consumption of energy carriers (coal, gas or uranium fuel) from 16 to 20 %;
- in all applications of fluorocarbons, the most valuable quality is essentially a higher level of safety for humans, machines and the environment.

Threats. Substances with a similar set of properties characteristic of fluorocarbons and SF_6 gas have not yet been found. For this reason, studies on the deep study of their properties, as well as on utilization and restoration of their primary properties after their use in energy cycles, will be relevant for the near future.

8. Conclusions

1. Based on the processing of mass balances according to IPCC-94 and IPCC-2013, conclusions are drawn on the estimated lifetime in the IPCC-94 for the most stable fluorocarbon CF_4, which gives grounds for removing restrictions on the use of fluorocarbons as a greenhouse hazard and creates conditions for research of technological properties of fluorocarbons.

2. Investigations of the thermal stability of fluorocarbon compounds (C_3F_8, C_4F_{10}) under constant and cyclic heating in the presence of structural materials containing catalysts in the ligature. Under these conditions, the temperature of the beginning of the thermal decomposition of octafluoropropane can be estimated at 630 °C, decafluorobutane at a level of 600 °C. The temperature of 600 °C can be considered as the boundary of the thermal corrosion resistance of structural materials presented in experimental studies of fluorocarbons during heating.

3. An estimate of the stability of C_3F_8 under the influence of α- and β-radiation with activity $1.2 \cdot 10^7$ and $3.2 \cdot 10^7$ Bq, respectively. No noticeable traces of the effect in the mass spectra of the gas after irradiation have been detected.

The effects of exposure to high doses of γ-irradiation on SF_6 and C_3F_8 have been determined experimentally. A conclusion is drawn about the analogy of the effects of γ-irradiation with an intensity of 80 Mrad and heat exposure for two hours at 650 °C for C_3F_8.

4. The validity of the technique for the use of the SiF_3^+ ion as an indicator of the appearance of a free ion of F^+, indicating the onset of the destruction of fluorocarbons and the occurrence of conditions of deep corrosion in structural materials, is confirmed.

References

1. Gohshtein, D. P. Nekotorye osobennosti parogazovyh shem s nevodianymi parami [Text] / D. P. Gohshtein, G. F. Smirnov, V. S. Kirov // Energetika. – 1964. – No. 11. – P. 20–24.
2. Moisan et Lebeau, C. R. Sur un nouveaucorps gazeux: le-perfluorure de soufre SF6 [Text] / C. R. Moisan et Lebeau. – Paris: Academie des sciences, 1900. – Vol. 130.
3. Morkin, M. S. Fizicheskaia model' radioliza gazoobraznogo ftoruglerodnogo rabochego tela [Text] / M. S. Morkin, V. V. Lemehov, Yu. S. Cherepnin // Doklady tret'ei mezhdunarodnoi nauchno-tehnicheskoi konferentsii «Innovatsionnye proekty i tehnologii iadernoi energetiki». – OAO »NIKIET», 2014. – Vol. 1. – P. 462–466.
4. Maksimov, B. N. Promyshlennye ftororganicheskie produkty [Text]: Handbook / B. N. Maksimov, V. G. Barabanov, I. L. Serushkin et al. – Ed. 2. – St. Petersburg: Himiia, 1996. – 544 p.
5. Brown, T. E. Chemistry: The Central Science [Text] / T. E. Brown, H. E. LeMay, B. E. Bursten, C. Murphy, P. Woodward. – Ed. 11. – Prentice Hall, 2011. – 1232 p.
6. Summary for Policymakers [Text] / Intergovernmental Panel on Climate Change // Climate Change 2013 – The Physical Science Basis. – Cambridge University Press, 2014. – P. 1–30. doi:10.1017/cbo9781107415324.004
7. Tapscott, R. E. Tropodegradable fluorocarbon replacements for ozone-depleting and global-warming chemicals [Text] / R. E. Tapscott, J. D. Mather // Journal of Fluorine Chemistry. – 2000. – Vol. 101, No. 2. – P. 209–213. doi:10.1016/s0022-1139(99)00161-x
8. Haywood, R. W. Analysis of Engineering Cycles [Text] / R. W. Haywood. – Elsevier, 1980. – 348 p. doi:10.1016/c2013-0-03329-4
9. Perelshtein, I. I. Termodinamicheskie i teplofizicheskie svoistva rabochih veshchestv holodil'nyh mashin i teplovyh nasosov [Text] / I. I. Perelshtein, E. B. Parushin. – Moscow: Liogkaia i pishchevaia promyshlennost', 1984. – 232 p.
10. Syvorotkin, V. L. Glubinnaia degazatsiia Zemli i global'nye katastrofy [Text] / V. L. Syvorotkin. – Moscow: Geoinformtsentr, 2002. – 250 p.
11. Molina, M. J. Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone [Text] / M .J. Molina, F. S. Rowland // Nature. – 1974. – Vol. 249, No. 5460. – P. 810–812. doi:10.1038/249810a0
12. Houghton, J. T. Climate Change 1994. Radiative Forcing of Climate Change and An Evaluation of the IPCCIS92 Emission Scenarios [Electronic resource] / ed. by J. T. Houghton, L. G. Meira Filho, J. Bruce, Hoesung Lee, B. A. Callander, E. Haites, N. Harris, K. Maskell. – Cambridge University Press, 1995. – 340 p. – Available at: \www/URL: https://www.ipcc.ch/pdf/special-reports/cc1994/climate_change_1994.pdf
13. SF6 recycling guide. Re-use of SF6 gas in electrical power equipment and final disposal [Electronic resource] // ELECTRA. – 1997. – ELT_173_3. – 29 p. – Available at: \www/URL: https://e-cigre.org/publication/ELT_173_3-sf6-recycling-guide-re-use-of-sf6-gas-in-electrical-power-equipment-and-final-disposal
14. Stekolnikov, I. S. Priroda dlinnoi iskry [Text] / I. S. Stekolnikov. – Moscow: AN SSSR, 1960. – 272 p.
15. Stekolnikov, I. S. Issledovanie prirody dlinnoi iskry [Text] / I. S. Stekolnikov, M. A. Bagirov // Izvestiia AN SSSR. OTN. – 1953. – No. 2. – P. 12–16.
16. Toepler, M. Zur Kenntnis der Gesetze der Gleitfunkenbildung [Text] / M. Toepler // Annalen der Physik. – 1906. – Vol. 326, No. 12. – P. 193–222. doi:10.1002/andp.19063261202

17. Schonland, B. F. J. The Pilot Streamer in Lightning and the Long Spark [Text] / B. F. J. Schonland // Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences. – 1953. – Vol. 220, No. 1140. – P. 25–38. doi:10.1098/rspa.1953.0169
18. Isidorov, V. A. Organicheskaia himiia atmosfery [Text] / V. A. Isidorov. – Leningrad: Himiia, 1985. – 264 p.
19. Doronin, A. The new cooling agents [Text] / A. Doronin, I. Mazurin, A. Stoljarevski // Proceedings of the 19th International congress of refrigeration, Hague, Netherlands, August 20–25, 1995. – Paris: Institut international du froid, 1995. – P. 914.

АНАЛИЗ ЭКОЛОГИЧЕСКИХ, ЗАКОНОДАТЕЛЬНЫХ И ТЕХНОЛОГИЧЕСКИХ АСПЕКТОВ ВЫБОРА НЕВОДНЫХ РАБОЧИХ ТЕЛ ДЛЯ ЭНЕРГЕТИЧЕСКИХ УСТАНОВОК

Представлен вариант решения задачи выбора рабочего тела с учётом ограничений Монреальского и Киотского протоколов для теплосилового контура энергетических установок на неводных рабочих веществах с возможностью значительного повышения энергоэффективности цикла и безопасности эксплуатации установок. Для фторуглеродных рабочих тел и SF_6 обнаружено несоответствие на четыре порядка величины для критерия Lifetime, полученного по данным IPCC-13, что дает основание для их применения без ограничений, отмеченных в Киотском протоколе.

Ключевые слова: энергетическая установка, рабочие тела энергетических циклов, стабильность веществ, гексафторид серы.

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