

Plasma-Chemical Treatment of Process Gases with Low-Concentration Fluorine-Containing Components

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Abstract The problems of recycling of the gases with low concentration of fluorine-containing components have been considered. The model of their plasma-chemical treatment with the heat recovery of effluent gases is proposed. The process thermodynamics for various compounds of reacting gases is considered. The heat- and mass transfer processes are simulated in the plasma-chemical reactor. Temperature and velocity profiles of treated gas flows have been obtained within the recovery zone, mixing area with the plasma jet as well as in the reactor working zone. The compliance of the resulting distributions and the temperature range needed for the full conversion is demonstrated. The experiments on the plasma-chemical treatment of carbon tetrafluoride and nitrogen trifluoride have been conducted. The resulting degrees of CF₄ and NF₃ decomposition turned out to be above 90% providing more than double reduction of specific energy cost as compared with the available facilities of similar purposes. An approach is proposed to reduce nitrogen oxide content in effluent gases at reactor outlet and to decrease in future the specific energy cost of conversion of halogen-containing gases.

Keywords Plasma-chemical reactor · Fluorine-containing compounds decomposition · Gas dynamics simulation · Recuperative heat exchange

Introduction

The compounds in which hydrogen atoms are completely or partially replaced by fluorine, or perfluoro-compounds (PFCs) including CF₄, C₂F₆, C₃F₈, CHF₃ (HFC-23), SF₆, and NF₃ etc., are commonly used for cleaning and etching of surface of semiconductor wafers, in

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display production, etc. [1–4], since they present the most safe and reliable source of fluorine. Earlier, chlorine- and fluorine-containing freons were produced commercially; they were utilized in refrigerators and heat exchangers of different purposes [5]. Moreover, heavy stocks of halogen-containing waste, including organic ones, have been accumulated [6]. These substances pertain to the greenhouse gases category and are directly related with the ozone layer degradation; thus they must be recycled. PFCs have the high global warming potential (GWP) and very long lifetime in the atmosphere: in particular, taking the carbon dioxide GWP as a unity (lifetime in the atmosphere is 50–200 years), the methane tetrafluoride CF_4 GWP (50,000 years) is 6500, and NF_3 GWP (740 years) is 11,700 [7].

The plasma-chemical method is the most promising way of conversion of halogen-containing components; it is being developed in recent years and combines the capability to heat the reacting mixture components up to high temperatures and a wide range of plasma gases [8]. A plasma heat source enables to decrease the facility overall dimensions and the effluent gas volume flow rate in comparison with conventional thermal treatment methods.

The major criterion of the completeness of halogen-containing compound decomposition is the ratio of decomposed molecules of this compound at the outlet of plasma-chemical reactor to the total number of the molecules of this substance at reactor inlet, the destruction and removal efficiency (DRE) [17]. DRE depends on the rate of mixing of reactants with each other and a heat-carrying gas, temperature level and residence time of reactants in the reactor working zone. Taking into account the value of the maximum permissible CF_4 concentration, the treatment of gases with low concentration of halogen-containing components, almost 100% DRE is not needed, as it is in the case of treatment of undiluted halogen-containing compounds. DRE = 90% is enough when initial CF_4 concentration in the gas mixture to be treated is max 1%. In this case, the economic aspect, energy cost per 1 m^3 of the treated gas, becomes especially important.

Numerous experimental and numerical investigations have been devoted to the plasma-chemical decomposition of the most chemically stable fluorocarbon, CF_4 , and other PFCs as well [9–18].

The authors of [9] fulfilled the experimental investigation of CF_4 decomposition in the atmospheric-pressure reactor in argon plasma jet, when the hydrogen–oxygen mixture was added both in plasma argon and beneath of the plasma torch output nozzle cross-section. It was found that the electric power of the plasma torch varied within the range of 6–9 kW under given operating conditions weakly affected the conversion degree, whereas the increased flow rate of CF_4 diminished this degree. With the Ar + CF_4 mixture, the DRE of pyrolysis did not exceed 25–27%, with specific energy cost being equal to $6.3 \text{ kW} \times \text{h/m}^3$. More hydrogen permitted increasing DRE up to 99%, but it was accompanied by occurrence of soot particles in the reducing atmosphere. Extra oxygen supplied by the ratio of $\text{CF}_4:\text{O}_2:\text{H}_2 = 1:2:4$ permitted reaching the DRE conversion degree of 95% at the specific energy consumptions of about $4.6 \text{ kW} \times \text{h/m}^3$.

The authors of [10] performed the numerical and experimental investigations and comparative analysis of decomposition of tetrafluoromethane in air and nitrogen plasmas at atmospheric pressure. The electric power of the plasma torch with hollow cylindrical electrodes ranged from 40 to 60 kW. According to the investigation results, higher heating degrees and longer residence times in the reactor zone were needed in the nitrogen-plasma case to reach the same conversion degree of 97.4–99.5% as it was the case in the air plasma [13, 17]. Specific energy cost was of $3.3\text{--}5.0 \text{ kW} \times \text{h/m}^3$ of the gas to be treated. Moreover, the layout of the facility of treated gas injection used in this case requires a

relatively high pressure of the gas, which is not always realizable in the conditions available in the electronic industry.

A number of tests on the high-temperature pyrolysis of CF_4 and other halogen-containing hydrocarbons (HFC-134a, HFC-32) were carried out in [11, 15]. A steam DC plasma torch with the power up to 2.5 kW was used as a plasma source. The optimal energy consumptions per the molar flow rate of the halogen-containing substance were determined for each decomposed substance; at this consumption level, the conversion degree of each substance reached 99%. The obtained results show good prospects of water steam plasma application for the problem of high-temperature conversion of the halogen-containing gases [14]. The very high water steam equivalence rate (more than $30\times$) over the stoichiometry, plus high specific energy consumptions (dozens of $\text{kW} \times \text{hour}$ per cubic meter of the treated gas) are the disadvantages of this technique.

In [16], the authors tried to use the recuperative heat of the effluent gases with the purpose of reducing the energy cost. To do this, they simulated the high-temperature hydrolysis of HFC-23 (CHF_3) in a nitrogen plasma jet and compared the results with experimental findings. The reactor consisted of three coaxial tubes: the central one, along which the flow of nitrogen plasma was supplied, and two external tubes; note that the mixture of water vapour and air was supplied between the central and middle tubes whereas the mixture of air and HFC-23 was injected between the middle and external ones. Both separated mixtures moved in opposite direction to that of main flow in the central tube and were gradually heated by the walls (the counter-flow recuperation); then, in the upper part of the reactor they were mixed and ejected by the plasma jet into the central tube wherein the HFC-23 conversion took place. Variations were provided by the distances from the plasma jet injection plane to the end-faces of the coaxial tubes, by the plasma torch arc current as the main parameters governing the resulting profiles of temperatures and velocities in the working zone of the reactor. The melting point of the coaxial tube material (Inconel alloy) served as a working temperature limitation, it ranged within 1600–1700 K. Simulation results enabled to propose the working mode of the plasma torch and reactor layout at which DRE reached 99%. Nevertheless, the energy consumptions were in this case even higher than in the case with the hollow cylindrical electrodes, they reached $9 \text{ kW} \times \text{h/m}^3$ of the treated gas. Such a high value of the energy cost seems to be caused by the missing thermal insulation of the reactor case and plasma torch low electric power which leads to the increased part of heat loss.

Thus, according to literature data, available setups of plasma-chemical treatment of halogen-containing gases provide the required level of DRE (in some cases it reaches 99%), but they have high specific energy consumptions, at least $3.3 \text{ kW} \times \text{h/m}^3$ of the treated gas.

The purpose of this work is the reduction of the energy consumptions for the plasma-chemical treatment of the gases with low concentration of fluorine-containing components providing required DRE level. CF_4 and NF_3 commonly used in the electronic industry as fluoride sources were considered as the objects to be decomposed.

The level of the energy consumptions for the gas plasma-chemical treatment depends on two factors:

1. The energy consumptions required to complete corresponding chemical reactions;
2. The heat losses in the plasma torch and plasma-chemical reactor (thermal efficiency of the plasma torch and plasma-chemical reactor).

The energy consumptions required for the chemical reactions depend on the temperature level needed based on thermodynamics, and on molar fraction of the treated components in

the mixture. Hence, to reduce these energy consumptions, one can use the recuperation of the hot effluent gas plus a reduction of the heat losses in both the plasma torch and plasma-chemical reactor.

In summary, this paper proposes the model of the plasma-chemical reactor for the conversion of the gases with low concentration of halogen-containing components; the basic principles are the following: (a) using the plasma torch with a high thermal efficiency; (b) preliminary treated gas heating by means of the counterflow recuperation into the reactor with the thermally-insulated case.

Experimental

Figure 1a shows the schematic of the plasma-chemical reactor. Figure 1b depicts the cylindrical channel of the plasma torch with self-establishing arc. Cathode 1 consists of hafnium insert embedded into a copper case. Here axial length of copper anode 2 is 70 mm, ID of the channel is equal to 6 mm. The gap between the cathode 1 and anode 2 is 2 mm. The plasma forming gas is supplied into the channel through the supply device in the electric insulator via orifices with the circumferential component of velocity, direction of plasma forming gas supply is shown by arrow. As seen from Fig. 1a the reactor consists of a central tube 1 and cylindrical case 2 coaxially assembled with central one. The case 2 has the external thermal insulation 3. The plasma torch 4 mounted to the reactor works as a heat source. The treated gas is supplied tangentially into the reactor bottom part 5 through two orifices 6 set symmetrically along the reactor axis. The treated gas goes upstream by the annular slot of the recuperation zone 7 and is heated from the external wall of the central tube 1 and internal wall of the reactor case 2; then it mixes with the plasma jet in the upper part 8 and goes into the reactor working part 9, wherein the fluoride conversion occurs. The high-speed plasma jet flowing out from the plasma torch promotes the ejection of the treated gas which guarantees the low flow friction in the gas-supply channel.

To quantify toxic gases Fourier Transform Infrared spectrometry is conventionally used because of its time-saving, credibility and convenience. Hence, FT-IR MIDAC Model I-4001 spectrometer (USA) has been attached at the outlet of the plasma-chemical reactor to detect a concentrations of fluorides (CF_4 and NF_3) and NO_x in the cycle of experiments. Thereby, variations of the concentrations have been detected.

To reduce the energy consumptions, the plasma torch must demonstrate the maximal efficiency and generated plasma enthalpy. To meet these requirements, the authors have chosen the the plasma torch with the vortex stabilization of the arc, an end-face cathode 10,

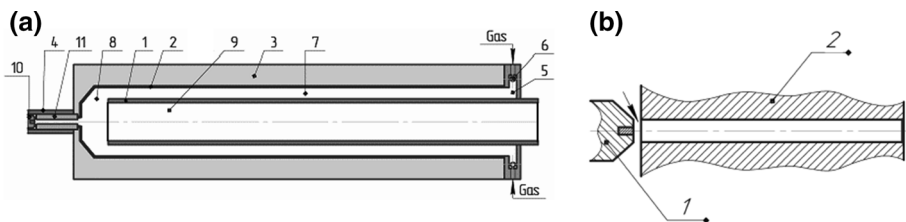


Fig. 1 a Schematic of the plasma-chemical reactor: 1 central tube, 2 reactor case, 3 thermal insulation, 4 plasma torch, 5 the area of the tangential supply of the treated gas, 6 orifices, 7 recuperation zone, 8 mixing zone, 9 working zone of the reactor, 10 cathode, 11 anode; b geometry the cylindrical arc chamber: 1 cathode, 2 anode

and anode 11 with a cylindrical arc chamber (see Fig. 1b). In contrast to the plasma torch with hollow cylindrical electrodes and efficiency below 52% used in [10, 13, 17], the efficiency of this one can reach 80–85% [19]. Actually, the measured thermal efficiency turned out to achieve this level when enthalpy of plasma forming nitrogen ranged within 12.0–18.7 MJ/kg. In experiments enthalpies were within this range, but estimated thermal efficiency of the plasma torch was 76–82% depending on operating mode of the plasma torch.

The temperature level and optimal chemical composition of the gas mixture supplied into the plasma-chemical reactor needed for the treatment, were estimated by means of the thermodynamic simulation. The geometry of the reactor and area of plasma jet and treated gas mixing were optimized based on results of the flowfield numerical simulation.

Thermodynamic Consideration of CF_4 and NF_3

There are two plasma methods of treatment of halogen-containing raw materials: the plasma thermal decomposition (pyrolysis) and plasma chemical conversion. In the first case, the halogen-containing substances are thermally decomposed in the medium of chemically inert gases, to yield elementary halogens. In the second case, the halogen-containing substance is disintegrated as result of chemical reaction, in particular, with water vapour.

Commercially available software package “Terra” was used for the analysis of the thermodynamically equilibrium composition for both methods. In Fig. 2a, b thermodynamic calculation of the substance equilibrium composition resulting from the pyrolysis in the corresponding systems $\text{CF}_4\text{--N}_2$ and $\text{NF}_3\text{--N}_2$ under the atmospheric pressure versus the temperature is presented (molecular nitrogen curve was omitted in the plots here and elsewhere). Evidently, NF_3 begins to dissociate even at 800 K, is completely decomposed at 1250 K, whereas CF_4 begins to dissociate only at 2000 K. The latter is confirmed by the thermodynamic calculations [17].

As seen from the Figure, the pyrolysis reaction is reversible in both cases, the resulting products should be quenched in order to prevent the reverse reaction. In spite of the high energy consumptions, necessity of quenching, and complexity of the sequential trapping of the resulting elementary fluorides, the plasma pyrolysis of NF_3 is technically realizable. For CF_4 , the pyrolysis is almost unrealizable owing to economic and engineering reasons.

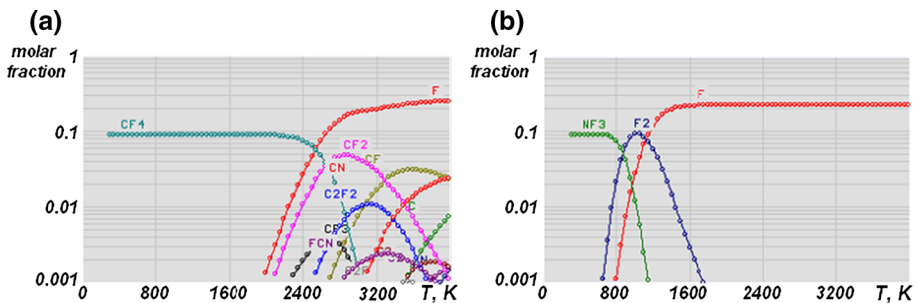


Fig. 2 Equilibrium substance composition as result of plasma pyrolysis of CF_4 (a) and NF_3 (b), $p = 0.1$ MPa

Numerical Modeling

Computational Domain

The completeness of the chemical reaction depends on the quality of mixing of the reacting components, temperature level, and temperature profile uniformity. The processes of heat and mass transfer in the reactor have been calculated for the optimization of geometry of the reactor and zone of mixing of the treated gas and plasma jet.

The reaction of water steam conversion of the fluorides under study is accompanied with the insignificant heat release. Thus, during the calculation of the heat and mass transfer in the plasma-chemical reactor in the case of treatment of the gases containing maximum 1% of halogen-containing components, it is possible to neglect the energy released as result of the chemical reactions; the energy consumptions in this case depend on the energy needed for the treated gas heating up to the required temperature. Having this in mind, nitrogen was taken as a plasma forming gas as well as gas to be treated in the calculations. The quality of gas mixing was evaluated by the uniformity of the temperature profiles in the reactor.

The calculation was carried out for the model of the reactor shown in Fig. 1. The internal diameter of the central tube of the reactor is 50 mm, its wall thickness is 5 mm. The axial stand-off distance of top plane of central tube from plasma torch exit plane is 35 mm. The total reactor length from the plasma torch anode end face to the reactor output section is 600 mm, the central tube length is 565 mm. The treated gas is injected tangentially through two holes of 6 mm in diameter set symmetrically about the reactor axis.

In the calculations, the plasma forming nitrogen flow rate is 36 l/min, which corresponds to the mass flow rate of 0.75 g/s. The plasma torch net capacity is taken to be 6.4 kW. The mean mass temperature of the plasma jet in the output section of the plasma torch nozzle is 5500 K, the mass-average velocity at the plasma torch nozzle exit plane is 461 m/s. The flow rate of the treated gas (nitrogen) is taken to be 2.5 normal l/s (3.125 g/s). As was mentioned above, the calculation ignores the presence of CF_4 and H_2O in the treated gas.

Five numerical grid patterns with 76175, 92411, 170092, 252925 and 320282 unstructured hexahedral cells of the computational domain have been considered. Based on results of grid sensitivity analysis, first coarse grid has been rejected. The fourth grid with 252925 cells has been preferred despite of faster and more stable convergence of solutions in case of 92411 or 170092 cells. The reason is explained in the section Results of simulation.

Figure 4a shows the geometry of the internal part of the reactor channel (domains 5 and 6, Fig. 1a), the output part of the plasma torch anode channel, and calculation grid. Grid refinement in the zone of plasma jet injection is shown in Fig. 4b and that of tangential injection of the nitrogen to be heated—in Fig. 4c. In the vicinity of both zones typical cell size is about 0.8 mm, growth rate between neighboring cells is factor of 1.06.

Calculation Model and Boundary Conditions

According to the evaluations of the Reynolds number, the flow field character in the mixing area is turbulent, thus the *realizable* k - ε model was chosen for the calculations; it includes the Navier–Stokes equations and two equations for the turbulent kinetic energy k and its dissipation ε [12, 20] in the axisymmetric statement. The simulation was carried

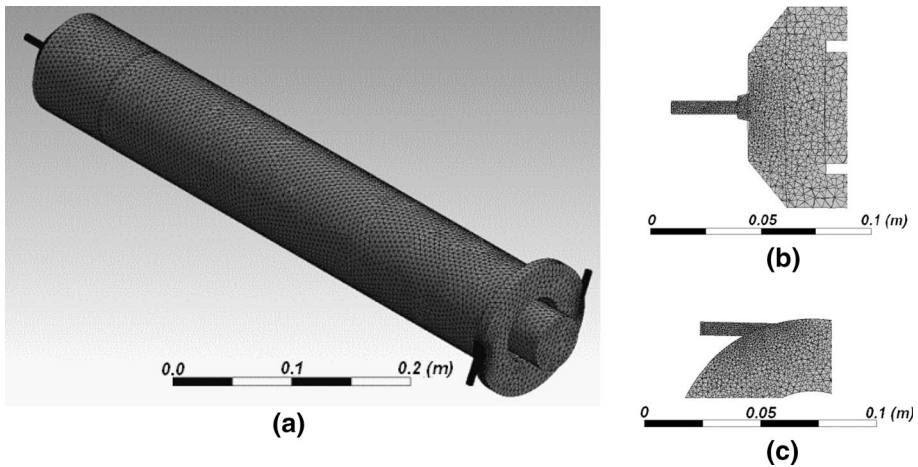


Fig. 4 Reactor channel geometry and generated grid in isometry: **a** general view, **b** central-axis plane of plasma jet outlet computational domain with refined mesh, **c** computational domain with refined mesh of tangential injection of treated gas

out using software package ANSYS Fluent 15.0 with implicit pressure-based solver. The *realizable* k - ϵ model with standard wall functions features the good convergence for turbulent and rotary flows [21]. The stationary solution for the incompressible ideal gas was sought with using SIMPLE scheme. Convective heat exchange with the heated reactor walls (in the recuperation region) followed by the mixing with the turbulent plasma jet in the reactor working part are main sources of heating of the treated gas in this model. The constant temperature and velocity plasma nitrogen (5500 K, 461 m/s) and transport nitrogen (300 K, 48.5 m/s) inlet boundary conditions have been set for numerical simulation. The turbulence intensity at the plasma torch nozzle exit plane was set within 10–20%. No-slip conditions implied on the reactor walls, the thermal flux was set in the heating area, from the walls to the gas, 4000 W/m^2 , its value is found from the preliminary evaluations, whereas in the upper part of the reactor and on the internal wall of the central tube, the thermal flux is directed from the plasma jet toward the walls, and it is also reaches 4000 W/m^2 . On the other walls, the heat fluxes are taken to be equal to zero. All computations have been performed in double precision.

Transport and thermodynamic properties of nitrogen have been taken into account, in particular, molecular viscosity and thermal conductivity, were varied within given temperature range as predicted in the basic work [22].

Results and Discussion

Results of Simulation

The results of simulation of stationary fields of velocity and temperature in the reactor are shown in Fig. 5.

As observed from Fig. 5a, the tangential component of velocity of the treated gas decays according as gas moves upstream in the recuperation region. The gas flows in the annular slot of the recuperation region toward the upper part of the reactor and is gradually

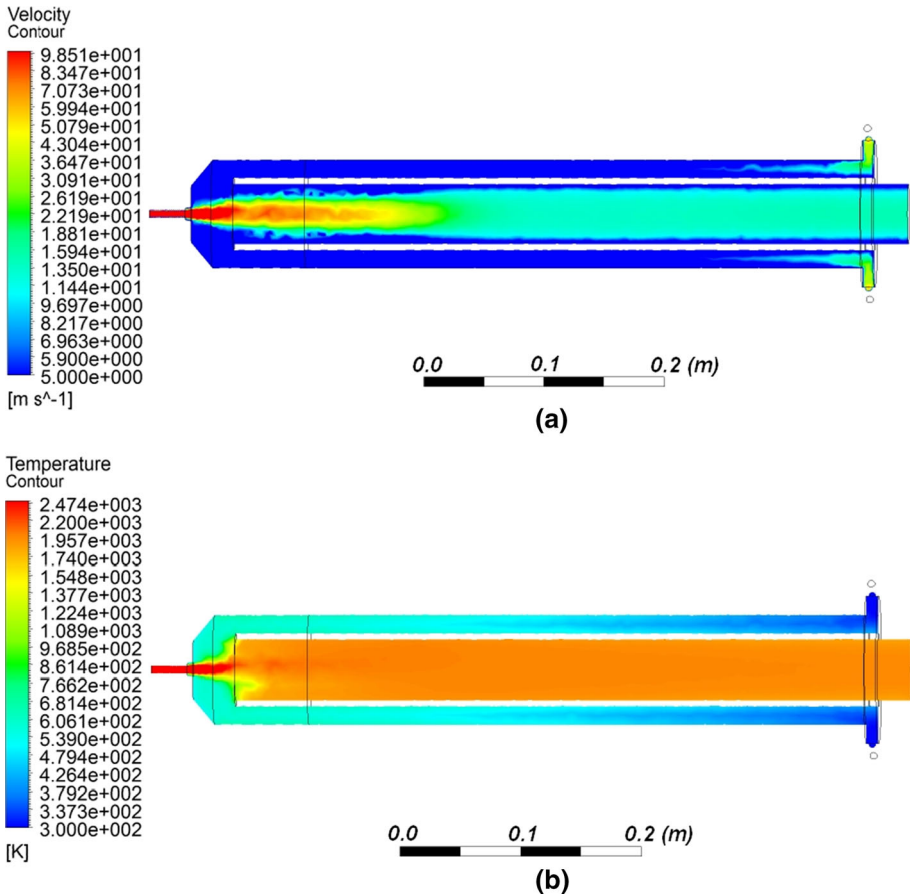


Fig. 5 Results of numerical simulation: **a** velocity profiles, **b** temperature profiles

heated from the walls (see Fig. 5b). Then, treated gas moves along the upper part of the reactor and is entrained by the plasma jet into the reactor working part. The high turbulence of the plasma jet provides good mixing and intensive heating of the treated gas [23, 24]. In the reactor geometry chosen, the plasma jet is localized in its central part and does not contact with the reactor case 2 (see Fig. 1), so it ejects the treated gas. There are neither noticeable dead zones, nor near-wall backflows occur. The treated gas flows along the walls of the reactor upper part and forms the gas shield around it, preventing it from the thermal load of the plasma jet. Full mixing of the plasma jet and treated gas is reached in the upper part of the central tube in the reactor.

It should be notified that steady-state solution obtained using the finest mesh and depicted in Fig. 5 is not absolutely stable whereas solutions converged in case of grids with 92411 and 170092 cells are quite steady and are the same as in this figure. The reason seems to be following. Since velocities of plasma jet and treated gas at the top of the reactor are extremely different, in the periphery of plasma flow Kelvin–Helmholtz instability occurs and small-scale vortices are formed. Corresponding estimate of Richardson number gives a value very close to zero which indicates the presence of such an instability.

When using a coarse mesh (92411 cells) these vortices are not resolved and well-converged steady solution is easily obtained. When using fine enough mesh (252925 cells) 3D inherently unsteady vortices are caught. Nevertheless, in compliance with results of simulation this small-scale inherent instability is localized in the periphery of plasma jet and does not occur in recuperation region of the reactor. It is the case partially owing to reactor geometry. In fact, local disturbances caused by this instability disappear at downstream axial distance of one diameter from top plane of the central pipe.

As evident from Fig. 5, the mixture in the reactor working part is heated up to 2000 K, which is enough for the fluorine-containing components conversion. According to the calculations of the temperature profiles in the reactor, with the heat recuperation being ignored, the temperature in the conversion region is 300–400 K lower in this case. The residence time of the treated gas components in the reactor working part is at least 20–30 ms, which is comparable to the characteristic times obtained in [12, 17]. The velocity and temperature fields in the transverse cross sections of the internal part of the reactor are almost uniform which provides the similar conditions of the conversion process.

Thus, lower energy consumptions for the gas treatment and low pressure loss in the injection unit are the advantages of this reactor configuration.

Experimental Results

In order to study the plasma-chemical conversion of carbon fluoride CF_4 and nitrogen NF_3 in the nitric plasma of atmospheric pressure, the tests were carried out in the plasma-chemical plant shown schematically in Fig. 1. The difference between the test plant geometry from the schematic shown in Figs. 1 and 4 is that the treated gas is injected through one tangentially set orifice with diameter of 25 mm rather than two ones. This difference is not critical, regarding the fast loss of the tangential velocity of the treated gas as it goes upstream in the recuperation region 7, Fig. 1.

As mentioned above, the plasma torch with vortex arc stabilization, end-face cathode and the anode with a cylindrical arc channel was used in order to reduce the heat losses. Nitrogen was used as a plasma forming gas.

The mixture of $\text{N}_2 + \text{CF}_4$ or $\text{N}_2 + \text{NF}_3$ was supplied in the plasma-chemical reactor. Both the thermal dissociation of fluorides and their water steam conversion were studied experimentally. For both kinds of conversion the liquid water (discharge of 100 g/h) was fed through a separate connecting pipe into upper heated part of recuperation region 7 in order to avoid water condensation upon the walls and then to mix with fluorine-containing gas. In the case of CF_4 conversion ratio of water discharge and CF_4 molar flow rate is about $1.4\times$ over the stoichiometry.

Table 1 presents the conditions and results of the tests on thermal dissociation (the 1st line) and CF_4 conversion (the 2nd line). Table 2 presents the conditions and results of the tests on thermal dissociation (first two lines) and NF_3 conversion (the rest). The enthalpies in experiments for CF_4 pyrolysis and CF_4 conversion were 15.7 and 18.2 MJ/kg with thermal efficiencies 79.1 and 76.0%, respectively (Table 1). For NF_3 pyrolysis the enthalpies were 18.2 and 17.8 MJ/kg (Table 2, 1st and 2nd line), accordingly, thermal efficiencies were 76.0 and 76.5%. In case of NF_3 plasma conversion—13.3 and 14.7 MJ/kg (Table 2, 3rd and 4th line), corresponding thermal efficiencies—81.8 and 80.3%. Evaluated mean mass temperatures at plasma torch outlet were 6100–6700 K, whilst mass averaged velocity varied within 380–650 m/s.

Table 1 shows that the conversion degree of carbon tetrafluoride is below 50% without water injection, and its content in the effluent gases exceeds significantly the permissible

Table 1 Data of CF₄ conversion experiments

Flow rate, N ₂ (l/min)	Flow rate, CF ₄ (l/min)	Input concentration of CF ₄ (ppm)	Electric power of plasma torch (Kw)	Flow rate of plasma forming, N ₂ (l/min)	Output concentration of CF ₄ (ppm)		DRE conversion degree, CF ₄ (%)	Output concentration of NO _x (ppm)
					Plasma torch off	Plasma torch on		
150	0.75	5000	16.5	40	4050	2200	45.7	–
150	0.75	5000	12.5	25	4250	350	91.8	330

Table 2 Data on NF₃ conversion experiments

Flow rate, N ₂ (l/min)	Flow rate, NF ₃ (l/min)	Input concentration of NF ₃ (ppm)	Electric power of plasma torch (kW)	Flow rate of plasma, N ₂ (l/min)	Output concentration of NF ₃ (ppm)		DRE conversion degree, NF ₃ (%)	Output concentration of NO _x (ppm)
					Plasma torch off	Plasma torch on		
300	3	9900	12.5	25	9050	720	92.0	–
300	3	9900	13.5	28	9000	220	97.6	–
300	3	9900	8.5	25	9050	300	96.7	5300
300	3	9900	9.5	25	9050	84	99.1	6100

level. With water on (line 2 in Table 1), concentration of CF₄ in the off-gases is 12× lower, and DRE is above 90%. It confirms the conclusions of the thermodynamic analysis of CF₄ conversion that the plasma chemical technique is preferable. As seen from Table 2, the acceptable DRE = 92–98% in the case of NF₃ pyrolysis reached at electric power consumptions of 12.5–13.5 kW. In the case of NF₃ conversion with water injection DRE = 96–99%, with lower electric power consumptions being within 8.5–9.5 kW. But the output NO_x concentration happened to be impermissibly high.

Figure 6 presents the time scanning of carbon tetrafluoride concentration at the reactor outlet. The figure evidently shows the effect of the recovered heat of the off-gases on the CF₄ conversion degree. CF₄ concentration goes down to the level of 1200 ppm almost immediately after the plasma torch switching on. Right after the plasma torch switching-on, the reactor walls remain cold, and the treated gas is not heated in the recuperation region. This mode corresponds to the mode of the reactor with a water-cooled case (without thermal insulation). As seen from the plot in Fig. 6, almost 3× drop of the CF₄ concentration in the off-gases down to ≈400 ppm occurs within 10 min after the plasma torch switching on. This time roughly correlates with the time of reactor walls heating up. As clear from the Figure, after a 1.5 min pause in the plasma torch work, during which the reactor walls do not cool down, almost immediately after the plasma torch next switch-on, the low CF₄ concentration is observed in the off-gases from the reactor. This is also a result of the heat recuperation effect.

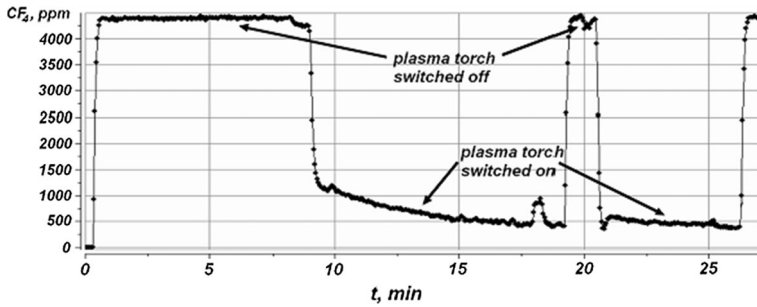


Fig. 6 CF_4 concentration time scanning of at the reactor outlet

Specific energy consumptions were about $1.4 \text{ kW} \times \text{h/m}^3$ in the case of treatment of the gas mixture $\text{N}_2 + \text{CF}_4$, which is more than $2 \times$ lower than obtained in [10], as well as by the results of [13] at the somehow lower DRE. In the case of $\text{N}_2 + \text{NF}_3$, the energy consumptions were $0.47\text{--}0.75 \text{ kW} \times \text{h/m}^3$.

According to the data of Tables 1 and 2, generation of nitrogen oxide is a disadvantage of water utilization as a reactant. This is especially the case subject to treatment of NF_3 -containing gases. The content of NO_x in the off-gases reached several 1000 ppm, which exceeds multiply the permissible level and in fact makes the plasma-chemical conversion of NF_3 using water steam unrealizable. This problem is solved by using hydrogen instead of water vapour as a reactant [25]. Contrary to treatment of the carbon-containing fluorides, the treatment of NF_3 does not require oxygen. In this case, it is desirable to supply hydrogen into the plasma torch as a plasma gas component. There will be atomic dissociation of hydrogen in the plasma torch channel (see Fig. 7a). The presence of atomic hydrogen in the reacting mixture makes the temperature of conversion start several times less [12], which may provide further reduction of the energy consumptions for fluoride treatment.

In the case of CF_4 treatment, the problem of NO_x occurrence is not that critical. Nitrogen oxide content in the off-gases is acceptable. Water steam supply into the plasma torch to decrease of the required conversion temperature is not advisable since it may cause the rise of NO_x concentration in the off-gases (see Fig. 7b). The technique of separate supply of hydrogen and oxygen instead of water steam appears to be better; note that hydrogen is supplied as a plasma-gas component, whereas oxygen is supplied in the mixture with the treated gas. This would allow us to prevent a generation of a large number

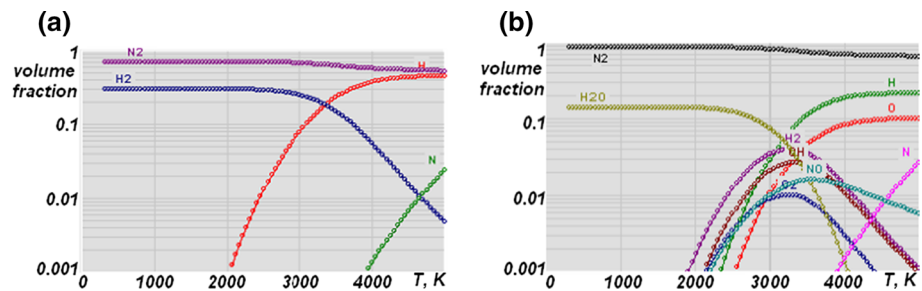


Fig. 7 Equilibrium composition of components in the system: **a** $\text{N}_2 = 70 \text{ vol\%}$; $\text{H}_2 = 30 \text{ vol\%}$; **b** $\text{N}_2 = 86 \text{ vol\%}$; $\text{H}_2\text{O} = 14 \text{ vol\%}$, $p = 0.1 \text{ MPa}$

of NO_x molecules in high-temperature zone of the plasma-chemical reactor. Similarly to the previous case, it can reduce the required temperature of CF₄ conversion and hence the NO_x concentration in the off-gases. It should be outlined that the concept of RQL combustor is based on the similar approach [26].

Conclusions

The proposed model of the plasma-chemical treatment of fluorine-containing gas mixtures with the low concentration of halogen-containing components involves the counterflow recuperation of the heat from the off-gases at the reactor outlet and the plasma torch with high thermal efficiency.

The processes of heat and mass transfer have been investigated numerically. Numerical investigation has shown that the reached average cross-sectional mixture temperatures (1800–2200 K) and residence time of reactants in the reactor working part are sufficient enough for the effective conversion of the low-concentration halogen-containing gases in the mixed gases flow.

According to the proposed approach, the plasma chemical treatment of the gas mixtures with the low concentration of fluorine-containing components has been studied experimentally. DREs of CF₄ and NF₃ decomposition exceed 90% at specific energy cost of $1.4 \text{ kW} \times \text{h/m}^3$ and $0.47\text{--}0.75 \text{ kW} \times \text{h/m}^3$, respectively, which means more than double reduction of the energy consumptions in the case of methane tetrafluoride conversion as compared to the available similar facilities.

The approach is offered to reduce the content of nitrogen oxide in the off-gases at reactor outlet as well as for the further decrease of the energy consumptions for the halogen-containing gases conversion.

The similar model of the plasma-chemical reactor can be used for the treatment of gases with the high concentration of halogen-containing components.

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