INFLUENCE OF CHEMICAL NONEQUILIBRIUM ON THE CHARACTERISTICS OF POWER UNITS OPERATING ON A CHEMICALLY REACTIVE GAS

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Flux parameter calculation features in the circuit of power units operating on a chemically-reactive N_2O_4 *mixture are reviewed in this paper. It was observed that, contrary to chemically inert heat-transfer agents, a change in the state of a chemically-reactive gas under the influence of external action depends both on the total magnitude of the action and on its specific value. The effect of chemical reaction kinetics on the thermodynamic characteristics of similar type units has been qualitatively and quantitatively analyzed.*

The study of the impact of chemical process kinetics and of oscillatory relaxation processes on the properties of the flux of reactive gas mixtures is of great scientific and practical significance. The research in this direction was to a considerable extent stimulated by the development of rocket-space studies, by the creation of powerful gas lasers, by problems of the optimization of fuel-combustion processes, by the development of optimal chemical-technological processes, etc. [1, 2].

When studying chemically-reactive mixtures based on N_2O_4 as heat-transfer agents and as the working media of power units, it is necessary to study features in the calculation of parameters of a chemically-reactive flux in a power unit circuit and to take into account the effect of chemical transformation kinetics on the characteristics of processes that take place in circuit elements and throughout the unit [3-5].

The following is a specific feature in the calculation of flux for the circuit using chemically-reactive mixtures as heat-transfer agents and as working media in comparison to chemically inert ones. When using chemically inert heat-transfer agents the state of the flux is characterized by independent parameters – temperature and pressure – whereas heat loads of the power unit equipment and its operating efficiency are uniquely defined based on the calculated or measured temperatures and on the heat-transfer agent's pressure and flow rate. It is sufficient to know the total magnitude of the external action to determine the change in the state of such a heat-transfer agent.

A similar approach is applicable in certain cases to power units employing reactive mixtures. The applicability is determined by the following: it is necessary to know the gas composition in addition to the temperature and pressure for calculating the reactive-gas thermodynamic function. During the equilibrium flow of the reacting mixture, its composition is determined on the basis of the law of mass action and is solely dependent on temperature and pressure [4, 5]. Only the availability of the equilibrium composition at the control and node points of the circuit makes it possible to apply traditional thermodynamic methods for determining the heat loads of circuit elements and power unit performance efficiencies [6].

For a nonequilibrium flow of the reactive gas, the finite velocity of chemical transformations should be taken into account when calculating flux parameters (temperature, pressure, and composition). Deviation from the thermo-chemical equilibrium in the unit with a reacting heat-transfer agent occurs at working sections (circuit elements) where the chemically-reactive system is subject to external actions and at the sections where the mixing of cold and hot fluxes takes place. At the same time, in contrast to chemically inert heat-transfer agents, the change in the state of a chemically-reactive gas exposed to an external action depends not only on the total action magnitude but also on its specific value $K = (G/F)/(dH_e/dz) = qV$ [7-9], where K is complex of external action; G is gas flow rate; F is flow cross section; and dH_e/dz is specific linear heat load.

The working sections of a power-unit circuit contain adiabatic volumes (inlet, outlet chambers, cavities, collectors) that are interconnected by thermoinsulated pipelines in which the chemical relaxation of the nonequilibrium gas takes place.

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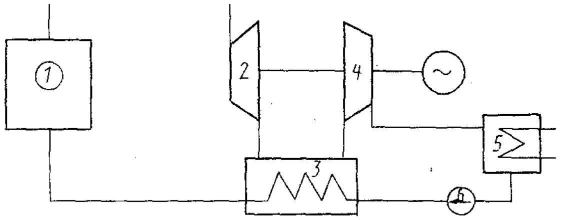

Fig. 1. Principal diagram of a power unit with a dissociative heat-transfer agent: 1) heater, 2) high-pressure turbine, 3) regenerator, 4) low-pressure turbine, 5) condensator, 6) feeder pump.

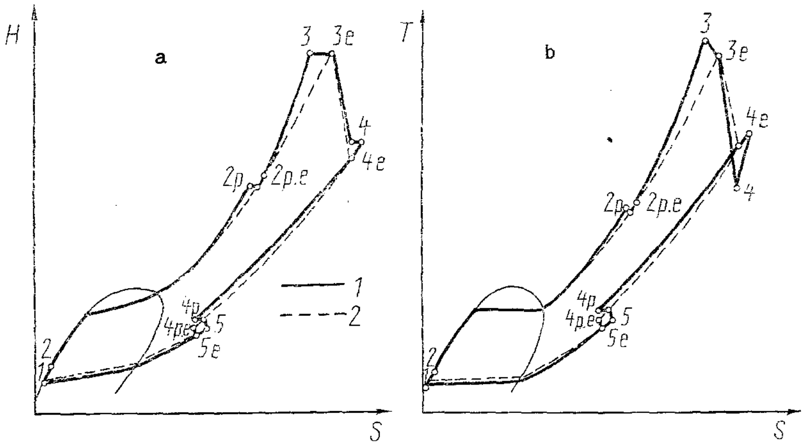

Fig. 2. Gas-liquid cycle with an intermediate heat regeneration of the chemically-reactive mixture NO_4-NO: chemical nonequilibrium (1) and equilibrium (2) in enthalpy-entropy H-S (a) and temperature-entropy T-S (b) diagrams.

Gas temperature and composition, as a result of relaxation and depending on process history, may change substantially, and, upon reaching quasi-equilibrium, they further remain practically unchanged on an adiabatic section of constant cross section [10]. At high temperatures and pressures, the equilibrium state of the reacting mixture is sometimes reached already in outlet chambers. Under other conditions, such a quasi-equilibrium state may be attained either in a connecting pipeline or might not occur at all by the time it enters the next working section. In similar cases the composition nonequilibrium both at the inlet and the outlet of each working section should be taken into account when computing thermodynamic processes in circuit elements.

Let us review the impact of chemical nonequilibrium on the characteristics of a power unit operating on a chemically-reactive gas.

From the thermodynamics point of view, the most ideal are equilibrium processes and working cycles of power units. Any nonequilibrium, including a chemical one, leads to energy dissipation, an irreversible entropy increase, and reduced working medium workability and unit performance efficiency [6, 11].

Let us analyze with respect to circuit elements the influence of chemical nonequilibrium on the flux parameters and on the characteristics of a power unit operating on a N_2O_4-NO mixture during the gas-liquid cycle with an intermediate heat regeneration (Fig. 1).

Heat-transfer agent compression in the pump takes place in the liquid phase in the region of the reaction equilibrium $N_2O_4 \rightleftarrows 2NO_2$.

Heat supply in the regenerator on the heated side takes place in the region of the reaction $N_2O_4 \rightleftarrows 2NO_2$ and at the beginning of the reaction $2NO_2 \rightleftarrows 2NO + O_2$; a possible nonequilibrium development of a second reaction leads to a higher temperature of the heat-transfer agent, to a lower regenerator temperature head, and to a reduced regeneration heat.

TABLE 1. Major Characteristics of the Experimental-Industrial "Vikhr'-2" and "BRIG-300" Units

Unit feature	"Vikhr'-2"	"BRIG-300"
Major unit features		
Unit diagram	Single-circuit	Single-circuit
Number of circuits	1	1
Cycle	Gas—liquid	Gas—liquid
First circuit's number of loops	1	1
Heater thermal power, MW	4.709	1110
Regenerator thermal power, MW	5.023	911.2
Electric power on turbine shaft, MW	0.9275	374.6
Heat-transfer-agent parameters		
Gas flow rate via heater, kg/sec	5.71	1266
Temperature at inlet—outlet from the heater	463/776	471/753
Pressure, MPa:		
at the inlet to the heater	6.42	17
in front of the turbine	6.00	15.0
after regeneration	1.98	2.1
Temperature in regenerator, K:		
on hot side, inlet—outlet	766.8/391	634/387
on cold side, inlet—outlet	348/463	312/471
Cycle minimum temperature, K	343	308
Cycle minimum pressure, MPa	0.726	0.22
Unit efficiency, %	17.1	31.8

TABLE 2. Impact of Chemical Nonequilibrium on "Vikhr'-2" and "BRIG-300" Power Unit Performance Indices ($\delta B = [(B - B_e)/B_e] \cdot 100$), %

Unit	High-pressure turbine			Regenerator	Heater	Efficiency of unit
	δG_T	$\delta\eta_{0i}$	δN_T	δQ_r	δQ_h	$\delta\eta_t$
"Vikhr-2"	+0,4	−1,4	−1,0	−1,9	+1,034	−4,3
"BRIG-300"	+0,74	−1,53	−0,8	−2,34	+1,024	−3,12

Heat-transfer agent heating in the heater, as a rule, occurs in the region of the $2NO_2 \rightleftarrows 2NO + O_2$ dissociation reaction; a nonequilibrium course of this reaction may cause a temperature increase of the heat-transfer agent and, consequently, an increase in the temperature of the walls of the heater's structural materials.

Gas expansion in a high-pressure turbine occurs in the region of the $2NO_2 \rightleftarrows 2NO + O_2$ recombination reaction; chemically nonequilibrium gas expansion leads to an irreversible increase in entropy, a decrease in the internal relative turbine efficiency and its useful work.

Heat removal in the regenerator on the heated side occurs in the region of nonequilibrium $2NO_2 \rightleftarrows 2NO + O_2$ recombination reaction and of equilibrium $N_2O_4 \rightleftarrows 2NO_2$ reaction; the nonequilibrium reaction results in a lower regenerator temperature head and in reduced heat regeneration.

N_2O_4-NO expansion in a low-pressure turbine occurs mainly in the region of $N_2O_4 \rightleftarrows 2NO_2$ equilibrium reaction. But, after the regenerator, the gas contains products of the $2NO_2 \rightleftarrows 2NO + O_2$ recombination reaction, the content of which almost does not change in the course of expansion due to the "freezing" of this reaction in the region of temperatures and pressures in which the low-pressure turbine operates.

In the condensator the heat is removed in the region of the $N_2O_4 \rightleftarrows 2NO_2$ equilibrium reaction. The presence of the $2NO_2 \rightleftarrows 2NO + O_2$ recombination nonequilibrium reaction products after the low-pressure turbine degrades the condensator performance conditions.

Summing up all these effects, nonequilibrium flow of chemical reactions in a power-unit circuit degrades the unit's thermodynamic efficiency. The qualitative impact of chemical nonequilibrium on N_2O_4-NO flux parameters in a gas-liquid cycle with an intermediate heat regeneration is shown in Fig. 2.

When designing units which are expected to use a N_2O_4-NO mixture as a heat-transfer agent and a working medium, great attention must be paid to reducing the level of nonequilibrium chemical reaction flow in circuit elements, and various methods have been employed to decrease such chemical nonequilibrium.

First of all, this refers to the choice of working temperature and pressure range of the units being designed, because the rates of chemical transformations depend, above all, on these parameters [12].

Much attention was paid to the heat conversion scheme in the power unit. From this point of view, the use of a scheme with an intermediate heat regeneration between turbines of low and high pressures in order to increase the heating gas pressure in the regenerator [5, 12] is technically justified. The value of the intermediate pressure in the unit's circuit was optimized and it was found that heat regeneration at the heating steam pressure of P_{4opt} = 2-2.5 MPa occurs with only minimal nonequilibrium [12].

When designing power units of the reviewed type, attention was also paid to providing an equilibrium gas composition at the inlet to its every element [12], because failure to meet this requirement degrades the work of both its separate elements and the unit as a whole. For this purpose, the connecting thermo-insulated pipelines, which play the role of relaxation volumes, should have requisite dimensions. The attainment of quasi-equilibrium composition at the inlet to major circuit elements was checked in [12] by the ratio of the "dwell" time to the chemical relaxation time t/τ_{rel}, which is practically identical to the condition obtained in [10] that $V_{ad}/V_{rel} \geq 1$, where V_{ad} is the adiabatic section volume and V_{rel} is the volume required for a "complete" chemical gas relaxation.

It was recommended in [13] that special adiabatic reservoirs (intermediate collectors) inside the work section be installed to reduce the level of nonequilibrium chemical reaction flow and to improve regenerator performance efficiency. This proposal may also be employed in other circuit elements.

The quasi-equilibrium flow criteria for adiabatic processes $K_{e\,=\,ad}$ and those for heat exchange $K_{e,q}$, obtained in papers [7, 9], made it possible to formulate the technical requirements for ensuring a quasi-equilibrium flow of thermodynamic processes: meeting the requirement $|K| \leq |K_e|$ in all circuit working sections is necessary for this effect. The only two limitations to the use of this requirement are as follows: 1) the possibility of technical implementation of such processes; 2) since the external-action complex K is related to specific power, the fulfillment of requirement $|K| \leq |K_e|$ will necessitate, in some cases, the use of larger-size power equipment, which brings about the issue of weight-dimensional and technical-economic optimization. Thus, the external-action complex K, which is used for the analysis of the state of a chemically-reactive gas in working processes, may be related to a number of the unit's characteristics that are subject to both thermodynamic and weight-dimensional optimization in the design of the power units under consideration.

When designing the "Vikhr'-2" and "Brig-300" power units, the above named means for nonequilibrium level reduction were to a variable extent applied both to separate circuit elements and to the unit as a whole. The use of the criteria obtained in papers [7, 9], namely, K_e- for quasi-equilibrium and K_f- for quasi-"frozen" flows and the external-action complex K, makes it possible to assess the impact of nonequilibrium chemical reaction flow in operation processes of such units on the following major characteristics:

a) on gas expansion work in high-pressure turbine; on the flow rate through the turbine, and on its internal relative efficiency;

b) on the amount of regenerating heat in the regenerator and on the resulting change of heater capacity;

c) on the thermal efficiency of the unit work cycle.

The parameters of the thermodynamic cycles of units "Vikhr'-2" and "BRIG-300" are specified in Table 1. Chemically nonequilibrium thermodynamic processes were compared to a hypothetical equilibrium process under the conditions of maintaining minimum temperature head in the regenerator and a maximum and a minimum temperature in the cycle.

The relative impact of chemical nonequilibrium on the characteristics of these units for nominal work duty is shown in Table 2.

The results of our comparative analysis show that the chemical nonequilbrium's contribution to reducing the thermal cycle efficiency of the said units amounts to ~3-4.5 % (rel.), which attests to the availability of a reserve for increasing the performance efficiency of units which use chemically-reactive mixtures as a heat-transfer agent and a working medium.

LITERATURE CITED

1. Nonequilibrium Physical-Chemical Processes in Aerodynamics [in Russian], edited by G. I. Maikapara, Moscow (1972).
2. S. Veilas, Chemical Kinetics and Industrial Reactor Design [in Russian], Moscow and Leningrad (1964).
3. V. B. Nesterenko, A. A. Mikhalevich, and B. E. Tverkovkin, Atomic Power Station Fast Reactors and Heat Exchange Units with Dissociating Heat-Transfer Agent [in Russian], Minsk (1978).
4. M. V. Mal'ko and V. B. Nesterenko, Kinetics and Mechanism of Chemical Reactions in Dissociating Heat-Transfer Agent NO_4 [in Russian], Minsk (1974).
5. M. A. Bazhin, V. P. Bubnov, V. B. Nesterenko, and N. M. Shiryaeva, Parameter Optimization of Power Units Using Dissociating Working Media [in Russian], Minsk (1970).
6. M. P. Vukalovich and I. I. Novikov, Technical Thermodynamics [in Russian], Moscow (1968).
7. G. É. Kostik and N. M. Shiryaeva, Vestsi AN BSSR, Series Physical-Power Sciences, No. 2, 101-109 (1979).
8. G. É. Kostik and N. M. Shiryaeva, Vestsi AN BSSR, Series Physical-Power Sciences, No. 4, 113-120 (1979).
9. M. V. Mal'ko and N. M. Shiryaeva, Vestsi AN BSSR, Series Physical-Power Sciences, No. 1, 72-76 (1991).
10. M. A. Bazhin, G. É. Kostik, and N. M. Shiryaeva, Dissociating Gases as Heat-Transfer Agents and Working Media of Power Units [in Russian], Part I, pp. 88-92, Minsk (1982).
11. R. Haaze, Thermodynamics of Irreversible Processes [in Russian], Moscow, (1967).
12. E. N. Bunin, Study of Gas-Liquid Cycles on N_2O_4 as Applied to Atomic Power Stations with Fast Reactors. Author's Abstract of Engineering Sciences Candidate Dissertation, Minsk (1981).
13. "A method of heat exchange," A. C. 832305, USSR, MKI^3 F28 F13/06.

MATHEMATICAL MODEL FOR SOOT FORMATION DURING NATURAL-GAS BURNING. 2. SOOT FORMATION PARAMETER AND POLYATOMIC CARBON COMPLEXES

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The first part of our work [1] was concerned with the elements of the mathematical model for methane dehydrogenation and its radicals. Relations were obtained for determining critical temperatures of the above process. The second part is aimed at finding a soot formation parameter and considers the mechanism of forming polyatomic hydrocarbon complexes that determine the concentration and the sizes of soot particles in a natural gas flame.

As shown in [1], the critical dehydrogenation temperatures, T_i^*, of methane molecules and its radicals regulate the number of free hydrogen atoms H that enter a gas volume. The final stage of this process is completed with the destruction of the radical $\dot{C}\ddot{H}$. As a result of an energetic break-up of the C−H bond in this radical, free carbon atoms, which are the nucleation centers for soot particles, enter the gas volume.

The development of the above process is determined by the probabilities $W_{(3-1)}$, $W_{(2-1)}$, and $W_{(1-1)}$ of the break-up of the C−H bonds in methane molecules and in its radicals. Naturally, the concentrations of the so-formed free hydrogen atoms are proportional to those of the initial compounds N_{CH_4}, $N_{\dot{C}H_3}$, $N_{C\ddot{H}_2}$ and $N_{\dot{C}\ddot{H}}$.

Considering [1], it may be written that

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