Development of Solid Gas Generating Compositions to Ensure Non Explosiveness of Spent Orbital Stages of Liquid Rocket of Space Launch Vehicles

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Abstract

The choice is discussed of solid gas generating compositions for venting by hot combustion products a fuel tank of the spent orbital stage of a space launch vehicle with a main liquid rocket engine. Non explosiveness is achieved via eliminating the possibility of freezing the drainage system when products of gasification (vapours of a propellant component + the remains of a gas boost + the hot products of combustion of solid gas generating compositions) are discharged from the tank into surrounding space. There are imposed requirements, constraints, and criteria for selecting solid gas generating compositions. When considering tank with the residues of liquid oxygen belonging to orbital spent stage of the launch vehicle «Zenith» the ways are shown how to ensure explosion safety, which on the basis of proposed approaches by selecting solid gas generating compositions (SGC) which generate oxygen and nitrogen. As a criterion of choice of SGC the total mass of the gasification system is adopted, which includes the SGC mass for gasification of liquid propellant residues, the mass of the gas generator and the mass of system to supply the combustion products of SGC into the tank. It is proposed use of residual heat in the condensed phase of the SGC combustion products to heat up the drainage system, which will increase the probability of a trouble-free operation of the drainage system.

1. Introduction

There is a problem of explosions in orbit of the spent stages of launch vehicles (LV) containing residues of liquid propellants in the tanks after turning off the main liquid rocket engine (LRE). Up to the current time, concerning orbits in the protected areas of near-earth space, there were more than 200 explosions of spent stages of launch vehicles. The main reason for these explosions is the presence of unused remains of propellants in the tanks and pipes of the LV.

In accordance with the recommendations of the Technical Subcommittee of the United Nations on the peaceful uses of outer space [1] and the Inter-Agency Space Debris Coordination Committee [2] in order to prevent explosions of propellant tanks of the orbital LV stages it is necessary to passivate unused remnants of the propellant components in tanks, for example, by discharge into surrounding space. However, when discharging the gas-vapor mixture, for example, from the oxygen tank (mixture of vapor of oxygen and pressurization gas, helium) through the drainage system into surrounding space – there is a sharp pressure drop and temperature decrease of the gases, leading to condensation of the vapors of oxygen and freezing. As a result, the drainage pipe is freezing.

An example of the implementation of dumping unused remnants of oxygen is the drainage system of the orbital second stage of the LV «Zenith» [1]. During the launch of the LV «Zenith» into orbit, at the conclusion of the second stage mission at the instant of LRE shutdown in the tanks may remain...
up to 4 tons of liquid oxygen, up to 2 tons of kerosene and 60 kg of gaseous helium. By 1996, in 21 successful launches 2 cases of destruction in orbit of the spent second stage of the LV «Zenith» were observed.

Post flight analysis showed that in these two cases the orbital spent second stages of the LV «Zenith» were in sunlit illuminated conditions during almost the entire time from the moment of launch until the moment of destruction (17–18 circuits around the Earth). These conditions likely caused a more intense evaporation of the oxygen leading to a rise of pressure inside the oxidizer tank to critical level, and that caused the destruction with the formation of a significant number of fragments. The existing drainage system was supposedly freeze due to the impact of the cooling gas flowing out from the tank containing helium and vapors of oxygen. On the basis of this analysis a modified oxygen tank drainage system in the second stage of the LV «Zenith» was developed providing for the installation of an extra pyro valve on the top of the tank, which is activated after completing the mission of the second stage of the LV by a special signal coming from the on board control system. After the introduction of these improvements six launches of the LV «Zenith» were carried out and cases of destruction of the spent second stage of the LV were not fixed. [1].

The Inter-Agency Space Debris Coordination Committee proposed general guidelines for the explosion protection of fuel tanks for cryogenic fuels [2], which consider the ventilation of fuel tanks and pipes, minimization of residual propellant at the time of the shutdown of the main LRE, etc. To implement venting of the fuel tank for the perspective LV with the main LRE it was proposed to consider the use of the technology of convective gasification for the remaining propellant, based on the supply of hot gases flow into the fuel tank. The implementation of this technology involves the development of gasification systems, which in turn is a part of the active on board deorbiting system of a spent LV stage [3, 4].

Getting hot gas (heat carrier, HC) on board of the spent stages of the LV for the system of gasification of residues of the propellant in the tank, after turning off the main LRE, to make venting the fuel tank is proposed on the basis of the combustion of gas generating compositions with desired physical and chemical properties [3]. Thus, a general statement of the research problem can be formulated as follows.

2. Formulation of the problem

In order to ensure the safe explosion of the orbiting spent stage of the LV with the residues of liquid propellant it is necessary to provide:
- venting the fuel compartment on the basis of the gaseous HC supply in the tank;
- evaporating propellant residues;
- discharge of gasification products (the vaporized component of the propellant – gas boost – HC) through the drainage system.

When discharging the gasification products into surrounding near-Earth space it is necessary to exclude the possibility of freezing the drainage system at the expense of the choice of the physical and chemical properties of the HC (products of the combustion of solid gas generating compositions).

3. Initial data, limitations, assumptions

1. Initial information on drainage systems, propellant components and pressurization gas in the oxidizer tank (liquid oxygen) referred to the orbital spent second stage of the LV «Zenith»:
- design and construction parameters of the drainage system of the fuel tank of the LV for discharging the gasification products (construction materials, diameters and length of drainage pipes and drainage safety valve settings);
- component of propellant – liquid oxygen (physical and chemical properties) of the gas-liquid phase, the residue mass in the tank after turning off the main LRE both in the liquid and gaseous states, the boundary conditions of propellant being in the tank, the temperature and pressure in the tank, including the oxygen partial vapor pressure;
- gas boost – helium, its temperature and partial pressure in the tank.

2. The solid gas generating compositions (SGC) are considered [3, 5], where:
- SGC combustion occurs in the gas generator, the pressure in the gas generator and the gas generator nozzle exits are taken the given values;
- thermodynamic equilibrium of SGC products of combustion is established;
- SGC combustion products (HC) do not react chemically with oxygen;
- heat carrier (HC) should not be composed of gas products, turning into a solid or liquid state at a temperature of oxygen boiling (90–120 K, depending on the pressure in the tank);
- as a result of the combustion of SGC the solid combustion products contain the minimum amount
of residual heat and mass and slag remains in the gasifier;
- HC contain nitrogen or oxygen containing gases, and it is necessary to exclude ingress of solid phase in the fuel tank;
- HC have a maximum specific heat;
- the burning rate of SGC or HC mass flow rate at steady state regime are selected from the condition of the fixed pressure conservation of in the tank, which is determined by its strength, when drainage system is open;
- the possibility is considered for the transfer of residual heat from the solid SGC combustion products (slag), remaining in the gas generator, through the thermal bridge to the drainage system to avoid its freezing during reset of gasification products.

3. The processes of heat and mass transfer are considered on the basis of the equations of heat balance, with the heat losses for heating the walls of the fuel tank and radiation in surrounding space being neglected; all the heat from the HC is consumed for heating of the gas boost and propellant vapor, as well as the evaporation of its liquid phase.

4. The criterion of choosing the optimal SGC at the accepted assumptions and constraints is the total mass of the system generating HC, which comprise mass of SGC, mass of gas generator, and mass of the HC supply system to the tank.

It is necessary to choose the composition of SGC, the combustion products of which, taking into account all limitations and assumptions, may provide:
- evaporation of liquid residues of propellant component in the tank;
- ventilation of the tank when discharging the gasification products through the drainage system without formation of the liquid or solid state gasification products.

4. The convective process of gasification in the tank of the spent stage of the LV

The processes of gasification of the residues of unused propellant components in the tanks after completing the LV stage mission are proposed both for low-boiling and high-boiling propellant components when designing new LV with the main LRE in their modernization to improve ecological safety and economic efficiency [4, 5].

The main technology process of gasification residues of oxygen in the tank of the second stage of the typical LV is implemented in the following sequence: after turning off the main PRE to the fuel tank with residues of oxygen (liquid and vapor phase) and gas boost helium with a total pressure of about 3 atm the products of combustion of SFGC are supplied, with a temperature of 1100 K to 1700 K and velocity of 900 m/s. The heating and evaporation of the liquid phase of oxygen are occurred, as well as increasing the pressure and the temperature alignment in the system «HC – the evaporated oxygen – gas boost helium».

In [6], the mathematical modeling is conducted of gas-dynamic flows within the typical designs of fuel tanks of the LV during the supply to the HC. Qualitative evaluation of the flow regimes for different typical designs of fuel tanks of the LV showed that the composition of gasification products is largely determined by the consumption rate of HC; the velocity vectors of flow can change their direction of movement; there may appear possible areas of turbulence, separated flows and stagnation zones.

After reaching the desired pressure in the tank determined by its strength a discharge (ventilation) of the products of gasification is performed from tank into surrounding space through the drainage system.

Impulse formulation of the problem of HC supply in the tank (the instantaneous combustion of the SGC) implies the fact that the pressure of gasification products reaches the values by several times exceeding the strength of the tank. This raises the need to determine the mass flow rate of HC in the tank. In accordance with the statement of the problem it is necessary to choose such physical and chemical parameters of SGC that the products of combustion (chemical composition, temperature, mass supply rate into the tank) provide conditions under which the gasification products, while moving through the drainage system with specified design parameters (diameters of pipelines, design of the drainage safety valve, the material of the drainage system, etc.), do not change the phase state (i.e. do not condense and convert to solid phase).

Figure 1 shows a typical tank with a drainage system that is installed on the top of tank, including the piping and drainage safety valve between them.

Figure 2 shows the phase diagram of oxygen [7] in the coordinates pressure – temperature.

As follows from the Fig. 2, at pressures and temperatures corresponding to the values above line 1, vapors of oxygen in the products of gasification, when going through the drainage will condense, while with the pressure and temperature
values above line 2, the vapors of oxygen will crystallize and, consequently, there is a possibility of the drainage system freezing with subsequent explosion of the tank.

The initial position of the points of a two-phase mixture in the tank after turning off a main LRE in Fig. 2 corresponds to: a) the gas-vapor mixture (vapor of oxygen); b) liquid oxygen residues.

When discharging the gasification products there is a depression in pressure and temperature levels. Upon motion of gasification products through the drainage system it may become possible transition of the system point in the domain of the liquid phase and then in domain of solid phase.

![Fig. 1. Typical drainage system of the LV.](image)

It is proposed to consider the use of SGC for ensuring thermodynamic properties of the system “HC + vapor of oxygen + gas boost helium” which eliminate the liquid and solid phases in the discharge process of gasification products through the drainage system.

![Fig. 2. Phase diagram of oxygen, the lines of equilibrium: 1 – liquid and gaseous phase, 2 – solid and gaseous phase, 3 – solid and liquid phases.](image)

<table>
<thead>
<tr>
<th># p/p</th>
<th>Investigation of the SGC</th>
<th>Temperature of combustion products, K</th>
<th>Composition of combustion products, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>64.7% NaNO₃ + 35.3% KMnO₄</td>
<td>1515</td>
<td>N₂: 41.7; Na₂O (s): 30.67; K₂O (s): 7.3; MnO₂ (s): 17.0.</td>
</tr>
<tr>
<td>2</td>
<td>67.6% NaNO₃ + 33.4% CrO₃</td>
<td>1798</td>
<td>N₂: 42.7; Na₂O (s): 28.46; Cr₂O₃ (s): 25.76.0.</td>
</tr>
<tr>
<td>3</td>
<td>50% NaNO₃ + 50% Fe₂O₃</td>
<td>1125</td>
<td>N₂: 32.3; Na₂O (s): 8.5; NaFeO₂ (s): 44.4; Fe (s): 12.5</td>
</tr>
<tr>
<td>4</td>
<td>60% NaNO₃ + 40% CaO₂</td>
<td>1740</td>
<td>N₂: 38.7; Na₂O (s): 27.3; CaO (s): 31.1; O₂: 1.6</td>
</tr>
<tr>
<td>5</td>
<td>64% NaClO₃ + 26% BaO₂ + 6% SiO₂ + 4% Mg</td>
<td>1499</td>
<td>O₂: 28.7; MgO (s): 6.63; BaO (s): 8.2; BaSO₄ (s): 21.3; NaCl (s): 32.2</td>
</tr>
<tr>
<td>6</td>
<td>86% NaClO₄ + 10% Na₂O₂ + 4% Si</td>
<td>1480</td>
<td>O₂: 42.4; NaCl (s): 35.85; Na₂SiO₃ (s): 14; Na₂Si₂O₅ (s): 2.5</td>
</tr>
<tr>
<td>7</td>
<td>77.5% NaClO₄ + 17% CaO₂ + 5.5% Mg</td>
<td>1457</td>
<td>O₂: 40.7; NaCl (s): 33.2; MgO (s): 9.0; CaO (s): 13.3</td>
</tr>
<tr>
<td>8</td>
<td>78% NaClO₄ + 7% BaO₂ + 4% SiO₂ + 9.5% Fe + 1.5% Mg</td>
<td>1475</td>
<td>O₂: 30.7; NaCl (s): 39.4; MgO (s): 0.45; BaSO₄ (s): 8.8; Mg₂SiO₄ (s): 3.5; Fe₂O₃ (s): 13.6</td>
</tr>
</tbody>
</table>
5. The selection of solid gas generating compositions to generate the heat carrier

As possible SGC there were selected compositions the combustion of which produces mostly gases: nitrogen and oxygen. The choice fell on the compounds generating nitrogen and oxygen because supplying in the tank with liquid oxygen the combustible gases (hydrogen, carbon monoxide [9]) is extremely dangerous due to the high explosivity of the resulting gas mixture. Use of carbon dioxide is ineffective, because its boiling point and melting point are substantially higher of the boiling point of oxygen, thus the carbon dioxide may freeze and clog the drainage system. For the same reason, even water should not be in the combustion products. Table 1 lists the possible compositions of SGC, formally satisfying these requirements, similar to the compositions described in [10‒15], temperature and composition of the HC, calculated according to [8] at a pressure of 2.5 atm.

When selecting the composition of the SGC, the content of components in known oxygen-generating mixtures was varied in order to get a lower boiling temperature up to ~ 1500 K. In Table 1 we included only the compositions described in [12, 13].

By special thermodynamic calculations it was shown that only below temperature 1500 K in the gas phase there is practically no NaCl vapor. Component variation of SGC is used everywhere when there is a need to provide a range of additional requirements, for example [14]. Therefore, sometimes the non-stoichiometry mixtures and the inert fillers (polymers, asbestos, and glass [15]) are used.

It should be noted that the use of nitrogen generating compositions do not cause big concerns about preventing the presence of condensed combustion products in the tank (via putting the filters like in inflators for airbags). But when using the oxygen generating compositions, many of which contain chlorates and perchlorates of alkali metals [16], one of the main products of combustion is corresponding metal chloride (NaCl, KCl) whose boiling point is between 1400 and 1500 K, which is often significantly lower than the combustion temperature, and thus NaCl or KCl can enter into the tank. For example, the composition NaClO$_3$ + CaO$_2$ + Mg [11] has calculated temperature 2036 K. As follows from the results in Table 1 the HC in the form of hot nitrogen gas (1125 K ...1798 K) enters the tank and solid products (s) can be filtered and remained in the gas generator having corresponding residual heat.

In the future, it is suggested to consider the use of residual heat contained in the solid products for heating the drainage system to prevent possible freezing when discharging the gasification products from the oxygen tank. To determine the amount of heat that is supplied to the tank by firing the SGC, the specific amount of SGC needed for the gasification of 1 kg of liquid oxygen was used in some studies [3, 5].

Table 2 presents preliminary estimates of specific energy and mass characteristics for SGC, given in Table 1.

<table>
<thead>
<tr>
<th>No. composition in Table 1</th>
<th>Gas mass fraction of SGC, %</th>
<th>The amount of heat that will be delivered by 1 kg of HC when cooling to the temperature 220 K, kJ/kg</th>
<th>The amount of HC necessary for gasification of 1 kg of liquid oxygen, kg</th>
<th>The amount of SGC needed for gasification of 1 kg of liquid oxygen, kg</th>
<th>Percentage of heat remaining in the solid slag relative to the total heat released in SGC combustion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.7</td>
<td>1470</td>
<td>0.074</td>
<td>0.18</td>
<td>67.7</td>
</tr>
<tr>
<td>2</td>
<td>42.7</td>
<td>1830</td>
<td>0.059</td>
<td>0.14</td>
<td>66.3</td>
</tr>
<tr>
<td>3</td>
<td>32.3</td>
<td>1000</td>
<td>0.109</td>
<td>0.34</td>
<td>69.9</td>
</tr>
<tr>
<td>4</td>
<td>40.3</td>
<td>1758</td>
<td>0.062</td>
<td>0.154</td>
<td>67.5</td>
</tr>
<tr>
<td>Compositions, which produce hot nitrogens</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>28.7</td>
<td>1302</td>
<td>0.081</td>
<td>0.28</td>
<td>73.3</td>
</tr>
<tr>
<td>6</td>
<td>42.4</td>
<td>1315</td>
<td>0.081</td>
<td>0.19</td>
<td>68.2</td>
</tr>
<tr>
<td>7</td>
<td>40.7</td>
<td>1290</td>
<td>0.082</td>
<td>0.20</td>
<td>66.4</td>
</tr>
<tr>
<td>8</td>
<td>30.7</td>
<td>1310</td>
<td>0.081</td>
<td>0.26</td>
<td>74.4</td>
</tr>
<tr>
<td>Compositions, which produce hot oxygen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As shown in Table 2, the most effective are the SGC under numbers 2 and 4. Those systems emit nitrogen. Systems that produce oxygen lose a little, but it is only because it was assumed that the temperature of combustion of the compositions containing chlorates or perchlorates must not exceed 1500 K. The last column shows the estimation of residual heat in the solid phase of SGC. It follows that the greatest loss corresponds to option number 8, which produces the lowest gas mass fraction in combustion products.

In the long term we consider a possibility of the transfer of heat from the gas generator housing to the drainage system via a thermal bridge to prevent freezing the oxygen vapors on the inner surface of the drainage pipe (Fig. 3).

6. Investigation of process parameters of heat and mass transfer while discharging gasification products

For calculations, the parameters of tank oxidizer (liquid oxygen) were taken from the second stage of the LV «Zenith». This tank was chosen because of the great volume of information available in open sources about its explosions in orbit [1] as a result of freezing the drainage pipe due to the condensed vapors of liquid oxygen.

Evaluation of the phase state of the vapor of oxygen was carried out with the following initial conditions: pressure 2.5 atm; the temperature of the gas phase 90 K; the volume fractions of helium/oxygen are 0.8/0.2.

When calculating, for the beginning of the discharge process of gasification products from the tank of spent stage of the LV, the thermodynamic systems were considered corresponding to 2 situations.

1. Original tank with heat and mass transfer caused by the thermal loading the tank of the spent stage of the LV due to radiation from the Sun upon the orbital motion. The increase in the internal pressure within the tank is caused by the temperature rise of the gas mixture (vapor of liquid oxygen + gas boost helium) and the evaporation of liquid oxygen [17]. In Fig. 4 curve 3 shows the change of partial pressure of oxygen as a result of the thermal loading the fuel tank.

2. Modified tank, when after turning off the main LRE the igniter starts in the gas generator containing SGC. As a result of burning SGC the nitrogen is supplied in the tank at an average temperature of 1500 K. The increase in internal pressure occurs as a result of mixing nitrogen, helium and the vapor of liquid oxygen. In Fig. 4 curve 4 shows the change of partial pressure of oxygen as a result of supplying HC to the tank.

The discharge process of gasification products from the tank of the LV of spent stage presents 2 situations.

1. When discharging the vapor oxygen and gas boost helium [15]. The phase state of the vapor oxygen corresponds to the appearance of the liquid phase. On the phase diagram of oxygen (Fig. 4 curve 5) this corresponds to the position of the
points, respectively, the initial position of point G1 and the end position L1;
2. When discharging mixture nitrogen + helium + vapor oxygen. It is seen that the phase state of the vapor of the oxygen gas phase corresponds to G4 (Fig. 4 curve 6).

From the results shown in Fig. 4 it follows that there is a possibility in principle of the SGC composition selection of to provide discharging the vapor oxygen, while it is in the gas phase, i.e., at conditions of the explosion safety of the spent stage of LV.

At subsequent stages of calculations optimization will be carried out to select the optimal SGC composition providing the gas state of the oxygen vapor upon discharge from the tank without residing in the domain of liquid and solid phases.

7. The results of calculations and their discussion

The calculations (Fig.4) showed hazardous possibility of freezing the drainage system when discharging the gas mixture (vapor of oxygen and gas boost helium) from the oxygen tank, for example, of the spent second stage of the LV “Zenith”. When using SGC of various compositions and supplying into the tank the appropriate HC there is a possibility of increasing the temperature and pressure providing existence of gaseous oxygen vapor and the phase avoiding formation of oxygen in the liquid phase and the subsequent freezing of the drainage system (Fig. 4 line 6).

Optimization of the SGC composition and possible modes of its combustion in the gas generator in the subsequent stages of the research will allow developing an effective system of gasification of propellant residues and venting the fuel tank. In subsequent phases of the study the issues of determining the burning rate of SGC and the optimal supply scheme of the SGC combustion products into the tank will be addressed.

8. Conclusions

1. It is proposed to carry out the process of ventilation of tanks of the orbital LV spent stage from unused remnants of the liquid propellant by means of supplying the hot SGC combustion products.
2. The calculations showed that for complete evaporation of 1 kg of liquid oxygen remaining in the fuel tank it is necessary to use 0.2–0.3 kg of SGC.
3. It is shown that the explosion protection of the tank can be achieved by eliminating the possibility of freezing the drainage system when discharging products of gasification (vapors of a propellant component + the remaining gas boost helium + hot products of combustion of the SGC) into surrounding space.
4. There are proposed options of SGC when the products of combustion do not enter into a chemical interaction with a propellant component and the condensed combustion products of SGC, and do not enter in the tank.
5. As a criterion of choice of SGC the total mass of the gasification system is adopted, which includes the SGC mass for gasification of liquid propellant residues, the mass of the gas generator and the mass of system to supply the combustion products of SGC into the tank.
6. It is proposed use of residual heat in the condensed phase of the SGC combustion products to heat up the drainage system, which will increase the probability of a trouble-free operation of the drainage system.
7. Taking for example the tank with the residues of liquid oxygen of spent orbital stage of the LV “Zenith”, the mathematical modeling was conducted of the process of discharge of the gasification products from the tank in near-earth space. It showed the possibility of freezing the drainage system and thus the possibility of exploding the tank to the original version (no SGC) and vice versa preventing freezing if using SGC that generate oxygen or nitrogen.

Acknowledgements

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References

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[7]. A.V. Novoselova, Fazovye diagrammy, ih postroenie i metody issledovanija [Phase diagrams: Their construction and methods of research], Moscow, Publishing house of Moscow University, 1987, p. 150 (in Russian).

[8]. B.G. Trusov, Program System Terra for Simulation Phase and Chemical Equilibrium, The XIV International Symposium on Chemical Thermodynamics, St-Petersburg, Russia, 2-5 July, 2002, P. 483–484.


