ANALYSIS OF POSSIBILITY OF POLYCHLORINATED BIPHENYLS (PCBS), POLYCHLORINATED DIBENZO-DIOXINES/FURANS (PCDDS/FS) FORMATION DURING RUSSIAN ROCKET SOLID PROPELLANT MOTORS DESTRUCT

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Introduction

In agreement with the Russian-American treaty START - 1 destruction of 916 rocket solid propellant motors (RSPM) with overall mass of rocket solid propellant equal to 17,5 thousand tons is being presupposed. The destruction is to be performed with the help of the technology developed by the American firm "Lockheed - Martin" [1]. This technology is based on burning of RSPM in a closed container under low pressure with subsequent scrubber purification of waste gases. As far as the question on the formation of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-dioxines/furans (PCDDs/Fs) was of primary importance when the project was tested, we made thermodynamic analysis of possibility of formation of the given compounds in the process of RSP burning.

Methods and Materials

For calculation of thermodynamic properties of PCBs and PCDDs/ Fs well known data published elsewhere were used [2]. The calculation of the thermodynamic properties was performed with the use of the additive-grouped method [3]. Calculation of ideal - gas heat capacity was performed by Rihani-Doraiswamy method:

$$C_p^o = \sum_i n_i a_i + \sum_i n_i b_i T + \sum_i n_i c_i T^2 + \sum_i n_i d_i \qquad (1)$$

where : n_i is a number of groups of the type: a_i, b_i, c_i, d_i — parameters are reference parameters for separate group in organic compounds. The received values are satisfyingly close to the well-known published data [2].

The received data were used for calculation of the standard entropy, enthalpy andGibb's energy of the reaction for determination of the direction of the process.

Results and Discussion

Russian RSPM, which are supposed to be destroyed by "Lockheed-Martin" technology, have the compositions of rocket solid propellants (RSP) as given in Table 1, according to [1].

The composition of rocket solid propellants burning products combustion products is given in Table 2, [1, 4].

Earlier direct studies of RSPM burning product and studies of soil around launching pad of solid propellant rockets had shown the possibility of formation of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-dioxines/ furans (PCDDs/Fs [2]. It seems that if the RSPM disposal plant works normally the mentioned compounds do not form in waste gases. However, the analysis of the technology tests conducted in the city of China-Lake (California)

showed that this technology had been used for the propellants having the compositions quite different than the Russian ones [3]. The Russian RSPM to be disposed have more power-generating fuels, containing cyclotetramethylene-tetranitroamine, the so-called octogene (about 85% of all the items). Besides, they have considerable mass - up to 49 tons of rocket solid propellants [1], for which the USA technology was not used either.

Table 1.Exemplary composition of the Russian rocket solid propellants (RSP) [1].

Components of RSP	Variant 1 (%)	Variant 2 (%)
Octogen	0	25
Aluminum	18	20
Polybutadiene	11.5	8.5
Ammonium perchlorate	70	46
Ferrocene	0.5	0.5

Table2 The composition of RSP combustion products [1, 4]

Combustion products	Variant 1 (g/kgRSP)	Variant 2 (g/kgRSP)
Al_2O_3	327.00	335.37
H_2	20.53	2.75
H_2O	86.44	36.69
HCl	163.01	86.74
N_2	83.13	138.43
CO	211.65	268.76
CO_2	20.66	9.59
O	2.23	1.17
H	3.81	4.62
OH	10.60	5.07
Cl	39.92	23.05
HCN	—	0.04
Fe	0.60	0.60

Probably for successful use the technology should be tested for these particular types of propellants to guarantee purification of toxical wastes, which is the main point of the project. Otherwise, waste gases formed during RSP burning may occur in the atmosphere without being properly purified.

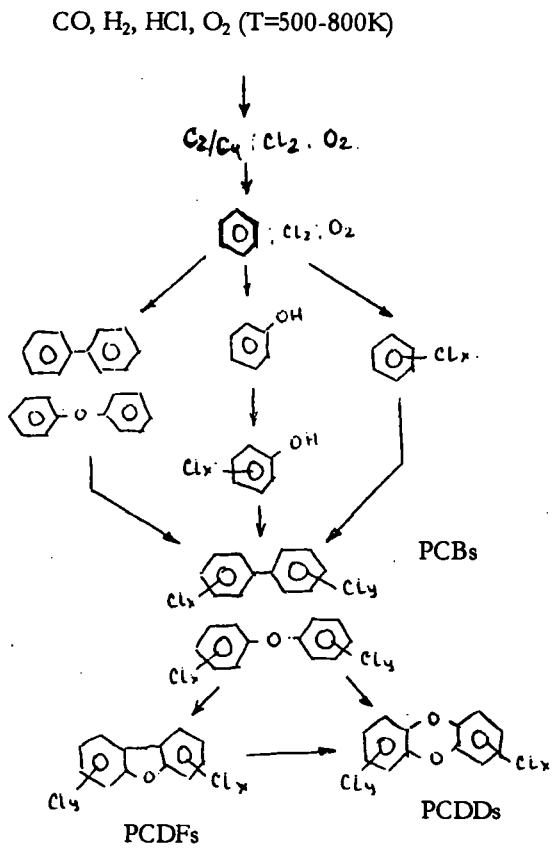
When RSP combustion products interact with the atmospheric air and the temperature of the air-gas mixture goes down lower than 900K, the reaction with chlorine formation takes place:

$$2HCl + 0.5O_2 \; f \quad Cl_2 + H \qquad (2)$$

If in the temperature of the air-gaseous mixture is in the range of 500 - 800 K chlorine formation causes occurrence of various organic chlorine compounds including PCBs, PCDD/F. The thermodynamic study of various possible reactions in air-gaseous mixture [7] that we

performed, showed the possibility of PCBs and PCDD/Fs formation according to the scheme given in fig. 1.

Fig. 1. The scheme of PCBs and PCDD/Fs formation for the air-gaseous mixture at the temperature of 500 - 800 K, made on the base of the thermo-dynamic calculations of the possible direction of the reactions [7].



Thus the above-mentioned thermodynamic analysis of the processes taking place during waste gases cooling when RSPs are burned in the open air showed the possibility of formation of PCDDs/Fs and PCBs, and chlorine aromatic compounds, which confirmed the data presented in [5].

Fig. 2 presents dependence POPs release versus time of RSP combustion products effluent into the atmosphere.

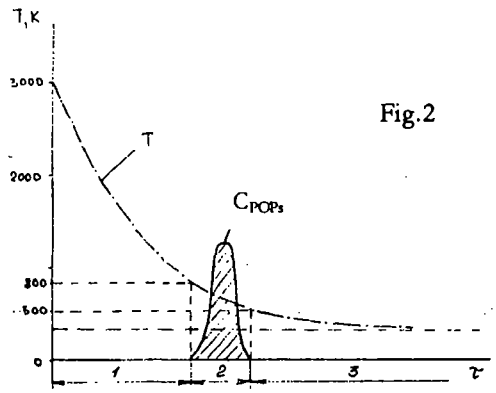


Fig.2

In case the applied technology does not allow deep purification from toxic wastes, the territory around the RSPM disposal plant can be polluted with these substances. This should be thoroughly analyzed as far as the plant is planned to be built in 4 km from the city ofVotkinsk with the population of 150 thousand people.

References

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