# THERMODYNAMIC PROPERTIES OF PROPELLANTS FOR GAS GENERATORS USED IN OIL AND GAS INDUSTRY

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Nowadays solid-propellant gas generators are used for formations breakdown and thermochemical treatment of oil-bearing beds by combustion products in order to improve or restore well bottom zone filtration properties [1]. During the process of solid fuel burning in a fluid-filled well, the high-pressure area creates for a short time period that allows not only cleaning clogged pores, but also creating new ones. In connection with this it is urgent to create propellants with high gaze inlet, burning rate and combustion product temperature.

**Table 1**

**Fuel compositions**

| Components | Compositions | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Chemical composition, mass percent | | | | | | | |
| AP | 70.8 | 69.2 | 67.9 | 67.9 | 67.9 | 68.3 | 68.3 |
| SRDM-80 | 14.2 | 15.8 | 17.1 | 17.1 | 17.1 | 16.7 | 16.7 |
| Al/B | 10/5 | - | - | - | - | - | - |
| Al | - | 15 | - | 5 | 5 | 10 | 5 |
| Ti | - | - | 15 | 10 | 5 | - | - |
| $Al_2O_3$ | - | - | - | - | 5 | - | - |
| Pb | - | - | - | - | - | 5 | 10 |
| α | 0.5 | 0.5 | 0.5 | 0.51 | 0.53 | 0.5 | 0.51 |

Water production of oil well could be limited by using metallized fuels that provide synthesis of metal oxides with melting temperature over 2000 K. In the temperature range from 923 to 1873 K metal oxides, capable to form a melt with siliceous and calcium rock will form a strong bond with these rocks after cooling. Thereby water-tight pressurizable screen arises.

This paper presents results of thermodynamic analysis for different solid fuel compositions. Solid propellants with excess oxidant ratio $\alpha$=0.5÷0.53 based on ammonium perchlorate (AP), inert fuel-binder (SKDM-80) and metal fuel (Al, Ti, $Al_2O_3$, Pb) in an amount of 15 weight percent were studied (Table 1).

**Table 2**

**Fuel compositions**

| Properties | Compositions | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Composition properties | | | | | | | |
| $T_{ad}$, K | 2919 | 3078 | 2592 | 2709 | 2519 | 2775 | 2395 |
| $I_{sp}$, s | 268 | 269 | 243 | 251 | 241 | 253 | 233 |
| W, m/s | 2371 | 2404 | 2177 | 2250 | 2153 | 2262 | 2091 |
| $MM_r$, g/mole | 19.324 | 18.354 | 18.729 | 18.457 | 19.097 | 20.051 | 21.880 |
| z | 0.255 | 0.271 | 0.237 | 0.247 | 0.222 | 0.187 | 0.094 |
| Decomposition products (mole/kg) | | | | | | | |
| HCl | 5.950 | 5.891 | 5.778 | 5.778 | 5.778 | 5.559 | 5.052 |
| CO | 9.985 | 10.698 | 10.506 | 11.065 | 10.294 | 10.592 | 9.469 |
| $H_2$ | 16.645 | 15.687 | 15.520 | 16.160 | 15.021 | 15.104 | 14.624 |
| $N_2$ | 2.834 | 2.903 | 2.539 | 2.660 | 2.562 | 2.765 | 2.283 |
| $CO_2$ | 0.077 | 0.613 | 1.474 | 1.038 | 1.709 | 1.296 | 2.553 |
| $H_2O$ | 0.520 | 3.308 | 4.176 | 3.540 | 4.676 | 4.507 | 5.619 |
| $Al_2O_{3\ condensed}$ | 1.854 | 2.779 | 0.783 | 0.927 | 1.417 | 1.853 | 0.927 |
| $Ti_4O_{7\ condensed}$ | – | – | 0.783 | 0.522 | 0.146 | – | – |
| $B_2O_{3\ condensed}$ | 0,958 | - | – | – | – | – | – |
| $TiO_{2\ condensed}$ | – | – | – | – | 0.459 | – | – |

Powder gas generators are used at bottom-hole temperatures up to 420 K and depths up to 6000 m [2]. Decomposition temperatures of AP and SKDM-80 are higher than operating temperature range for gas generators, that ensures safety use of fuels based on ammonium perchlorate. Selection of powdered metals for gas generators is limited by the presence of it production in our country and their calorific value.

On the basis of thermodynamic calculations, the following characteristics (Table 2) were found: adiabatic combustion temperature ($T_{ad}$), specific impulse ($I_{sp}$), combustion products outflow velocity (W), average molar mass of the gas phase ($MM_g$), combustion products composition and mass fraction of condensed phases (z). Calculations were conducted by using thermodynamic software "Astra-4" (Moscow State Technical university) under pressure ratio $p_k/p_a$=40/1, where $p_k$ and $p_a$ – pressure in gas generator and at the nozzle exit respectively.

Calculation results show high energy performance of investigated fuel systems. Moreover, combustion products contain considerable quantity of chlorine that increases efficiency of such fuels by the active chemical effect on the bank.

Aluminum and mixed metal fuel Al/B significantly increase energy characteristics (compounds 1, 2). These compositions are characterized by high values of adiabatic combustion temperature, specific impulse and combustion products flow rate. Compositions 1, 2 have the highest mass fraction of condensed phases. Simultaneous mechanical, thermal and physicochemical impact of combustion products onto rocks, saturating fluids and solid deposits in the wellbore zone and cracks will increase oil production. Total or particular replacement of Al by Ti, $Al_2O_3$, Pb decreases adiabatic temperature, specific impulse, combustion products flow rate and mass fraction of condensed phases (compounds 3 – 7). It should be taken into account, that well fluid is a mixture of oil, soft or saline water. Moreover, acid treatments of adjacent layers are possible. Replacement of aluminum by titanium powder provides generation during burning process oxides $TiO_2$ and $Ti_4O_7$, forming low-melting systems with siliceous and calcium rock base and having sufficient acid resistance, that is notably for water production isolation in oil wells. Partial replacement of aluminum powder by lead one saves sufficiently high energy characteristics for this kind of fuel and allows forming fusible compounds based on PbO that react with rock components and form strong acid-resistant adherence substance.

Thermodynamic calculations demonstrate the possibility of component optimal ratio selecting. Reliable performance of gas generators used in oil&gas industry is provided by; a) improving of propellant/fuel energy properties: b) combustion products temperature increasing; c) high burning rate ensuring, d) generating in combustion products metal oxide condensates that are able to form low-temperature eutectic melt with rocks. Results of this research may be useful in further studies fuel combustions based of ammonium perchlorate and an inert binder.

## References

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# LIGHTWEIGHT VERMICULITE-CONTAINING GROUTING MORTAR

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On a number of oilfields well drilling is complicated by the presence of high-permeable layers and layers with low formational pressure. Implementation of lightweight grouting mortars is one of the most effective technological solutions to improve well cementing quality significantly [1].

In order to reduce grouting mortat density for well cementing in complex geological conditions vermiculite air-entraining admixture can be applied. Vermiculite is hydromica group mineral, has low thermal conductivity and considerable absorbency, is not susceptible to biological decomposition, acid and alkalis action. It should be noted that vermiculite is non-toxic environmentally friendly material [2]. Efficiency of lightweight vermiculite-containing grouting mortars is caused by vermiculite and cement physicochemical interaction that leads to new hydrated phase formation reinforcing composite material structure. In comparison with widespread gel-cement slurry vermiculite-containing grouting mortar has better plugging ability, lower thermal conductivity providing better facilities for cement hardening, and relaxing ability increasing frost resistance and fracture strength [3, 4].

At the first stage of this study the selection of grouting mortar receipt providing the lowest density while maintaining the required flowability of cement slurry in accordance with the requirements of GOST 1581-96 was carried out. ПЦТ-IG-CC-1 was used as the cement component. Experimental results are shown in Table1.

**Table 1**

**Density and flowability of cement slurry**

| Parameters | Composition I (90% cement, 10% vermiculite) | | | Composition II (87,5% cement, 12,5% vermiculite) | | | Composition III (85% cement, 15% vermiculite) | | | GOST 1581-96 |
|---|---|---|---|---|---|---|---|---|---|---|
| | water-cement ratio | | | water-cement ratio | | | water-cement ratio | | | |
| | 0.65 | 0.75 | 0.8 | 0.65 | 0.75 | 0.8 | 0.65 | 0.75 | 0.8 | |
| Density, g/cm$^3$ | 1.6 | 1.55 | 1.5 | 1.57 | 1.53 | 1.48 | - | 1.46 | 1.44 | 1.4-1.5 |
| Flowability, mm | 145 | 170 | 250 | 120 | 150 | 210 | - | <90 | 165 | >180 |

In accordance with experimental results, composition I (90% cement, 10% vermiculite, water-cement ratio about 0.8) is accepted to be optimal.

At the second stage thecomposition of lightweight grouting was tested for compliance with GOST 1581-96. Experimental results are shown in Table 2.