Composition of the gas-plasma phase in the radioactive graphite - water vapor system

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Abstract. In this work, the composition and thermophysical properties of the “Reactor graphite-H₂O” system at temperatures from 2123 to 3223 K are calculated. It was found that the main components of the vapor phase at a temperature of 2123-2923 K: carbon dioxide, carbon monoxide, water vapor, hydroxide, hydrogen, atomic hydrogen. At temperatures above 3223 K, oxygen and atomic oxygen are added to the gases present. The balances of uranium and plutonium are considered. Uranium at temperatures above 2123 K is present in the system in the form of gaseous and ionized uranium dioxide and trioxide. Plutonium at temperatures above 2123 K is present in the system in the form of gaseous and ionized plutonium oxide, gaseous plutonium dioxide. The calculation of thermophysical properties for the considered system is carried out.

1. Introduction
Reactor graphite in the form of blocks is used as a neutron reflector in nuclear reactors of various generations. Various types of structural elements of technological equipment are also made from reactor graphite: graphite rings of contact between the process channel and the graphite block; graphite bushings for fuel assemblies; displacers of rods of the control and protection system, etc [1].

In addition to thermal, chemical and mechanical loads, reactor graphite is exposed to powerful radioactive radiation during operation, which leads to its degradation. The activity of graphite in the reactor core is due to: neutron activation of carbon in the graphite matrix; contamination of graphite with products of activation of the gas filling the masonry; hitting the masonry with coolant, products of erosion and corrosion; and fission products and nuclear fuel getting into masonry during a “wet” accident. The level of activation by neutrons depends on its chemical composition graphite, duration of irradiation, flux and spectrum of neutrons. The activated impurities in gases are ³H, ¹⁴C, ³⁶Cl, ⁴¹Ar, ¹³N, ¹⁶N. Radioactive products of corrosion and erosion that contaminate graphite in their mutual contact with structural elements (channels, rods, supports, etc.) are mainly radioisotopes of zirconium and
niobium, the concentration of which is low. Contamination of graphite with a fuel composition and fission products during “wet” accidents occurs due to the ingress of gamma-emitting nuclides into the graphite stack: $^{134}\text{Cs}$, $^{137}\text{Cs}$, $^{60}\text{Co}$, $^{55}\text{Fe}$, $^{154}\text{Eu}$, $^{151}\text{Sm}$, $^{244}\text{Am}$, $^{243}\text{Am}$, $^{239}\text{Pu}$, $^{106}\text{Ru}$, $^{90}\text{Sr}$. Most often, such contamination is observed on the surface of graphite blocks [2].

The largest amount of radioactive graphite is found in UK (eighty-six thousand tons), the USA (fifty-five thousand tons), the Russian Federation (sixty thousand tons), France (twenty-three thousand tons). A smaller part of radioactive graphite is located in Ukraine (5.7 thousand tons), Lithuania (3.8 thousand tons), Spain (3.7 thousand tons), North Korea (3.5 thousand tons), Italy (three thousand tons), Japan (three thousand tons). tons), Belgium (2.5 thousand tons), Germany (two thousand tons) [2].

For most of the nuclear reactors included in the decommissioning programs, a delayed decision was adopted, which provides for mothballing and controlled maintenance for a long time. At the moment, no final decision on the problem of using radioactive graphite has been made in the world. There are the following options for the processing of reactor graphite are considered: heat treatment (up to 1400 °C), high-temperature oxidation, acid treatment, washing of graphite with synthetic surfactants, in molten salts, the use of spark erosion, plasmification, reuse of deactivated graphite, processing in boiling bed, gasification processing, gasification of graphite using superheated steam [2].

The aim of the work is to conduct a thermodynamic analysis of the “Reactor graphite-$\text{H}_2\text{O}$” system. The task of the work is to conduct a thermodynamic analysis of the “Reactor graphite-$\text{H}_2\text{O}$” system at temperatures from 2123 to 3223 K.

2. Calculation Method
Exploring System Behavior “Reactor graphite-$\text{H}_2\text{O}$” is studied using the method of thermodynamic modeling. The thermodynamic modeling method is a computational experiment that allows you to analyze states and processes and draw conclusions about the behavior of the objects under study based on model concepts. It follows from the laws of thermodynamics that in a state of equilibrium the entropy of an isolated system is maximum. Therefore, the problem of thermodynamic calculation is reduced to finding the coordinates of the conditional maximum of entropy. Thermodynamic modeling was performed in the TERRA software package. TERRA allows for thermodynamic calculations of the phase composition of arbitrary heterogeneous systems, as well as their thermodynamic and transport properties. To carry out thermodynamic calculations, thermodynamic databases were used: IVTANTHERMO, HSC Chemistry, etc [3 – 9].

To carry out thermodynamic modeling of the “Reactor graphite-$\text{H}_2\text{O}$” system, the following initial composition was selected: condensed phase – 25.003 % (C – 24.999 %, Eu – 1.999·10^{-6} %, Am – 2.499·10^{-6} %, Sr – 2.499·10^{-6} %, Cs – 9.999·10^{-7} %, Ni – 1.999·10^{-6} %, Pu – 1.799·10^{-5} %, Ca – 6.749·10^{-5} %, Cl – 0.0004 %, U – 0.002 %); vapor phase ($\text{H}_2\text{O}$ - 74.997%). The investigated temperature range: 2123-3223 K, with a step of 100 K. Constant pressure is 0.1 MPa.

3. Results and discussion
Table 1 shows composition of the vapor phase of the “Reactor graphite-$\text{H}_2\text{O}$” system at temperatures from 2123 to 3223 K.

Table 1. Composition of the vapor phase (atm.) of the “Reactor graphite-$\text{H}_2\text{O}$” system at temperatures from 2123 to 3223 K

| T (K) | CO₂ | CO | H₂O | OH | H₂ | H | O₂ | O   |
|------|-----|----|-----|----|----|---|----|-----|
| 2123 | 0.044 | 0.2889 | 0.2887 | 0.0002 | 0.3759 | 0.0023 | 3.4·10⁻⁷ | 1.05·10⁻⁶ |
| 2223 | 0.042 | 0.2905 | 0.2901 | 0.0005 | 0.3728 | 0.004 | 1.2·10⁻⁶ | 3.75·10⁻⁶ |
| 2323 | 0.0403 | 0.2917 | 0.2908 | 0.0009 | 0.3694 | 0.0068 | 3.9·10⁻⁶ | 1.2·10⁻⁵ |
system at temperatures from 2123 to 3223 K

Table 2 shows the distribution of uranium and plutonium in vapor phase of the “Reactor graphite-H₂O” system at temperatures from 2123 to 3223 K.

| T (K) | UO₂ | UO₃ | UO₂⁺ | UO₃⁺ | PuO | PuO₂ | PuO⁺ |
|-------|-----|-----|------|------|-----|------|------|
| 2123  | 4.0489 | 75.5938 | 8.2983 | 12.0589 | 1.9303 | 97.046 | 1.0237 |
| 2223  | 4.7136 | 72.89 | 8.901 | 13.4951 | 2.3881 | 96.3252 | 1.2866 |
| 2323  | 5.4069 | 70.2571 | 9.4387 | 14.8968 | 2.8967 | 95.5173 | 1.5859 |
| 2423  | 6.12 | 67.6897 | 9.9749 | 16.2143 | 3.4534 | 94.6227 | 1.9238 |
| 2523  | 6.8465 | 65.1651 | 10.5462 | 17.4403 | 4.0555 | 93.6411 | 2.3033 |

The pressure of carbon monoxide rising from 0.2888 to 0.29242 atm., water vapor from 0.28869 to 0.290741 atm., atomic hydrogen from 0.00228 to 0.01097 atm., while the pressure of hydrogen is dropping from 0.37588 to 0.36537 atm., carbon dioxide from 0.04401 to 0.03877 atm. with an increase in temperature from 2123 to 2423 K. The pressure of atomic hydrogen rising from 0.01097 to 0.07158 atm., hydroxide from 0.00166 to 0.018 atm., while the pressure of carbon monoxide dropping from 0.29242 to 0.28557 atm., water vapor from 0.29074 to 0.26349 atm., hydrogen from 0.36537 to 0.32631 atm., carbon dioxide from 0.03877 to 0.0317 atm., with an increase in temperature from 2423 to 2923 K. The pressure of atomic hydrogen rising from 0.07158 to 0.16021 atm., hydroxide from 0.018 to 0.04394 atm., atomic oxygen from 0.00251 to 0.0152 atm., oxygen from 0.00079 to 0.00413 atm., while the pressure of carbon monoxide dropping from 0.28557 to 0.26853 atm., water vapor from 0.26349 to 0.202 atm., hydrogen from 0.32631 to 0.2825 atm., carbon dioxide from 0.0317 to 0.02432 atm., with an increase in temperature from 2923 to 3223 K.

Table 2 shows the distribution of uranium and plutonium in vapor phase of the “Reactor graphite-H₂O” system at temperatures from 2123 to 3223 K.
Let us consider the distribution of uranium in the vapor phase. Ionized uranium trioxide reaches 20.6131 mol%, ionized uranium dioxide - 10.0601 mol%, vaporous uranium dioxide - 10.0602 mol%, at the same time, vaporous uranium trioxide decreases to 55.8854 mol% with an increase in temperature from 2123 to 2923 K. Ionized uranium dioxide reaches 20.9731 mol%, vaporous uranium dioxide to 13.6674 mol%, at the same time, vaporous uranium trioxide decreases to 47.9796 mol%, ionized uranium trioxide - 17.3203 mol% with an increase in temperature from 2923 to 3223 K.

Let us examine the distribution of plutonium in the vapor phase. Vaporous plutonium oxide reaches 10.3271 mol%, ionized plutonium oxide to 8.8797 mol%, at the same time vaporous plutonium dioxide decreases to 80.7887 mol% with an increase in temperature from 2123 to 3223 K.

Table 3 shows the thermophysical characteristics of the “Reactor graphite-H2O” system at temperatures from 2123 to 3223 K.

| T (K) | Number of moles (mol/kg) | Internal energy (kJ/kg) | Entropy (kJ/(kg K)) | Enthalpy (kJ/kg) | Volume (m³/kg) |
|-------|--------------------------|-------------------------|---------------------|-----------------|---------------|
| 2123  | 62.5223                  | -4199.295               | 15.5571             | -3250.665       | 11.03615      |
| 2223  | 62.585                   | -3959.57                | 15.69175            | -2957.945       | 11.5676       |
| 2323  | 62.68625                 | -3700.45                | 15.8293             | -2645.075       | 12.10765      |
| 2423  | 62.84375                 | -3413.765               | 15.97315            | -2303.47        | 12.66075      |
| 2523  | 63.0809                  | -3088.6                 | 16.1274             | -1921.65        | 13.23315      |
| 2623  | 63.42835                 | -2710.555               | 16.2971             | -1484.42        | 13.83365      |
| 2723  | 63.9263                  | -2260.715               | 16.48855            | -971.763        | 14.47415      |
The number of moles increases to 63.0809 mol/kg with an increase in temperature from 2123 to 2523 K according to a linear law. The number of moles increases more intensively to 71.06905 mol/kg (14.3 times) with an increase in temperature from 2523 to 3223 K.

Internal energy increases to $-3088.6$ kJ/kg with an increase in temperature from 2123 to 2523 K. Internal energy increases more intensively to $2183.095$ kJ/kg (4.7 times) with an increase in temperature from 2523 to 3223 K.

Entropy increases to $16.1274$ kj/(kg K) with an increase in temperature from 2123 to 2523 K. Entropy increases more intensively to $18.10865$ kj/(kg K) (3.4 times) with an increase in temperature from 2523 to 3223 K.

Enthalpy increases to $-1921.65$ kj/kg with an increase in temperature from 2123 to 2523 K. Enthalpy increases more intensively to $3911.925$ kj/kg (4.3 times) with an increase in temperature from 2523 to 3223 K.

Volume increases to $13.23315$ m$^3$/kg with an increase in temperature from 2123 to 2523 K according to a linear law. Volume increases more intensively to $19.05005$ m$^3$/kg with an increase in temperature from 2523 to 3223 K.

4. Conclusion

The work carried out a thermodynamic study of the composition and thermophysical properties in vapor phase of the “Reactor graphite-H$_2$O” system.

The results of thermodynamic calculations are presented in the following tables: Composition of the vapor phase of the “Reactor graphite-H$_2$O” system at temperatures from 2123 to 3223 K; Distribution of uranium and plutonium in vapor phase of the “Reactor graphite-H$_2$O” system at temperatures from 2123 to 3223 K; Thermophysical characteristics of the “Reactor graphite-H$_2$O” system at temperatures from 2123 to 3223 K.

Analyzing the tables, the following conclusions can be drawn: at $T > 2923$ K, the main components of the vapor phase for the system under consideration are: carbon dioxide, carbon monoxide, water vapor, hydroxide, hydrogen, atomic hydrogen, oxygen, atomic oxygen; uranium at temperatures above 2123 K is present in the system in the form of ionized and vaporous uranium dioxide, vaporous and ionized uranium trioxide; plutonium at temperatures above 2123 K is present in the system in the form of ionized and vaporous plutonium oxide, vaporous plutonium dioxide; at $T = 2123$-2523 K, the thermophysical properties of the vapor phase of the system under consideration change linearly, and at temperatures above 2523 K, they change significantly.

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