Thermodynamic modeling of the gas-plasma phase in the processing of radioactive graphite in a gas plasma furnace

N M Barbin$^{1,2}$, A M Kobelev$^1$ and D I Terent’ev$^3$

$^1$Research department of the educational and scientific complex for fire fighting and rescue operations, Ural Institute of the State Fire Service EMERCOM of Russia, 22 Mir Street, Yekaterinburg 620062, Russia
$^2$Institute of Physicochemical Problems and Technosphere Safety, Ural State Agrarian University, 42 Karl Liebknecht Street, Ekaterinburg 620075, Russia
$^3$Research department of the educational and scientific complex of ensuring fire safety of objects and settlements, Ural Institute of the State Fire Service EMERCOM of Russia, 22 Mir Street, Yekaterinburg 620062, Russia

E-mail: nmbarbin@mail.ru

Abstract. The method of thermodynamic modeling was used to determine composition and thermophysical properties of a gas-plasma phase of a system of radioactive graphite – water vapor in the temperature range from 1000 to 3200 K. It has been established that in the temperature range from 1000 to 1100 K, the main components of the gas-plasma phase are $\text{H}_2$, CO, $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{CH}_4$. In the temperature range from 1100 to 2200 K – $\text{H}_2$, CO, $\text{H}_2\text{O}$, $\text{CO}_2$. At temperatures from 2200 to 2600 K those are $\text{H}_2$, CO, $\text{H}_2\text{O}$, $\text{CO}_2$, H. In the temperature range from 2600 to 3000 K those are $\text{H}_2$, CO, $\text{H}_2\text{O}$, $\text{CO}_2$, O, OH. In the temperature range from 3000 to 3200 K those are $\text{H}_2$, CO, $\text{H}_2\text{O}$, H, $\text{CO}_2$, OH, O, O$_2$. The thermophysical properties of the system under consideration have been calculated: specific volume, entropy, enthalpy, total internal energy, number of moles in the system.

1. Introduction
About 10% of the world production of energy falls on nuclear power plants which contribute in fight against global warming that prevents emission of about 32 billion tons of carbon dioxide in the atmosphere [1]. In total, 450 nuclear power units with a total electric capacity of 398 GW are in operation in the world [1].

By now works on decommissioning of the following uranium-graphite reactors have been conducted: Obninsk NPP, Beloyarsk NPP, Biblinsky NPP, and Leningrad NPP. In the nearest future the resource of power uranium-graphite stations in Russia will be over (the year when the last power unit will be decommissioned is 2035) [2].

By different estimates, the total amount of the irradiated reactor graphite in Russia reaches 60 thousand tons. Except for Russia, the problem of treatment of the irradiated reactor graphite is relevant for Great Britain (86 thousand tons), the USA (55 thousand tons) and France (23 thousand tons). The total amount of the irradiated graphite which is saved up around the world makes about 250 thousand tons [3].

Treatment of the irradiated graphite, including its conditioning for burial is one of relevant tasks.
The solution of a question on burial is aggravated with existence in structure of graphite products of long-living radionuclides (for example, a half-life period of $^{241}$Am – 7370 years).

Now the most perspective ways of treatment of the fulfilled graphite materials are burning [4].

Different ways of combustion of graphite are offered: traditional; in the boiling layer; by means of the plasmochemical reactor; gasification of graphite by means of superheated water vapor (pyrolysis); in the melt of one of the alkali metal carbonates or mixtures thereof in the presence of metal oxide [4–15].

The purpose of work is determination of composition and heatphysical properties of a gas-plasma phase of a system radioactive graphite – water vapor in the high-temperature range. The task of work consists in carrying out thermodynamic modeling of the considered system.

No information was found in the literature on the thermophysical properties of the gas plasma phase formed during the processing of radioactive graphite in the gas plasma furnace.

2. Calculation Method

Thermodynamic modeling of a gas-plasma phase when processing radioactive graphite in the gas-plasma furnace was carried out by means of the program TERRA complex.

The model of thermodynamic balance is widely used in scientific and industrial practice when studying behavior of systems, difficult on the chemical composition, at the increased temperatures. The program TERRA complex is intended for determination of structure of phases, thermodynamic and transport properties of any systems with chemical and phase transformations. The software package allows you to simulate the extremely equilibrium states of arbitrary complex systems. The determination of the parameters of the equilibrium state consists in finding all the dependent variables, including the number of moles of the components and phases at which the entropy (S) reaches its maximum. In the calculations of the equilibrium phase composition and equilibrium parameters, we used a reference database of the properties of individual substances (TERRA database, HSC, etc.) [5–10, 12, 14, 16–18].

The equilibrium condition of any closed and isolated thermodynamic system is defined by values of two parameters of a state [16 – 18]. Parameters of an equilibrium condition of the considered “graphite-water vapor” system were set by two parameters: temperature range (100 – 3200 K, a step of temperature 100 K), pressure (0,1 MPas). Composition of an initial system radioactive graphite - water vapor, loaded into the TERRA program: a gas phase (water vapor – 100% mass), condensed phase (carbon – 99.986% mass, uranium – 0.011% mass, chlorine – 0.0018% mass, calcium – 0.0002% mass, plutonium – 7.199·10$^{-5}$% mass, beryllium – 1.199·10$^{-5}$% mass, nickel – 7.998·10$^{-6}$% mass, caesium – 3.999·10$^{-6}$% mass, strontium – 9.998·10$^{-6}$% mass, americium – 9.998·10$^{-6}$% mass, europium – 7.998·10$^{-6}$% mass.

3. Results and discussion

Table 1 presents the composition of the gas-plasma phase of the radioactive graphite - water vapor system. In the temperature range from 1000 to 1100 K, the main components of the gas-plasma phase are: H$_2$ (p ~ 0.45 atm), H$_2$O (p ~ 0.2 atm), CO (p ~ 0.2 atm), CO$_2$ (p ~ 0.13 atm), CH$_4$ (p ~ 0.02 atm).

In the temperature range from 1100 to 2200 K, the H$_2$ pressure decreases to ~ 0.38 atm., CO$_2$ to ~ 0.04 atm. and CO pressure increases to ~ 0.29 atm., H$_2$O to ~ 0.29 atm. At temperatures from 2200 to 2600 K, the pressure of H$_2$ decreases to ~ 0.36 atm., CO$_2$ to ~ 0.036 atm. and CO pressure increases to ~ 0.292 atm., H$_2$O to ~ 0.292 atm., H to ~ 0.018 atm., OH to ~ 0.003 atm. In the temperature range from 2600 to 3200 K, the H$_2$ pressure decreases to ~ 0.296 atm, CO$_2$ to ~ 0.021 atm, H$_2$O to ~ 0.224 atm, CO to ~ 0.275 atm. and pressure H increases to ~ 0.132 atm, O to ~ 0.009 atm, O$_2$ to ~ 0.003 atm, OH to ~ 0.04 atm.
Table 1. Composition of the gas-plasma phase of the radioactive graphite – water vapor system.

| T (K) | O (atm) | O₂ (atm) | H (atm) | H₂ (atm) | OH (atm) | H₂O (atm) | CO (atm) | CO₂ (atm) | CH₄ (atm) |
|-------|---------|----------|---------|----------|----------|-----------|----------|-----------|-----------|
| 1000  | 2.4·10⁻²² | 6.1·10⁻²³ | 3.7·10⁻¹⁰ | 0.458    | 2.4·10⁻¹³ | 0.202     | 0.184    | 0.146     | 0.014     |
| 1100  | 1·10⁻¹⁹  | 2.8·10⁻²⁰ | 5.3·10⁻⁹  | 0.451    | 8·10⁻¹²  | 0.215     | 0.213    | 0.12      | 0.0009    |
| 1200  | 1.7·10⁻¹⁷ | 4.8·10⁻¹⁸ | 4.8·10⁻⁸  | 0.435    | 1.5·10⁻¹⁰ | 0.231     | 0.23     | 0.1       | 9.5·10⁻⁵  |
| 1300  | 1.3·10⁻¹⁵ | 3.7·10⁻¹⁶ | 3.1·10⁻⁷  | 0.422    | 1.8·10⁻⁹  | 0.244     | 0.244    | 0.089     | 1.3·10⁻⁵  |
| 1400  | 4.9·10⁻¹⁴ | 1.5·10⁻¹⁴ | 1.5·10⁻⁶  | 0.412    | 1.5·10⁻⁸  | 0.254     | 0.254    | 0.079     | 2.4·10⁻⁶  |
| 1500  | 1.2·10⁻¹² | 3.5·10⁻¹³ | 5.9·10⁻⁶  | 0.404    | 9·10⁻⁸    | 0.262     | 0.262    | 0.071     | 5.7·10⁻⁷  |
| 1600  | 1.8·10⁻¹¹ | 5.6·10⁻¹² | 1.9·10⁻⁵  | 0.397    | 4.4·10⁻⁷  | 0.269     | 0.269    | 0.064     | 1.6·10⁻⁷  |
| 1700  | 2·10⁻¹⁰  | 6.3·10⁻¹¹ | 5.6·10⁻⁵  | 0.392    | 1.7·10⁻⁶  | 0.274     | 0.274    | 0.059     | 5.4·10⁻⁸  |
| 1800  | 1.6·10⁻⁹  | 5.4·10⁻¹⁰ | 0.0001   | 0.388    | 5.9·10⁻⁶  | 0.278     | 0.278    | 0.054     | 2.1·10⁻⁸  |
| 1900  | 1.1·10⁻⁸  | 3.7·10⁻⁹  | 0.0003   | 0.384    | 1.8·10⁻⁵  | 0.282     | 0.281    | 0.051     | 8.7·10⁻⁹  |
| 2000  | 6.3·10⁻⁸  | 2·10⁻⁸    | 0.0007   | 0.381    | 4.7·10⁻⁵  | 0.285     | 0.285    | 0.048     | 4.1·10⁻⁹  |
| 2100  | 2.9·10⁻⁷  | 9.6·10⁻⁸  | 0.0013   | 0.378    | 0.0001   | 0.287     | 0.287    | 0.045     | 2.1·10⁻⁹  |
| 2200  | 1.1·10⁻⁶  | 3.9·10⁻⁷  | 0.0025   | 0.375    | 0.0002   | 0.287     | 0.289    | 0.043     | 1.1·10⁻⁹  |
| 2300  | 4.2·10⁻⁶  | 1.4·10⁻⁶  | 0.0044   | 0.372    | 0.0005   | 0.290     | 0.290    | 0.041     | 6.3·10⁻¹⁰ |
| 2400  | 1.3·10⁻⁵  | 4.5·10⁻⁶  | 0.0074   | 0.368    | 0.001    | 0.291     | 0.292    | 0.039     | 3.7·10⁻¹⁰ |
| 2500  | 4·10⁻⁵   | 1.3·10⁻⁵  | 0.012    | 0.364    | 0.002    | 0.291     | 0.292    | 0.038     | 2.3·10⁻¹⁰ |
| 2600  | 0.0001   | 3.5·10⁻⁵  | 0.018    | 0.359    | 0.003    | 0.292     | 0.292    | 0.036     | 1.5·10⁻¹⁰ |
| 2700  | 0.003    | 8.8·10⁻⁵  | 0.02     | 0.353    | 0.005    | 0.286     | 0.292    | 0.035     | 9.8·10⁻¹¹ |
| 2800  | 0.0006   | 0.0002   | 0.04     | 0.345    | 0.008    | 0.281     | 0.29     | 0.034     | 6.6·10⁻¹¹ |
| 2900  | 0.001    | 0.0004   | 0.05     | 0.335    | 0.01     | 0.273     | 0.288    | 0.033     | 4.5·10⁻¹¹ |
Table 2 presents the calculated thermophysical properties of the gas-plasma phase.

**Table 2. Thermophysical properties of the gas-plasma phase.**

| T (K) | V (m$^3$/kg) | S (kJ/(kg K)) | I (kJ/kg) | U (kJ/kg) | M (mole/kg) |
|-------|--------------|---------------|-----------|-----------|-------------|
| 1000  | 5.1381753    | 13.509689     | -6269.4121 | -6630.0782 | 61.782983   |
| 1100  | 5.706395     | 13.838124     | -5928.6269 | -6344.6079 | 62.392681   |
| 1200  | 6.2296152    | 14.071467     | -5661.1236 | -6129.3128 | 62.438347   |
| 1300  | 6.7492429    | 14.278572     | -5402.7    | -5922.8384 | 62.443043   |
| 1400  | 7.2684994    | 14.468284     | -5147.0348 | -5719.0932 | 62.443781   |
| 1500  | 7.7877302    | 14.644271     | -4892.2748 | -5516.2559 | 62.444162   |
| 1600  | 8.307028     | 14.808952     | -4637.2556 | -5313.1667 | 62.445005   |
| 1700  | 8.8265117    | 14.964392     | -4381.0037 | -5108.8556 | 62.447045   |
| 1800  | 9.3464053    | 15.112237     | -4122.4524 | -4902.2851 | 62.451598   |
| 1900  | 9.8671517    | 15.254041     | -3860.2332 | -4692.111  | 62.460969   |
| 2000  | 10.389507    | 15.391477     | -3592.3871 | -4476.4589 | 62.47899    |
| 2100  | 10.914687    | 15.52628      | -3316.0931 | -4252.6021 | 62.511444   |
| 2200  | 11.444596    | 15.660631     | -3027.1681 | -4016.5364 | 62.567014   |
| 2300  | 11.982231    | 15.797146     | -2719.7721 | -3762.6788 | 62.657661   |
| 2400  | 12.531743    | 15.939133     | -2385.9112 | -3483.4113 | 62.799889   |
| 2500  | 13.098853    | 16.090462     | -2014.846  | -3168.5296 | 63.015672   |
In the temperature range from 1000 to 2600 K, the specific volume of the system increases from 5.138175 to 13.69172 m$^3$/kg. In the temperature range from 2600 to 3200 K, the specific volume of the system increases more intensively (1.52 times) from 13.69172 to 18.75034 m$^3$/kg.

In the temperature range from 1000 to 2600 K, the entropy of the system increases from 13.50969 to 16.25598 kJ/(kg K). In the temperature range from 2600 to 3200 K, the entropy of the system increases more intensively (1.58 times) from 16.25598 to 17.99551 kJ/(kg K).

In the temperature range from 1000 to 2600 K, the enthalpy of the system increases from -6269.41 to -1592.35 kJ/kg. In the temperature range from 2600 to 3200 K, the enthalpy of the system increases more intensively (2.8 times) from -1592.35 to 3547.152 kJ/kg.

In the temperature range from 1000 to 2600 K, the total internal energy of the system increases from -6630.1 to -2804.5 kJ/kg. In the temperature range from 2600 to 3200 K, the total internal energy increases more intensively (3.1 times) from -2804.5 to 1846.78 kJ/kg.

In the temperature range from 1000 to 2600 K, the number of moles of components in the system increases from 61.783 to 63.3338 mole/kg. At temperatures from 2600 to 3200 K, the number of mole components increases more intensively (12.93 times) from 63.3338 to 70.4577 mole/kg.

Conclusions

Thus, the work carried out thermodynamic modeling of the gas-plasma phase during the processing of radioactive graphite in a gas-plasma furnace. The composition and thermophysical properties of the gas-plasma phase of the radioactive graphite – water vapor system are determined. The calculation results are presented in the form of reference tables, which are necessary for the design of gas-plasma furnaces for the processing of radioactive graphite. Computer simulation showed that at temperatures above 2600 K the main components of the gas-plasma phase are: H$_2$, CO, H$_2$O, H, CO$_2$, OH, O, O$_2$. In the temperature range from 1000 to 2600 K, the thermophysical properties of the gas-plasma phase of the radioactive graphite-water vapor system vary linearly. In the temperature range from 2600 to 3200 K, a significant change in the thermophysical properties of the system under consideration is observed. It can be explained with thermal dissociation of the gases which are logging in.

References

[1] Skachek M A 2014 *Radioactive Components of Nuclear Power Plants: Management, Processing, and Localization: Textbook for Higher Schools* (Moscow: Publishing House MEI) p 25

[2] Reprocessing of reactor graphite of decommissioned uranium-graphite reactors for disposal, https://www.atomic-energy.ru/articles/2016/06/08/66585 (addressed May 04, 2020)

[3] Processing of Irradiated Graphite to Meet Acceptance Criteria for Waste Disposal, https://www-pub.iaea.org/MTCD/Publications/PDF/TE-1790_web.pdf (addressed May 04, 2020)

[4] Tsyganov A A, Khvostov V I, Komarov E A, Kotlyarevsky S G, Pavlyuk A O, Shamanin I V and Nesterov V N 2007 *Izv. Tomsk. Politekh. Univ.* 310 94
[5] Barbin N M, Kobelev A M, Terent’ev D I and Alekseev S G 2017 *Radiochemistry* **59** 507
[6] Barbin N M, Kobelev A M, Terent’ev D I and Alekseev S G 2016 *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **59** 16
[7] Barbin N M, Kobelev A M, Terent’ev D I and Alekseev S G 2016 *MATEC Web of Conf.* **59** 04005
[8] Barbin N M, Kobelev A M, Terent’ev D I and Alekseev S G 2019 *Radiochemistry* **61** 192
[9] Barbin N M, Kobelev A M, Terent’ev D I and Alekseev S G 2018 *Russian metallurgy (Metally)* **2018** 700
[10] Barbin N M, Kobelev A M, Terent’ev D I and Alekseev S G 2020 *Russian metallurgy (Metally)* **2020** 145
[11] Vitushko A G, Kudrinskiy A A, Anpilov S V, Bobrakov A N, Markelov A Yu and Shiryaevskij V L 2017 *Thermal processes in engineering* **9** 131
[12] Bobrakov A N, Kudrinskiy A A, Pereslavcev A V, Shiryaevskij V L and Krutyakov Yu A 2013 *Ecology and industry of russia* **3** 46tm
[13] Bobrakov A N, Kudrinskiy A A, Pereslavcev A V and Shiryaevskij V L 2014 *Ecology and industry of russia* **4** 4
[14] Bobrakov A N, Kudrinskiy A A, Pereslavcev A V, Shiryaevskij V L and Artyomov A V 2012 *Russian chemical magazine* **56** 65tm
[15] Bobrakov A N, Kudrinskiy A A, Pereslavcev A V, Polkanov M A, Artyomov A V and Shiryaevskij V L 2013 *Russian chemical magazine* **57** 97
[16] Belov G V 2002 *Thermodynamic modeling: methods, algorithms, programs* (Moscow: Scientific world) p 128
[17] Belov G V and Trusov B G 2013 *Thermodynamic Modeling of Chemically Reacting System* (Moscow: Mosk. Gos. Tekh. Univ. im. N.E. Baumana) p 5
[18] Trusov B G 2012 *Engineering Herald* **8** 1