Processing of radioactive graphite by gas-generating method

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Abstract. Using the method of thermodynamic modeling the composition and quantity of generator gas formed during the processing of radioactive graphite in water vapor in the temperature range from 773 to 1073 K were determined. It has been established that the main components of the gas phase are CO, H₂, CO₂, CH₄, H₂O, HCl. The technological scheme and the scheme of a gas generator for the processing of radioactive graphite are developed.

1. Introduction

Among the entire mass of accumulated radioactive waste, graphite occupies a special place. After prolonged irradiation, graphite does not acquire any properties that could create a field of useful application for it [1].

Graphite is used in the form of non-replaceable products (in the form of graphite blocks) and replaceable elements: contact rings between masonry and technological channels, bushings of fuel assemblies, etc. [2].

The total amount of irradiated reactor graphite in Russia is about 60 thousand tons. In addition to Russia, the problem of handling graphite is relevant for the UK – more than 86 thousand tons, for the USA – more than 55 thousand tons and France – more than 23 thousand tons. The total amount of irradiated graphite accumulated worldwide is about 250 thousand tons [2].

Treatment of the irradiated graphite, including its conditioning for burial is one of the main objectives.

The solution of the burial issue is aggravated by the presence of long-lived radionuclides in the composition of graphite materials (for example, the half-life of ³⁶Cl is 0.3·10⁶ years, etc.) [2].

There is no final decision in the world on the disposal of spent graphite [3].

Currently, the most promising methods for managing spent graphite materials are incineration [1].

According to experts, the burning of spent graphite will result in radioactive waste, ready for long-term disposal, with a volume of 1 – 2% of the initial volume of graphite [1].

Different methods for burning graphite are proposed: traditional, in a fluidized bed, using a plasma chemical reactor, gasification of graphite using superheated water vapor (pyrolysis), in a melt of alkali metal carbonates in the presence of metal oxide [1].

The paper considers the possibility of processing reactor graphite using a gas generator.

The purpose of the gas generator processing of reactor graphite is to produce artificial combustible gases as a result of incomplete combustion of carbon-containing substances [4]. Process of gas-generating processing of reactor graphite is presented in figure 1. The gas-generating process is carried out at a temperature not lower than 500 °C [5].
In view of the composition of the gas supplied to the plant, the artificial gas generated is divided into air gas, steam-air gas, water gas and coke gas. Steam-air generated gas contains much more carbon monoxide than air gas [5].

Graphite layings of uranium-graphite reactors of nuclear power plants can be a specific source of raw materials [5].

![Figure 1. The process of gas generator processing of reactor graphite.](image)

One power unit of the RBMK nuclear power plant contains 1850 tons of reactor graphite. After disintegrating electrochemical processing of RBMK-1000 graphite blocks (removal of the most radioactive outer layer of graphite blocks ~ 1 mm), about 1.5·10^6 m^3 of generator gas can be produced. For the processing of the graphite masonry of one RBMK reactor, it will take from 3 to 6 years of continuous operation with a gas generator capacity of 20 to 50 m^3/h [4, 5].

The dilution coefficient of the residual specific radioactivity during the transition of a radioactive substance from solid to gaseous is proportional to the ratio of the corresponding densities, taking into account the mass fraction of the radioactive element in the gas molecule (equation (1)):

\[
K = \frac{\rho_r \cdot m_{co}}{\rho_{co} \cdot m_e}
\]

Provided that the density of graphite reactor grades is on average 1.7 g/cm^3 and the density of carbon monoxide is 1.25 g/l under normal conditions, the dilution coefficient of the residual specific radioactivity will be 3170. Thus, the residual specific radioactivity of the generator gas will be 3170 times less than the radioactivity of the burned reactor graphite. The ash content in this case will not exceed 0.2·10^{-3}%, which means that combustible gas will be an environmentally friendly product. The permissible concentration of carbon-14 in 1 g of reactor graphite will be 7·10^{-3} Ci/l which is safe for the environment [4, 5].

Depending on the method of gasification of carbon-containing materials, there are the following gas-generators: direct gasification process gas-generators, reverse gasification process gas-generators, transverse gasification process gas-generators, fluidized bed gas-generators, electric heating based gas-generators, rotary bed gas-generators [6 – 10].

2. Calculation Method
The composition and amount of generator gas generated during the processing of reactor graphite can be calculated by thermodynamic modeling using the TERRA software complex. The TERRA software package is designed to calculate the phase composition, thermodynamic and transport properties of arbitrary systems with chemical and phase transformations. This program simulates extreme equilibrium states. The determination of the parameters of the equilibrium state consists in finding all dependent variables, including the number of moles of components and phases at which the entropy reaches its maximum. The equilibrium state of any closed and isolated thermodynamic system is determined by the values of two state parameters. It has been determined that as such characteristics it is sufficient to consider any two of the following six thermodynamic quantities: pressure, temperature, specific volume, entropy, total enthalpy, and total internal energy. The range of change can be assigned to both the first and second parameters, or simultaneously for both parameters. The database open for expansion is built in the program TERRA complex [11 – 19].
The parameters of the equilibrium state of the considered system «graphite – water vapor» were set by two parameters: temperature range (773 – 1073 K, temperature step 100 K), pressure (0.1 MPa). The composition of the initial system of radioactive graphite – water vapor, loaded into the TERRA program: 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 ~ 7.19·10^{-5} mass%, beryllium ~ 1.19·10^{-5} mass%, nickel ~ 7.99·10^{-6} mass%, cesium ~ 3.99·10^{-6} mass%, strontium ~ 9.99·10^{-6} mass%, americium ~ 9.99·10^{-6} mass%, europium ~ 7.99·10^{-6} mass%.

3. Result and discussion
Distribution of volume of the formed connections of a gas phase of a system reactor graphite - water vapor in the range of temperatures from 773 to 1073 K is presented in table 1. In the temperature range from 773 to 1073 K, the main components of the gas phase are: CO (~ 0.68 m³), H₂ (~ 1.77 m³), CO₂ (~ 4.42 m³), CH₄ (~ 0.16 m³), H₂O (~ 1.08 m³), HCl (~ 9.16·10^{-6} m³). In the temperature range from 773 to 873 K, the volume of CO₂ increases to ~ 4.05 m³, H₂ to ~ 1.58 m³, CO to ~ 0.48 m³, HCl to ~ 9.66·10^{-6} m³ and the volume of H₂O decreases to ~ 0.96 m³, CH₄ to ~ 0.23 m³. At a temperature from 873 to 1073 K CO₂ volume to ~ 5.56 m³, H₂ to ~ 2.49 m³, CO to ~ 1.21 m³, H₂O to ~ 1.22 m³, HCl to ~ 1.18·10^{-5} m³ increases and CH₄ volume to ~ 0.003 m³ decreases.

Table 1. The distribution of the volume of the formed compounds depending on the temperature.

| Types of compounds that form in the gas phase | Volume of the gas phase of the system radioactive graphite-water vapor at temperatures from 773 to 1073 K (m³) |
|---------------------------------------------|--------------------------------------------------------------------------------------------------|
|                                             | 773           | 873           | 973           | 1073          |
| CO                                          | 0.0959        | 0.4863        | 0.9537        | 1.2121        |
| H₂                                          | 0.7596        | 1.5865        | 2.2714        | 2.4896        |
| CO₂                                         | 3.1033        | 4.0581        | 4.9803        | 5.5647        |
| CH₄                                         | 0.3965        | 0.2371        | 0.0356        | 0.003         |
| H₂O                                         | 1.1227        | 0.9608        | 1.0251        | 1.2183        |
| UO₃                                         | 1.24·10^{-23} | 4.8·10^{-23}  | 7.05·10^{-20} | 6.11·10^{-18} |
| UO₃⁻                                        | 1.04·10^{-17} | 3.11·10^{-15} | 2.89·10^{-13} | 1.17·10^{-11} |
| UO₂⁺                                        | 1.23·10^{-23} | 1.4·10^{-23}  | 1.56·10^{-23} | 1.72·10^{-23} |
| UO₂                                         | 1.23·10^{-23} | 1.4·10^{-23}  | 3.84·10^{-23} | 4.12·10^{-20} |
| HCl                                         | 4.33·10^{-6}  | 9.66·10^{-6}  | 1.07·10^{-5}  | 1.18·10^{-5}  |
| Ca(OH)₂                                     | 1.01·10^{-19} | 2.71·10^{-16} | 1.37·10^{-13} | 8.97·10^{-12} |
| CaOH⁺                                       | 1.23·10^{-23} | 1.4·10^{-23}  | 1.56·10^{-23} | 4.26·10^{-23} |
| CaOH                                        | 1.23·10^{-23} | 1.39·10^{-23} | 9.51·10^{-20} | 4.45·10^{-20} |
| Ca                                          | 1.23·10^{-23} | 1.39·10^{-23} | 1.82·10^{-23} | 2.72·10^{-20} |
| Ca⁺                                         | 1.23·10^{-23} | 1.39·10^{-23} | 1.56·10^{-23} | 1.72·10^{-23} |
| PuO₂                                         | 1.24·10^{-23} | 1.4·10^{-23}  | 1.56·10^{-23} | 7.27·10^{-23} |
| PuO                                          | 1.23·10^{-23} | 1.39·10^{-23} | 1.56·10^{-23} | 1.72·10^{-23} |
| PuO⁺                                         | 1.23·10^{-23} | 1.39·10^{-23} | 1.56·10^{-23} | 1.72·10^{-23} |
| Be(OH)₂                                     | 4.95·10^{-14} | 2.05·10^{-12} | 4.89·10^{-11} | 7.35·10^{-10} |
| BeOH                                         | 1.23·10^{-23} | 1.39·10^{-23} | 4.48·10^{-22} | 1.07·10^{-19} |
At the seventh stage, after purification, the generator gas enters the gas tank, where it accumulates and then to the gas piston unit, where it is burned and the electric energy is generated that goes to consumers. After processing, the working chamber is cooled to a safe temperature.

At the eighth stage, the crucible is removed and purified from radionuclides.

At the ninth stage, the mixture of radionuclides is included in borosilicate glass (25% - waste, 75% - crushed borosilicate glass) for its fixation in a stationary state in an insoluble, stable matrix.

At the first stage in tight installations there takes place crushing of the rest (after removal of the inner layer – 10 mm (the 10-fold stack is put)) the graphite block to the sizes of pieces ~ 10 mm.

At the second stage, a pipe with a stand for supplying water vapor is inserted into the refractory crucible, and crushed reactor graphite is loaded from above. After that, the crucible is placed in the oxidizing chamber of the furnace. The pipe is connected to the steam generator.

At the third stage, the oxidizing chamber of the furnace with the help of heaters is heated to ~ 600 °C. After heating the furnace, water vapor is supplied to the crucible. At the same time, gaseous products (H₂O, CO₂, CO, CH₄, H₂, HCl) are removed from the space of the oxidizing chamber of the furnace.

In the fourth stage, the generated gaseous products enter the cyclone for dust removal. The resulting dust is fed back into the crucible for afterburning.

At the fifth stage, the dust-free mixture of gases is fed to a gas-water heat exchanger, where the generator gases are cooled. The water generated in this process is removed through a drain device.

At the sixth stage, gaseous products enter the filter system for purification of HCl gas.

Based on the results of thermodynamic modeling of the radioactive graphite – water vapor system, a technological scheme for processing reactor graphite has been developed, which consists of ten stages.
At the eleventh stage, preparations are made for the storage of radionuclides. For the storage of radioactive waste, containers made of reinforced concrete, steel, lead or polyethylene enriched with bromine are used, which are then placed in dry barrels.

At the twelfth stage, radioactive waste is disposed of.

As a prototype of a plant for gasification of reactor graphite, a gas generator with a direct scheme for gasification of raw materials based on electric heating is used [10].

Housing of gas-generating furnace is made of refractory material.

A temperature sensor is installed in the upper part of the furnace oxidation chamber. At the bottom of the heat exchanger, gas monitoring sensors are installed. To control the supply of water vapor to the steam generator, a valve with an electric actuator is connected. The furnace is heated by electric heating elements, which are located in an oxidizing chamber. The equipment listed above is connected to a programmable logic controller. The PLC is connected to a personal computer on which a computer program is installed («GRAFIT-GAS»). The operator by means of the computer program, manages process of gas-generating processing of reactor graphite [20].

Thus, in the work, using the method of thermodynamic modeling, the composition and amount of generator gas generated during the processing of reactor graphite in water vapor were determined. The main components of the gas phase in the temperature range from 773 to 1073 K are: CO, H₂, CO₂, CH₄, H₂O, HCl. Based on the results of thermodynamic modeling and literature data, a technological scheme for processing reactor graphite has been developed. The scheme of a gas generator is developed. As a prototype of a plant for gasification of reactor graphite, a gas generator circuit with a direct gasification scheme for raw materials based on electric heating was taken.

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