Thermophysical properties of the radioactive graphite-nitrogen system

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Abstract. This article presents the thermophysical properties of the radioactive graphite–nitrogen system, which can be used as reference data to determine the operating parameters of the high-temperature processing method.

1. Introduction

One of the necessary conditions for the further effective development of nuclear energy is to ensure the safe decommissioning of NPP units and the associated processing of generated radioactive waste.

To date 110 nuclear power units have been shut down and are in various stages of decommissioning, apart from experimental, industrial, research, and transport reactors [1]. Besides, in Russia, according to the concept of preparing and decommissioning units of nuclear power plants, by 2028, 12 units should be permanently stopped for decommissioning at 5 nuclear plants [2]. Most of them are first-generation uranium-graphite reactors, namely high-power channel reactors – RBMK (according to the IAEA classification – a graphite-water nuclear reactor).

For RBMK rectors there is a problem that is currently difficult to resolve. This is due to the need to utilize reactor graphite, which is a moderator and reflector of neutrons in reactors of this type. Thus, the mass of graphite masonry of only one RBMK-1000 reactor is 1700 tons. In total, 17 power units with RBMK were launched. Eleven of them are now quite successfully operating in Russia at three nuclear power plants, namely, Leningrad, Smolensk, and Kursk NPPs, giving a little less than half of the total amount of nuclear-generated electricity produced by all nuclear power plants in Russia [3].

Besides Russia and the CIS countries, industrial and research reactors with graphite moderators are operated in the UK, France, and Japan. In total, there are more than 100 nuclear reactors with graphite elements in the world [4].

Not a single country operating uranium-graphite reactor has developed technology for conditioning reactor graphite before the disposal stage. Thus, in France, such reactors are stopped and waiting better times for the appearance of technological solutions [1].

The activity of the graphite masonry of the reactor is determined by the long-lived isotope \textsuperscript{14}C with a half-life of 5400 years. This is 95% of all graphite activity. The graphite masonry of RBMK reactors will have a radioecological hazard for a long time [1, 5].

Given the combustibility of graphite, its storage requires special safety measures [1]. In connection with the massive technical obsolescence of uranium-graphite power units of nuclear power plants, the issue of safe utilization of reactor graphite is becoming more acute.
The team of authors [6] proposed a method for high-temperature processing of reactor graphite. The essence of the method is the heating of irradiated reactor graphite in a nitrogen atmosphere at a temperature of 2600 – 2650 °C, which allows creating the necessary conditions for the transition of radionuclides accumulated in reactor graphite into the gaseous phase. The vacuum system removes the resulting volatile compounds from the furnace chamber and passes them through a filter system to trap.

2. Modeling
This article presents the thermophysical properties of the radioactive graphite-nitrogen system. The simulation was carried out using the TERRA software package, which proved to be effective in the study of high-temperature processes [7, 8] since experimental methods do not always allow obtaining complete and reliable information about the properties and behavior of substances at $T > 2000$ K due to difficulties in conducting physical experiments and measurement errors.

The numerical simulation was carried out within the temperature range from 373 to 3673 K and a pressure of one technical atmosphere. In the simulations, components with a concentration of at least $10^{-18}$ mole were taken into account. The time required to change the phase state, gas exchange with the environment, and the reaction rate was neglected.

3. Result and Discussion
The change in specific entropy ($S/M$) in the system under consideration with increasing temperature is shown in fig. 1. The graph shows that with an increase in temperature from 373 to 3273 K, the specific entropy also increases from 0.16 to 0.237 KJ/K·mole. The temperature range 3273–3573 K is accompanied by a sharp increase in specific entropy to 0.285 KJ/K·mole, while at $T > 3573$ K, it continues increasing slightly.

![Figure 1. Temperature dependence of the specific entropy of the system.](image-url)

The temperature dependence of the specific enthalpy ($H/M$) of the system on temperature is shown in fig. 2. At 373 – 3173 K, the specific enthalpy increases linearly from 2 to 110 KJ/mole. Heating of the system within the temperature range from 3173 to 3573 K leads to a significant increase of this value to 188 KJ/mole, while at 3573 – 4273 K, it continues increasing linearly.
Figure 2. Temperature dependence of the specific enthalpy of the system.

A sharp increase in the system of specific entropy and specific enthalpy at a temperature of 3173 K indicate a phase transition of carbon in the system from condensed to a gaseous state. Therefore, the high-temperature method for processing reactor graphite must be carried out below a given temperature.

The temperature dependence of the specific volume ($v/M$) of the equilibrium system is shown in fig. 3.

The ratio of volume to one mole of the substance of the system linearly increases from 0.025 to 0.22 m$^3$/mole with increasing temperature from 373 to 3273 K.

Within the range of 3373–3573 K, a jump of the considered value to 0.3 m$^3$/mole is observed, which is explained by the complete combustion of carbon in the system. With further heating from 3573 to 4273 K, growth continues in a straight line.

Figure 3. Temperature dependence of the specific volume of the system.
The temperature dependence of the mass fraction of the condensed phase is shown in fig. 4. When the system is heated to 2973 K, the fraction of the condensed phase changes insignificantly and amounts to about 0.09, a further increase in temperature from 2973 to 3573 K leads to a rapid decrease in the condensed phase due to the combustion of radioactive graphite in a nitrogen atmosphere. And within the range of 3573 – 4273 K, the mass fraction of the condensed phase is zero, which indicates the absence of condensed substances in the system.

![Figure 4. Temperature dependence of the mass fraction of the condensed phase](image)

**Conclusion**

The obtained data on the thermophysical properties of the radioactive graphite-nitrogen system make it possible to determine the operating temperature of the proposed method for processing reactor graphite. The temperature dependence curves show that in the system under consideration above 2973 K, an intense transition of carbon to a gaseous state is observed. Therefore, the optimal temperature for this method is 2873 – 2923 K, which creates the necessary conditions for the transition of radionuclides into the gaseous phase, in addition to carbon and its isotope $^{14}$C.

Decommissioning nuclear power units after the end of the design service life is a natural and necessary stage of their life cycle. For nuclear facilities with graphite elements, the decommissioning issue is associated with the totality of problems concerned with the need to select the best ways and methods of handling accumulated radioactive waste.

**References**

[1] Album K, Bodrov O, Braend T, Ivanov Yu, Korshunova Yu, Lorentzen I, Muratov O, Pikshris S, Popova L 2008 The concept of the decommissioning plan for nuclear power plants that have developed a design resource. Proposals of public environmental organizations (St. Petersburg: Network of non-governmental organizations to study the world experience of withdrawal from the operation of NPP power units) p 99

[2] The concept of preparation and decommissioning of nuclear power plant units of Rosenergoatom Concern JSC KCP 1.2.2.04.1240 – 2017 p 49

[3] Rosatom: history and modernity. Encyclopedia of the Nuclear Industry Electronic Materials http://edu.strana-rosatom.ru

[4] Blinova I, Blinova I, Sokolova I 2012 Atomic engineering abroad Electronic Materials vol 6 pp 3–14

[5] Skachek M 2007 Management of spent nuclear fuel and radioactive waste from nuclear power plants (Moscow: Publishing House House of MPEI) p 448
[6] Barbin N, Dalkov M, Shavaleev M A 2018 Method of processing reactor graphite Patent for invention RU 2658306 C2

[7] Barbin N, Shavaleev M, Terentyev D, Alekseev S 2015 The behavior of uranium and carbon when heating radioactive graphite in a nitrogen atmosphere. Thermodynamic modeling News of higher educational institutions Electronic Materials Series: Chemistry and Chemical Technology vol 58 5 34–6

[8] Barbin N, Shavaleev M, Terentyev D, Dalkov M, Alekseev S 2018 Thermophysical properties of a high-temperature system of radioactive graphite-nitrogen in the temperature interval from 2773 to 4273 K Electronic Materials Journal of Physics p 012151