Influence of vacuumetric pressure on thermal properties of high-temperature radioactive graphite-nitrogen system

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Abstract. To improve and specify the method proposed by the authors for high-temperature processing of reactor graphite in a nitrogen atmosphere, the thermodynamic data of the formed nitride compounds are supplemented and the system is calculated at a vacuum pressure of 0.5 atm. The data obtained are compared with the values at atmospheric pressure.

1. Introduction

The IAEA reports highlight that nuclear power technologies continue to evolve and the number of nuclear plants and the amount of nuclear material is increasing worldwide. Technologies related to the safety of these facilities, in particular nuclear power plants (hereinafter referred to as NPPs), also have to keep up with the times in order to maintain their efficiency [1].

As the fleet of nuclear power plants ages and their operating life is extended, safety issues should be addressed. These include managing the physical aging and obsolescence of safety equipment, ensuring the availability of qualified personnel and making the necessary safety upgrades, including radioactive waste management [2].

Currently, more than two thirds of all power reactors operating in the world have been in operation for more than 30 years. Keeping a fleet of nuclear power plants running is critical, as nuclear power accounts for approximately 10 percent of total electricity generation and a third of low-carbon electricity generation [2].

Some types of reactors of the first and second generation provide for the presence of graphite as a moderator and a reflector. These types include high-power channel reactors - RBMK (according to the IAEA classification, graphite-water nuclear reactor), power heterogeneous loop reactor - EGP, and gas-fired reactors with spherical filling [3]. In total, in the world, there are more than 100 nuclear reactors with the presence of graphite elements in the reactor [4].

In connection with the decommissioning of uranium-graphite reactors, there is a problem of reprocessing and utilization of graphite elements, since during their operation they accumulate radionuclides and form a long-lived carbon isotope 14C.

Currently, after removal from the reactor, this radioactive waste is placed for several years in special storage facilities built right at the power plant [3]. This method does not ensure a decrease in the volume of radioactive graphite; therefore, high-temperature heat treatment technologies in various gaseous environments are considered as an effective alternative.
The authors of [6-9] considered a new method for processing reactor graphite in a nitrogen atmosphere. This method was proposed on the basis of the obtained results of computer thermodynamic modeling.

In order to improve and specify the processing of reactor graphite by this method, the thermodynamic data of the formed nitride compounds are supplemented and the calculations of the reactor graphite-nitrogen system are carried out at a vacuum pressure of 0.5 atm.

2. Experiment
Modeling is carried out using the Terra program. Calculations of the phase composition and equilibrium characteristics are carried out using the reference database on the properties of individual substances IVTANTHERMO and HSC.

When heating the reactor graphite-nitrogen systems, the conditions for the complete oxidation of carbon in a nitrogen atmosphere, the temperature ranges of the transition of radionuclides into the gaseous phase and their formed volatile compounds are determined. The modeling is carried out under conditions of normal atmospheric and vacuum pressure - 0.5 atm.

3. Result and Discussion
As an example of the obtained simulation results, the balances of the distribution of carbon and plutonium by heating the reactor graphite-nitrogen system at a pressure of 0.5 atm are presented.

The carbon balance is shown in fig. 1. The graph shows that up to a temperature of 2673 K, carbon is completely in the condensed phase. A further increase in temperature in the system from 2673 to 3473 K leads to the disappearance of the condensed phase and the appearance of a gaseous phase in the form of CNC, C\textsubscript{3}, CN, C\textsubscript{2}N, C and C\textsubscript{2}. In the range 3473 - 4273 K, a decrease in the concentration of C\textsubscript{3} and an increase in the content of CN, C, C\textsubscript{2} are observed.

![Figure 1. Carbon balance.](image)

The behavior of plutonium in equilibrium phases and the compounds formed is shown in Fig. 2. When the system is heated from 373 to 1073 K, plutonium is present in the form of a condensed compound of plutonium carbide PuCl\textsubscript{3}. Under temperature conditions from 1073 K to 1573 K, an increase in the concentration of plutonium nitride PuN is observed due to a decrease in plutonium carbide PuCl\textsubscript{3}. Further heating of the system from 1573 to 1973 K leads to a decrease in the concentration of PuN nitride with a simultaneous increase in the content of plutonium oxide PuC\textsubscript{2}.

When the temperature reaches 1973 K and up to 2473 K, a decrease in condensed plutonium compounds in the form of PuN, PuC\textsubscript{2} and the formation of gaseous Pu and ionized Pu\textsuperscript{+} are observed in
the system. At temperatures of 2473-4273 K, plutonium in the system is presented entirely in the gaseous phase in the form of Pu vapor and Pu⁺ ion vapor.

Figure 2. Plutonium balance.

The table shows the obtained data on the distribution of radionuclides by phase states with the compounds formed under the conditions of heating reactor graphite at various pressures.

| Element    | Temperature range of phase distribution, K (in the form depending on which compound the element is in) |
|------------|---------------------------------------------------------------------------------------------------|
|            | only condensed phase | transitional interval (in system of two phases) | only condensed phase |
|            | 1 atm. | 0.5 atm. | 1 atm. | 0.5 atm. | 1 atm. | 0.5 atm. |
| Carbon     | < 2773 (C) | < 2673 (C) | 2773-3473 | 2673-3573 | > 3473 (CNC, C₃, C₂N, CN, C, C₂) | > 3573 (CNC, C₃, C₂N, CN, C, C₂) |
| Uranium    | < 573 (UN₂, UCl₃) | < 573 (UN₂, UCl₃) | 573-2673 | 573-2773 | > 2873 (U, U⁺) | > 2773 (U, U⁺) |
| Plutonium  | < 1773 (PuC₂, PuCl₃, PuN) | < 1773 (PuC₂, PuCl₃, PuN) | 1773-2673 | 1773-2473 | > 2673 (Pu, Pu⁺) | > 2473 (Pu, Pu⁺) |
| Americium  | 873 < (Am) | 773 < (Am) | 873-2573 | 773-1073 | > 1073 (Am) | > 973 (Am) |
| Europium   | 1473 < (EuCl₂) | 1473 < (EuCl₂) | 1473-1873 | 1473-1873 | > 1873 (Eu, Eu⁺) | > 1873 (Eu, Eu⁺) |
| Strontium  | 973 < (SrCl₂) | 973 < (SrCl₂) | 973-1373 | 973-1373 | > 1373 (SrCl₂, Sr, Sr⁺, SrCl) | > 1373 (SrCl₂, Sr, Sr⁺, SrCl) |
| Caesium    | 673 < | 573 < | 673–973 | 573–973 | > 973 | > 973 |
The simulations of the heating of radioactive graphite-nitrogen systems show differences in the behavior of radionuclides, namely, their transition from a condensed state to a gaseous state at lower temperatures.

The thermophysical characteristics of the system in the considered intervals are also analyzed.

Figure 3 shows changes in the specific entropies of the reactor graphite-nitrogen systems at pressures of 1 atm. and 0.5 atm. The graphs show that the behavior of the curves is similar, and the difference lies in the displacement of the line of the system with vacuum pressure relative to the atmospheric pressure upward over the entire considered interval.

![Figure 3](image-url)

**Figure 3.** Temperature dependence of specific entropies of systems.

The temperature dependence of the mass fractions of the condensed phase of the systems under consideration is shown in Figure 4. The behavior of these curves differs in the temperature range from 2673 to 3473 K. It can be seen that in the system with vacuum pressure the process of a decrease in the condensed phase and an increase in the gaseous phase occurs more intensively at lower temperatures.
4. Conclusion

Sustainable energy sources such as nuclear power are becoming increasingly important for many countries as they strive to produce energy and build pollution-free future. At the same time, technological progress helps to improve sustainability, profitability, reliability and safety of nuclear power.

The method of processing reactor graphite in a nitrogen atmosphere has a number of competitive advantages, however, the disadvantages of this method include a relatively high processing temperature - 2773 K. At a temperature of 2673 K, the same compounds of radionuclides are formed.

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