Thermophysical properties of high-temperature system of radioactive graphite-nitrogen in the temperature interval from 2773 to 4273 K

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Abstract. Results of thermodynamic modeling of radioactive graphite-nitrogen system heating which can be applied as reference data and can be used in technological processes of high-temperature processing of reactor graphite are given in the article.

1. Introduction
Radioactive graphite as one of solid radioactive waste is a significant problem of reliability and profitability of nuclear power plants. As nuclear power plant uses graphite, this substance accumulates itself a small amount of uranium, transformation elements, and radionuclides (such as tritium and \textsuperscript{14}C)\textsuperscript{1}. Thus, reactor graphite is radiation source that considerably increases the volume of solid radioactive waste of nuclear power plants.

There are various ways of its processing including high-temperature processing, however its low efficiency requires its improvement on the basis of the new obtained data. The authors have offered a new method of high-temperature processing of radioactive graphite in arc furnaces \textsuperscript{2} that limit a possibility of transition \textsuperscript{14}C in volatile compounds to which about 90\% of radioactivity of graphite elements are fallen, detaining this element in the furnace \textsuperscript{3}.

The offered method of high-temperature processing of reactor graphite is based on its heating to 2873 K in the inert nitrogen atmosphere that creates necessary conditions of radionuclides transition to gaseous phase without carbon emissions. Along with this process, the vacuum system deletes the formed volatile compounds from the furnace and passes them through the filtering system for catching or condensing in special apparatus.

The present article deals with thermophysical properties of high-temperature processing of radioactive graphite.

2. Experiment
Thermodynamic modeling was carried out by means of the Terra program within the range of temperatures from 2773 to 4273 K under atmospheric pressure. Calculations of phases composition

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and imbalance characteristics were performed with the reference database on properties of personal substances (IVTANTERMO – Russian and HSC).

Thermodynamic balance calculation of any systems is performed by maximizing system entropy accounting to all potentially possible individual substances in balance. Components with concentration not less than $10^{-10}$ mole were considered in these calculations. Time required for phase changing, gas exchange with the environment and reaction rate were neglected. The initial structure of system is presented in table 1 [4 - 6].

| Phase          | Phase composition | Contents, % masses |
|----------------|-------------------|--------------------|
| Gas (90.9 %)   | N₂                | 100                |
| C              |                   | 99                 |
| U              |                   | $1,16 \cdot 10^{-2}$ |
| Cl             |                   | $1,9 \cdot 10^{-3}$ |
| Ca             |                   | $2,7 \cdot 10^{-4}$ |
| Pu             |                   | $7,3 \cdot 10^{-5}$ |
| Be             |                   | $1,2 \cdot 10^{-5}$ |
| Ni             |                   | $8,2 \cdot 10^{-6}$ |
| Cs             |                   | $3,4 \cdot 10^{-6}$ |
| Am             |                   | $9,3 \cdot 10^{-6}$ |
| Sr             |                   | $1,1 \cdot 10^{-6}$ |
| Eu             |                   | $1 \cdot 10^{-6}$  |
| Condensed (9.1 %) |                   |                    |

3. Results and Discussion
The realized thermodynamic modeling allows defining the formed connections and temperature intervals on the basis of which balances of elements distribution in the analyzed system have been constructed.

The balance of carbon is shown in figure 1. It is evident that carbon completely is in the condensed phase above the temperature of 2773 K. Further increase of temperature from 2773 to 3573 K results in transition of carbon from the condensed phase into gaseous forming the compounds such as CN, C₃, C₂, and C. From 3573 to 4273 K we observed the decrease of concentration of C₃ and increase of content of CN, C, C₂.

![Figure 1. Carbon balance.](image-url)
Table 2. Distribution of elements within the temperature ranges of reactor graphite heating in the nitrogen atmosphere.

| Element      | Temperature range of phase distribution, K (in the form depending on what compound is there an element) | transitional interval (in system of two phases) | only gaseous phase (vapours) |
|--------------|-----------------------------------------------------------------------------------------------------|-----------------------------------------------|-------------------------------|
|              | only condensed phase                                                                                   |                                               |                               |
| Carbon       | 2773 < (C)                                                                                             | 2773–3573                                    | 3573–4273 (CN, C, C2, C3, C2N) |
| Uranium      | (UC, UCl3, UCl4, U2C3, UC2)                                                                            | 2373–2873                                    | > 2873 (U, U\textsuperscript{+}) |
| Plutonium    | 1673 < (PuCl3, PuC2, PuC)                                                                             | 1673–2573                                    | > 2573 (Pu, Pu\textsuperscript{+}) |
| Americium    | 1373 < (Am)                                                                                            | 1373–2573                                    | > 2573 (Am)                   |
| Europium     | 1473 < (EuCl\textsubscript{2})                                                                         | 1473–1873                                    | > 1873 (Eu, Eu\textsuperscript{+}) |
| Strontium    | 973 < (SrCl\textsubscript{2})                                                                           | 973–1373                                     | > 1373 (SrCl\textsubscript{2}, Sr, Sr\textsuperscript{+}, SrCl) |
| Caesium      | 673 < (CsCl)                                                                                            | 673–973                                      | > 973 (CsCl, Cs\textsuperscript{+}) |
| Nickel       | 1273 < (Ni, Ni\textsubscript{3}C)                                                                      | 1273–1473                                    | > 1473 (Ni, NiCl, Ni\textsuperscript{+}) |
| Chlorine     | 773 < (UCl\textsubscript{3}, CaCl\textsubscript{2})                                                     | 773–1273                                     | > 1273 (UCl\textsubscript{4}, UCl\textsubscript{3}, Cl, CaCl\textsubscript{2}, BeCl\textsubscript{2}) |
| Beryllium    | 873 < (Be\textsubscript{3}N\textsubscript{2})                                                           | 873–1073                                     | > 1073 (BeCl\textsubscript{2}, BeC\textsubscript{2}, Be) |
| Calcium      | 973 < (CaCl\textsubscript{2})                                                                          | 973–1373                                     | > 1373 (CaCl\textsubscript{2}, CaC, Ca, Ca\textsuperscript{+}) |

By analogy with balance of carbon data we have obtained data on the formed compounds and phase transitions of the radionuclides available in radioactive graphite. They are represented in the summary table 2.

Changes of thermophysical characteristics of system in the considered temperature intervals have been analyzed. Change of specific entropy of reactor graphite-nitrogen system is presented in figure 2a. The diagram shows that within the range of temperatures from 3273 to 3573 K is followed by spasmodic increase of specific entropy up to 0.284 KJ / K-mole (increase by 27%) that is caused by transition of carbon to a gaseous phase. At temperatures from 3573 to 4273 K specific entropy continues increasing almost linearly.

The temperature dependence of mass fraction of the condensed phase is determined in figure 2b. When heating the system from 2773 to 3573 K we observed the zero interaction of condensed phase because of radioactive graphite combustion in the nitrogen atmosphere that is confirmed by the balance of carbon (figure 1) given above. At temperatures from 3573 to 4273 K a mass fraction of the condensed phase is equal to zero that demonstrates the lack of the condensed substances in system including radionuclides.
Figure 2. Temperature dependence: a) specific entropy of the system; b) mass fraction of the condensed phase.

4. Conclusion

Results obtained approve that at 2773 K the system being in the condensed phase contains only carbon and its isotopes. Information on the formed gaseous compounds allows finding the appropriate filtering systems for catching elements.

Originality of the offered processing method consists in essentially different approach to reactor graphite processing that allows holding isotope $^{14}$C in the condensed state, eliminating a set of various radionuclides from it.

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