Behavior of Eu, Pu, U in utilization of radioactive graphite by ignition method in oxygen

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Abstract. The behavior of some radionuclides (U, Eu, Pu) in the utilization of radioactive graphite by the combustion method in oxygen is considered. The study was carried out by thermodynamic modeling in the temperature range 300-3300 K. The main physicochemical processes occurring during oxidation were established.

1. Introduction

To date, the Russian Federation has 35 power units with a total installed capacity of 27.9 GW, of which,
- 18 power units with WWER reactors (of which 12 VVER-1000 power units, 1 WWER-1200 power units and 5 WWER-440 power units of various modifications);
- 15 power units with channel reactors (11 reactors with RBMK-1000 reactors and 4 power units with EGP-6 reactors);
- 2 power units with fast neutron reactors with sodium cooling (BN-600 and BN-800). [1]

In accordance with the General Scheme for the location of energy facilities until 2035, approved by the decree of the Government of the Russian Federation of June 9, 2017 №1209-p the RBMK-type power units should be decommissioned [2]. Thus, by 2035 the Rosenergoatom concern will need to dispose of about 20 thousand tons of radioactive graphite.

Technologies for the disposal of nuclear energy waste, for the most part, are based on the principle of isolating radioactive graphite from the environment [3]. However, this principle does not reduce their number. In this regard, it is promising to develop methods for high-temperature heat treatment, for example incineration. In recent years, this method has been considered as a replacement for existing ones, since it provides a significant reduction in the volume of waste [4].

2. Research technique

The study of the equilibrium composition of the system was carried out by the method of thermodynamic modeling. This method is a set of methods, procedures, conditions and assumptions, which makes it possible to calculate the composition of a model equilibrium system as close as possible to the equilibrium composition of the real system [5,6]. The criterion for the onset of an equilibrium state in the system is the condition for achieving an extremum of its characteristic function - a minimum of the Gibbs energy or a maximum of the entropy of the system (for closed systems) under the specified conditions. Thermodynamic modeling can be realized using a computer program...
of complete thermodynamic analysis and a database of thermodynamic properties of individual substances. In this case, the calculation was performed with the help of the TERRA software package [7] using the IVTANTHERMO database expanded due to information from the HSC5 database. Thermodynamic modeling using TERRA is successfully used in thermophysical calculations.

Thermodynamic modeling using the TERRA software complex has been successfully used in thermophysics [8-11].

In the TERRA complex, the calculation of the equilibrium composition is based on the compilation of the Lagrange function of the entropy of the components of all phases of the system and the determination of its maximum by numerical methods.

$$S = \sum_{g=1}^{G} \left[ S_{g}^0(T) - R \ln \frac{RT}{V} n_g \right] n_g + \sum_{c=1}^{C} S_{c}^0(T) n_c + \sum_{i=1}^{X} \sum_{r=1}^{K} \left[ S_{rx}^0(T) - R \ln w_{rx} \right] n_{rx} \Rightarrow S_{\text{max}}.$$  \hspace{1cm} (1)

Here: \( n_i \), \( S_i^0 \) - is the number of moles and the standard entropy (at temperature \( T \), K, and pressure \( 0/1 \) MPa) of gas (\( i = g \)), condensed (c) phases and ideal solution (rx) \( J / (\text{mol} \ \text{kg}) \) (index \( x \) refers to the solution, \( r \) - to the solution component);

\( G, \ C, \ X \) - the amount of gaseous, condensed components and solutions in the thermodynamic system, respectively, mole;

\( w_{rx} \) - is the mole fraction of the component in the solution, mol. part;

\( R \) - the universal gas constant, \( 8.314 \text{ J} / (\text{mol} \ \text{K}) \);

\( V \) - the specific volume, \( \text{m}^3 / \text{kg} \).

The radioactive graphite-oxygen system was studied in the temperature range 373-3273 K. The temperature varied in steps of 100 K. Only components with a concentration of at least \( 10^{-10} \) mol were taken into account in the calculations.

The initial system of radioactive graphite - oxygen consists of gas and condensed phases. The gas phase contains oxygen, condensed - is radioactive graphite. Information on the initial composition of radioactive graphite is given in Table 1.

### Table 1. Composition of the initial system.

| Phase          | Phase composition | Content, \% mass |
|----------------|-------------------|-----------------|
| Gas (90,91 \%) | O\(_2\)            | 100             |
| C             | 99.98             |
| U             | \( 1.16 \times 10^{-3} \) |
| Ca            | \( 1.89 \times 10^{-3} \) |
| Cl            | \( 2.69 \times 10^{-3} \) |
| Ni            | \( 7.99 \times 10^{-6} \) |
| Cs            | \( 3.99 \times 10^{-6} \) |
| Pu            | \( 7.19 \times 10^{-5} \) |
| Be            | \( 1.18 \times 10^{-7} \) |
| Np            | \( 9.99 \times 10^{-6} \) |
| Sr            | \( 1.99 \times 10^{-5} \) |
| Eu            | \( 7.99 \times 10^{-6} \) |

Condensed (9,09 \%)

This work is devoted to the study of the behavior of Eu, Pu, U radionuclides’. The considered radioactive elements present in the reactor graphite and their chemical versions necessary for thermodynamic modeling are given in Table 2.
Table 2. Forms of radionuclide existence in graphite and the equilibrium system.

| Radionuclide in graphite | Type of connection in the equilibrium system |
|-------------------------|---------------------------------------------|
| \( ^{239}\text{Pu}, ^{240}\text{Pu}, ^{241}\text{Pu}, ^{242}\text{Pu} \) | \( \text{Pu}(g), \text{PuO}(g), \text{PuO}_2(g), \text{PuO}^+(g) \) |
| \( ^{238}\text{U}, ^{236}\text{U}, ^{235}\text{U} \) | \( \text{UO}(g), \text{UO}_2(g), \text{UO}_3(g), \text{UO}_5(g), \text{UO}_3(g), \text{UO}_2^+(g), \text{UO}_3^+(g) \), \( \text{CaUO}_4(g) \) |
| \( ^{154}\text{Eu}, ^{155}\text{Eu}, ^{152}\text{Eu} \) | \( \text{Eu}(g), \text{EuO}(g), \text{EuOCl}(g), \text{EuCl}_3(g), \text{Eu}_2\text{O}_3(g), \text{Eu}^+(g) \) |

Notes. (s) is the condensed phase, (g) is the gas phase.

3. Result and Discussion

The distribution of Eu in the system is shown in Fig. 1. The condensed EuOCl remains the prevailing compound up to 800 K, then its amount begins to decrease to a temperature of 1500 K. An increase in the amount of condensed EuOCl is observed in the temperature range 900-1300 K and a decrease of 1800-2500 K. The growth of the gaseous EuO occurs from 2000 K to 2500 K. With further heating up to 3300 K, a decrease in the amount of EuO vapor with a simultaneous increase in the number of Eu\(^+\) ions and gaseous Eu occurs.

The distribution of Pu in the system is shown in Fig. 2. Up to a temperature of 1800 K, condensed PuO\(_2\) predominates in the system. With increasing temperature, the content of condensed PuO\(_2\) begins to decrease, while the content of gaseous PuO\(_2\) increases. At a temperature of 2200 K, the content of gaseous PuO\(_2\) is \(\approx 99\) mole. %, while the content of condensed PuO\(_2\) decreases to 0 mol %. Further heating of the system to 3300 K leads to a decrease in the content of gaseous PuO\(_2\) and an increase in the content of Pu\(^+\) ions, gaseous PuO.

![Figure 1. Europium’s balance](image-url)
The balance U is shown in Fig. 3. Up to a temperature of 2000 K, condensed CaUO$_4$ is observed to decrease. With a simultaneous increase in gaseous UO$_2$. With further heating together with the content of gaseous UO$_2$, the content of the following elements also increases: ions of UO$_3^-$ and gaseous UO$_3$.

**Figure 2. Plutonium’s balance**

4. Conclusion
As a result of the thermodynamic simulation of the process, it was established that when burning radioactive graphite in an atmosphere of O$_2$ uranium, plutonium and europium will be present as oxygen compounds. An increase in temperature above 2000 K leads to the evaporation of these compounds. This must be taken into account when utilizing radioactive graphite by combustion.

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