# Investigation of Radioisotopes Behavior during Thermal Decomposition of Irradiated Graphite Produced from KRR-2

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## 1. Introduction

Graphite has been used as a moderator and reflector of neutrons in more than 100 nuclear power plants as well as many experimental reactors and plutonium production reactors in various countries. Radioactive graphite dismantling, handling, conditioning and disposal are a common part of the decommissioning activities. The existing processing technologies for irradiated graphite are based mostly on the isolation of the radioactive graphite from the environment. They are, however, not able to provide for a significant volume reduction [1]. For this reason, the high-temperature thermal decomposition technologies such as an incineration are considered as effective alternative technologies, sine they provide a substantial reduction of the waste volume. However, the irradiated graphite waste includes various radionuclides such as such as tritium and $^{14}C$, as well as corrosion/activation products [2]. Therefore, while an incineration is considered as an effective tool for the integrated management of the radioactive graphite waste, the environmental acceptability of the emissions of the radioactive elements is a major criterion for the successful development of the incineration process.

The decommissioning of Korean Research Reactor 2 (KRR-2), which started in 1997, generated 3 tones of radioactive graphite waste [3].

In this study the vaporization and condensation of radioactive isotopes during thermal decomposition of irradiated graphite were investigated based on the thermodynamic analysis and experiment.

## 2. Methods and Results

### *2.1. Thermodynamic Analysis*

An important partitioning mechanism is the distribution of elements as a result of the chemical reactions within the thermal destruction system. In the absence of the reaction rate data, it is often assumed that all the reactions achieve chemical equilibriums in a relatively short period of time when compared to the total residence time of the reactants [4]. The equilibrium model analysis of this study is based on the following assumptions: (1) a thermodynamic equilibrium is maintained in the thermal destruction furnace and (2) all the radioactive species present in the irradiated graphite waste or vapor-phase elements in the furnace are intimately mixed. If a given mixture of species undergoes a change that minimizes the total Gibb's free energy, which change represents an equilibrium state, and corresponds to a complete conversion of the reactants to products [5]. The Gibbs function of a system is:

$$G = \sum_{k=1}^{K} \bar{g}_k N_k \qquad (1)$$

where $\bar{g}_k$ is the partial molar Gibbs function and $N_k$ is the number of moles of each species k in the system. $K$ is the total number of species. For ideal-gas mixtures or ideal solutions, the partial molar Gibbs function is given by:

$$\bar{g}_k = g_k(T,P) + RT \ln X_k \qquad (2)$$

where $g_k$ (T,P) is the Gibbs function for the pure species $k$, evaluated at the system temperature and pressure; R is the universal gas constant; and $X_k$ is the mole fraction of the *k*th species. The equilibrium solution at a given temperature and pressure is the distribution of $N_k$ that minimizes the system Gibbs function, *G*, subject to atomic population constraints (and non-negative $N_k$). The atomic population constraints are:

$$\sum_{k=1}^{K} n_{jk} N_k = p_j, \quad j = 1,...M \qquad (3)$$

where $n_{jk}$ is the number of the *j*th atoms that appear in the *k*th molecule, $p_j$ is the total population in moles of the *j*th atom in the system, and *M* is the total number of different element that are present in the system. HSC-Chemistry 5.1 software was used for the model calculation. HSC software makes conventional thermodynamic calculations based on the minimization of the Gibbs free energy in order to simulate the chemical reaction equilibrium and processes.

The radioactive carbon ($^{14}C$) will exist mostly in the form of $CO_2$ in the excess air incineration furnace and it will exist in the form of both CO and $CO_2$ in the hydrothermal oxidation furnace. Tritium ($^{3}H$) will exist as a water vapor ($H_2O$) in an incinerator but it will exist as a water vapor ($H_2O$) together with hydrogen molecules ($H_2$) in the hydrothermal oxidation atmosphere. Radioactive chlorine will mostly be present as hydrogen chloride (HCl) in the excess air incineration as well as the hydrothermal oxidation atmospheres.

The equilibrium distributions of the cobalt, cesium and europium species under the incineration atmospheres are shown in Fig. 1. CoO is the most stable cobalt species at temperatures above 600ºC and $Co_3O_4$ is the most stable cobalt species at temperatures below 600ºC.

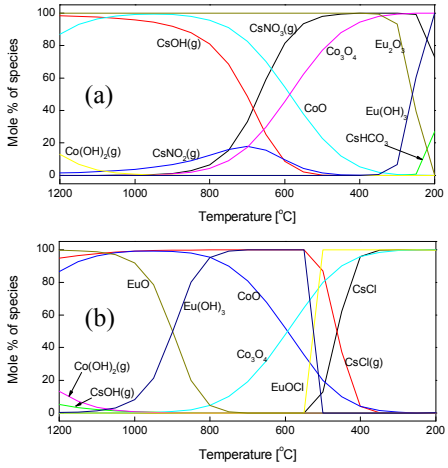


Figure 1. Equilibrium distributions of cesium, cobalt and europium species under the incineration atmospheres: (a) in the absence of HCl(g) and (b) in the presence HCl(g)

*2.2. Experimental Investigation*

The lab-scale incinerator was used to investigate the behavior of radionuclides in irradiated graphite block from KRR-2 during thermal destruction. The incinerator is composed of reaction part, off-gas cooling part, sampling part and filtering part.

As shown in Table 1, the most radionuclides such as $^{60}Co$, $^{152}Eu$ and $^{154}Eu$ were concentrated in ash as stable oxidants. However $^{134}Cs$ was emitted in gaseous form during incineration and then remained in condensed water.

Table 1. The experimental results of radionuclides behavior in the irradiated graphite from KRR-2

| | Co-60 | Cs-134 | Eu-152 | Eu-154 |
|---|---|---|---|---|
| Ash | 78.50% | | 80.77% | 86.82% |
| Condensed Water | 2.72% | 84.01% | 1.09% | 2.56% |
| Dust | 0.21% | 4.01% | 0.11% | 0.25% |

## 3. Conclusion

The behavior of the radioisotopes in the irradiated graphite was investigated by the thermodynamic equilibrium model analysis and experiment.

The beta nuclides are emitted as gaseous form. It is therefore suggested that the off-gases from the graphite thermal treatment furnace should be passed through a suitable isotope separation process.

Cesium is expected to be the most troublesome radionuclide under the incineration atmospheres. In the absence of HCl(g), cesium is expected not to condense before the off-gas cleaning systems.

Other radioisotopes such as $^{60}Co$, $^{152}Eu$ and $^{154}Eu$ are not expected to vaporize under the graphite waste thermal destruction conditions.

## REFERENCES

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