

Thermal Behavior of the Nuclear Graphite Waste Generated from the Decommissioning of the Nuclear Research Reactor

연구로 해체시 발생하는 흑연 폐기물의 열적 거동

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Abstract

This study investigated the thermal behavior of the nuclear graphite waste generated from the decommissioning of the Korean nuclear research reactor. The first part study investigated the decomposition rate of the nuclear graphite waste up to 1000 °C under various oxygen partial pressures using a thermo-gravimetric analyzer (TGA). Tested graphite waste sample not easily destroyed in the oxygen-deficient condition. However, the gas-solid oxidation reaction was found to be very effective in the presence of oxygen. No significant amount of the products of incomplete combustion was formed even in the limited oxygen concentration of 4% O₂. The influence of temperature and oxygen partial pressure was evaluated by the theoretical model analysis of the thermo-gravimetric data. The activation energy and the reaction order of graphite oxidation were evaluated as 128 kJ/mole and 1.1, respectively. The second part of this study investigated the behavior of radioactive elements under graphite oxidation atmosphere using thermodynamic equilibrium model. ²²Na, ¹³⁴Cs and ¹³⁷Cs were found be the semi-volatile elements. Since volatile uranium species can be formulated at high temperatures above 1050 °C, the temperature of incinerator furnace should be minimized. Other corrosion/activation products, fission products and uranium were found to be the non-volatile species.

Key Words : irradiated graphite waste, incineration, thermogravimetric analysis, thermodynamic equilibrium model

1. Introduction

Graphite has been used as a moderator and reflector of neutrons in many nuclear

reactors. The old graphite moderated reactors are already shut down and therefore a huge amount of radioactive graphite waste is generated. The radioactive graphite waste has different characteristics compared to other radioactive waste due to its physical and chemical properties. It includes various radionuclides such as tritium and ^{14}C , as well as corrosion/activation products (^{57}Co , ^{60}Co ; ^{54}Mn ; ^{59}Ni ; ^{63}Ni ; ^{22}Na), fission products (^{134}Cs , ^{137}C ; ^{90}Sr ; ^{152}Eu , ^{144}Ce) and small amount of uranium and transmutation elements (^{238}Pu , ^{239}Pu ; ^{241}Am , ^{243}Am)[1]. Therefore the development planning of an appropriate treatment technology for the waste nuclear graphite has to consider the safe management of these radioactive elements included in the graphite waste, as well as the volume reduction with an economic point of view.

The decommissioning of the research reactors (KRR-1&2) in Korea, which started in 1997, generated 3 tones of radioactive graphite waste[2]. The current status of the processing technologies has been analyzed to select an appropriate management system for the radioactive graphite generated from the decommissioning of KRR-1&2. Although the existing processing technologies are based mostly on the isolation of radioactive graphite from the environment, they are not able to provide for a significant volume reduction[1]. For this reason, the high-temperature thermal treatment process such as an incineration is considered as a promising technology, since it provides a substantial volume reduction.

This study investigated the thermal destruction characteristics of irradiated graphite waste from KRR 1&2 (Korea Research Reactor 1&2) and the behavior of the radioactive elements during the graphite incineration atmosphere. The purpose of this study is to get some kinetic data that are required to design a thermal treatment furnace such as an incinerator and to know the behavior of radioactive elements that are required to design off-gas system for graphite thermal treatment system.

2. Oxidative Decomposition Characteristics of Nuclear Graphite

2.1. Kinetic Model

The influence of temperature and that of the partial pressure of oxygen on the oxidation reaction of graphite can be described with an Arrhenius equation and a power law approach, respectively[3]. The reaction rate of the high-temperature oxidation of the graphite is thus described as:

$$\frac{dX}{dt} = k_0 (P_{O_2})^n \exp\left(-\frac{E}{RT}\right) f(X) \quad (1)$$

$$X = \frac{w_0 - w(t)}{w_0 - w_{ash}} \quad (2)$$

The function $f(X)$ represents the influence of the conversion on the conversion rate. The most simple of these equations is:

$$f(X) = (1 - X)^\beta \quad (3)$$

in which $\beta = 1$ represents a homogeneous reaction model and $\beta = (2/3)$ a shrinking core reaction model. In the case of a non-isothermal reaction and the applied heating rates are

constant the temperature can be expressed as:

$$T = Bt + T_0 \quad (4)$$

The constant ramp, B, is given as:

$$\frac{dT}{dt} = B \quad (5)$$

Using this transformation equation 1 can be rewritten as:

$$\frac{dX}{dT} = \frac{k_0}{B} (P_{O_2})^n \exp\left(-\frac{E}{RT}\right) f(X) \quad (6)$$

Separation of variables results in:

$$\frac{dX}{f(X)} = \frac{k_0}{B} (P_{O_2})^n \exp\left(-\frac{E}{RT}\right) dT \quad (7)$$

which can be rewritten as:

$$F(X) = \frac{ZE}{BR} p(y) \quad (8)$$

in which:

$$F(X) = \int \frac{1}{f(X)} dX \quad (9)$$

and:

$$Z = k_0 (P_{O_2})^n \quad (10)$$

In Equation (8), p(y) is a function of the temperature following from the temperature integral on the right hand side of Equation (7), which can be approximated as:

$$\ln[p(y)] = -2.315 - 0.457 \frac{E}{RT} \quad (11)$$

The activation energy of the reaction, at different levels of conversion, can now be determined by:

$$E = \frac{-R}{0.457} \left(\frac{d \log B}{d\left(\frac{1}{T}\right)} \right) \quad (12)$$

Once the activation energies have been calculated, equation (8) can be used, both to find the conversion model (f(x)) as well as the Z-values, which are different for each oxygen partial pressure. The reaction order with respect to oxygen partial pressure, n, can be calculated as the slope from a graph of the logarithmic of Z versus the logarithmic of the oxygen partial pressure[4].

2.2. Materials and Methods

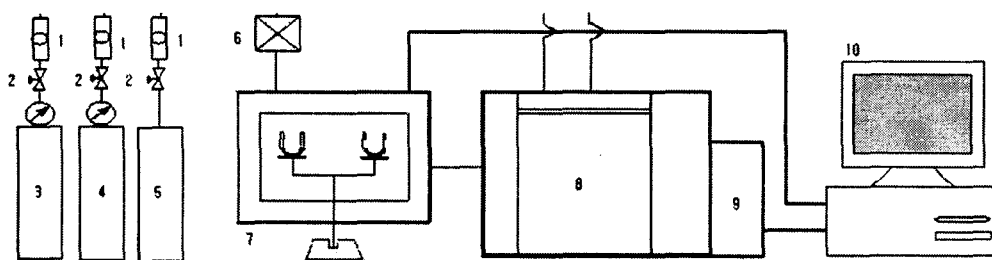
Sample graphite material was obtained from the neutron-modulating graphite rods used in Korea Research Reactor 1&2. It is one of the standard nuclear graphite. The analyzed compositions of graphite sample are shown in Table 1. The sample graphite was analyzed to

contain over 99.99% carbon, 190 ppm chlorine and about 20 ppm ash.

Experimental system, which is shown in Figure 1, consists of a gas conditioning system, a thermo-gravimetric furnace system (SDT-6120, TA instruments) and a gas chromatography (HP-5890 II) - mass spectrometer system (HP-5972). After the powdered sample graphite in the size range of 47-106 μm was placed in the thermo-balancer, the conditioning gas was fed and the furnace was heated to 1000 $^{\circ}\text{C}$.

Table 1. The compositions of sample nuclear graphite (dry weight basis)

Proximate analysis	Volatile matter		Fixed carbon		Ash
	2.2%		99.8%		<500ppm
Ultimate analysis	C	H	O	N	Cl
	>99.98%	<0.001%	<0.001%	-	190ppm



1. flow meter 2. valve 3. O_2 4. N_2 5. He 6. gas mixer 7. TGA 8. GC-MS

Figure 1. A schematic diagram of experimental system.

The first investigated variable is oxygen percent of conditioning gas. The tested oxygen percents were selected as 4%, 12%, 21% 100% and <0.1% with remainder consisting of pure nitrogen. Other investigated variables are the rate of heating and the size of graphite sample. At each tested gaseous atmosphere, sample graphite was heated up to 1000 $^{\circ}\text{C}$ with a heating rate of 3 $^{\circ}\text{C}/\text{min}$, 20 $^{\circ}\text{C}/\text{min}$ and 100 $^{\circ}\text{C}/\text{min}$. The compositions of furnace off-gas under various gaseous atmospheres were also analyzed using GC-MS system.

2.3 Thermal Behavior of Nuclear Graphite

The behaviors of sample graphite up to 1000 $^{\circ}\text{C}$ in various atmospheric gaseous conditions and at three different heating rates are shown in Figures 2. The decomposition reaction started at about 450 $^{\circ}\text{C}$, 500 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$ at a heating rate of 3 $^{\circ}\text{C}/\text{min}$, 20 $^{\circ}\text{C}/\text{min}$ and 100 $^{\circ}\text{C}/\text{min}$, respectively. The heating rate did not influence the decomposition rate but the oxygen concentration greatly influenced the decomposition rate of sample graphite. In the oxygen-deficient condition ($\text{N}_2 > 99.9\%$), the weight loss of graphite up to 1000 $^{\circ}\text{C}$ was extremely small, regardless of

the tested heating rate. Total weight loss of graphite up to 1000 °C in the oxygen deficient atmosphere did not exceed 2%. This suggested that the tested nuclear graphite is very thermally stable under oxygen-deficient condition. The flue gas compositions measured by GC-MS were in agreement with this suggestion. Only two carbon-containing species were detected during the weight loss of sample nuclear graphite. Less than 900 ppm of CO₂ and about 420 ppm of C₃H₄ were detected by the gas analysis during the weight loss of graphite sample in 99.9% N₂ condition. No other carbon-containing species was detected as a decomposed or volatilized species even under this oxygen-deficient condition. A trace amount of oxygen and water vapor adsorbed in the inner graphite structures or those in the flowing N₂ gas (>99.9% N₂) could react with graphite to form CO₂ and C₃H₄. However, the weight loss of graphite in the 99.9% N₂ atmosphere was very small. Tested graphite did not easily destructed in the oxygen-deficient condition. It is therefore noted that the pyrolysis of tested graphite in the absence of oxygen is practically impossible.

However, the oxidation reaction in the presence of oxygen was found to be effective and no significant amount of the products of incomplete combustion (PICs) was found even in the limited oxygen concentration of 4% O₂. No carbon monoxide was found and less than 100 ppm of C₃H₄ was emitted in this oxygen-limited condition, regardless of the heating rate. The measured BET surface area of tested graphite powder was 7.996 m²/mg. This large surface area can afford to complete reaction with gaseous oxygen through gas-solid incineration mechanism and therefore no significant amount of PICs is generated. It could therefore be positively said that the direct incineration would be easily applied to reduce the volume of graphite waste.

2.4 Kinetic Analysis

Two tests with a heating rate of 8 °C/min and 13 °C/min were additionally performed in the air atmosphere (21% O₂). The weight loss per unit time in the air, which is proportional to the rate of graphite oxidation reaction, is plotted in Figure 3 as a function of temperature. The increase in heating rate causes the reaction rate curves to shift toward higher temperatures. It is found that the heating rate is the important factor in determining the initiation temperature of decomposition reaction. This also suggests that the kinetic parameters at low heating rates could not be properly applied to the real incinerator in which fed waste is heated at a much higher heating rate.

The reaction rates shown in Figure 3, together with equation (12), were used to determine activation energy, as given in Figure 4. Figure 4 shows a series of lines created from the four curves in Figure 3. If the decomposition mechanisms were the same at all conversion levels, the lines would all have the same slope. This is the case here. The determined activation energy calculated from the slope in Figure 4 using equation (12) is 128 kJ/mol. This process was repeated for different O₂ % conditions and the similar results were obtained.

Assuming that the reaction follows first-order reaction, F(X) versus p(y) for 21% O₂ condition is plotted in Figure 5. From the obtained slopes in Figure 5, Z value was obtained. This process was also repeated for different O₂ % conditions, and finally the reaction order was determined from the intercept and the slope in Figure 6. The reaction order of the graphite oxidation was evaluated as 1.1.

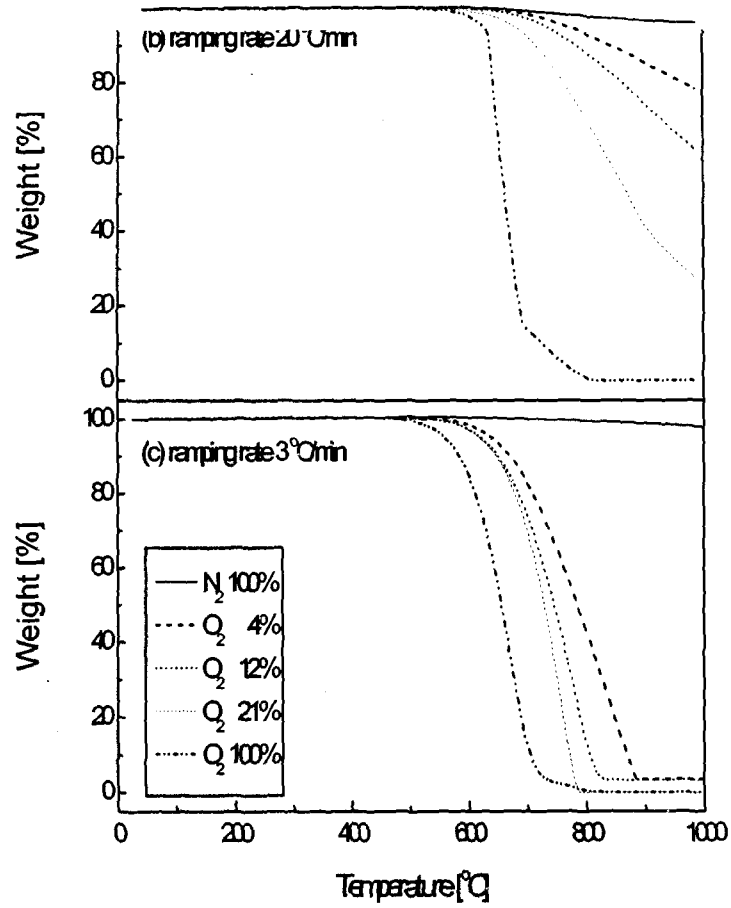


Figure 2. The weight loss of nuclear graphite at various heating conditions.

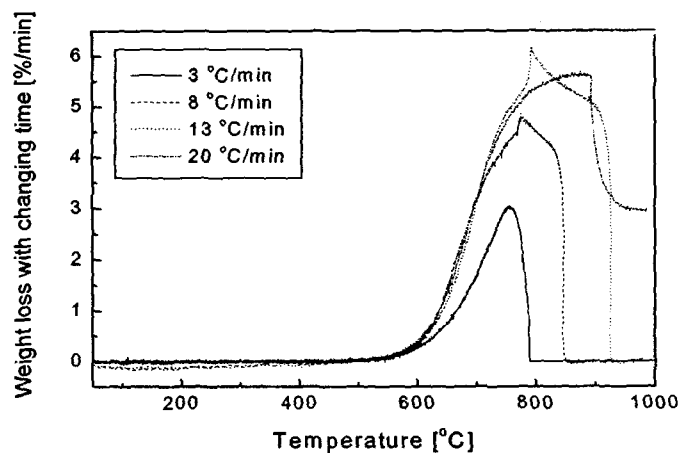


Figure 3. Weight loss patterns of nuclear graphite in an atmospheric air condition.

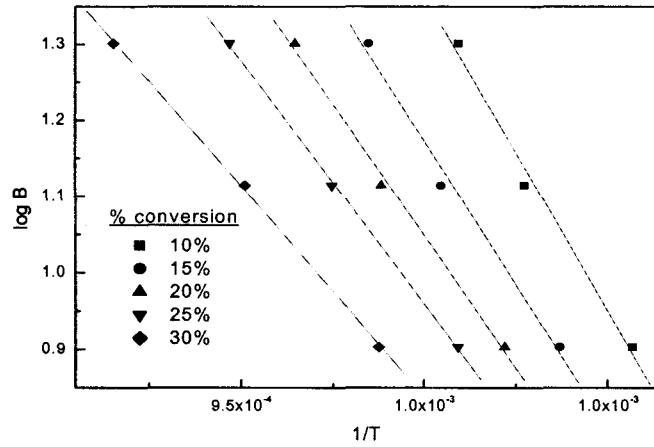


Figure 4. Calculation of activation energy for graphite oxidation.

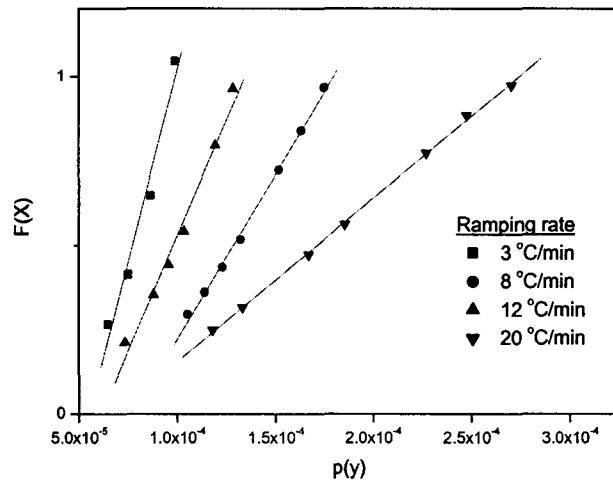


Figure 5. Plot of $F(X)$ versus $p(y)$ assuming first order reaction.

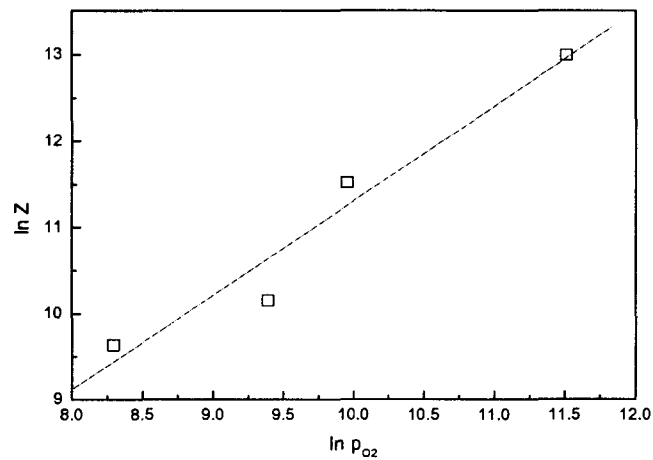


Figure 6. Estimation of reaction order of graphite oxidation.

3. Thermal Behavior of Radioactive Elements

3.1 Radionuclide Partitioning Model

As discussed, incineration is found to be an attractive of treating nuclear graphite. However, for safety reasons during incineration, and because of environmental impact of the incinerator, it is important to know how the radioactive elements in the graphite waste partitioned between the incinerator furnace, the fly ash, and the stack emission[5]. The model analysis on the radionuclide partitioning during incineration is based on following two simple assumptions:

1. Thermodynamic equilibrium is maintained in the incinerator furnace.
2. All radioactive species present in the waste or vapor-phase element in the off-gas are intimately mixed.

Equilibrium model calculations using a computer code Chemkin 3.6 were performed to observe the behavior of radioactive elements at the temperature range of 700-1300 °C[6]. Graphite incineration furnace atmosphere was simulated to be 12% O₂, H₂O 4%, CO₂ 5%, 100ppm Cl₂ and the remainder consisting of N₂, considering graphite composition.

3.2. Behavior of Corrosion/Activation Products

The equilibrium distributions of investigated corrosion/activation products are shown in Figure 7. Sodium (²²Na) was found to be volatile radioactive elements under the graphite incineration atmosphere. Sodium converts into sodium chlorides (NaCl) in the presence of chlorine. Since the nuclear graphite waste includes a significant quantity of chlorine, sodium species may convert into NaCl(g) in the incinerator furnace. Gas-phase NaCl subsequently condense out into fly ash particles as the off-gas cools down to the dew point temperature of NaCl. Other investigated corrosion or activation products, such as ⁵⁴Mn, ⁵⁷Co, and ⁶³Ni, which are included in the nuclear graphite waste, are present as non-volatile species up to 1300 °C under the graphite combustion atmosphere.

3.3. Behavior of Fission Products

The equilibrium distributions of investigated fission products are shown in Figure 8. Cesium (¹³⁴Cs and ¹³⁷Cs) was found to be volatile radioactive elements under the graphite incineration atmosphere. The behavior of cesium is similar to that of sodium. Cesium converts into cesium chloride (CsCl) in the presence of chlorine. Gas-phase CsCl condenses out into fly ash particles as the off-gas cools down to the dew point temperature of CsCl. Other investigated fission products, such as ⁹⁰Sr, ¹⁵²Eu, and ¹⁴⁴Ce is present as non-volatile species up to 1300 °C under the graphite combustion atmosphere. The behavior of strontium species is very interesting. The most stable strontium species is strontium carbonate (SrCO₃) up to 1000 °C. At higher temperatures, it converts into the strontium oxides. Some gas-phase strontium hydroxide can be formed at the temperatures above 1100 °C, but its fraction is negligible.

3.4. Behavior of Uranium and Transmutation elements

The equilibrium distributions of uranium, plutonium and americium are shown in Figure 9. The most stable species of each element are found to be UO₃, PuO₂OH, and AmO₂ at relatively low temperatures. These species convert to each of their high-temperature stable oxides such as UO₂, PuO₂ and Am₂O₃, as the temperature increases. One volatile uranium species is found as UO₃(g) at the temperatures above 1050 °C and its fraction increases greatly as the temperature increases. It is therefore noted that temperature of graphite incineration furnace should be maintained as low as possible.

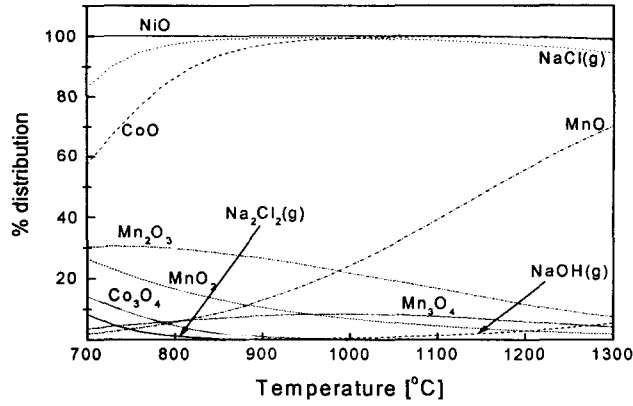


Figure 7. Equilibrium distribution of corrosion/activation products under graphite incineration atmosphere.

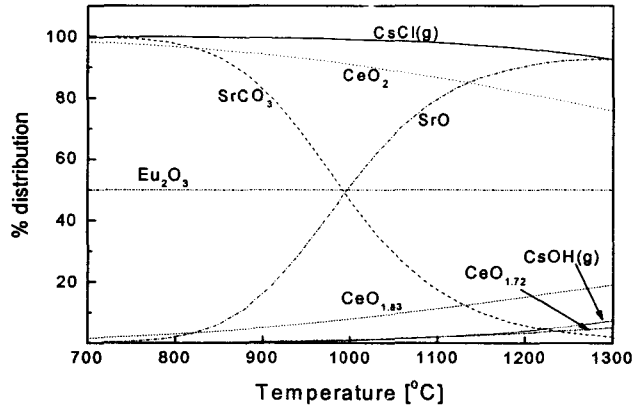


Figure 8. Equilibrium distribution of fission products under the graphite incineration atmosphere.

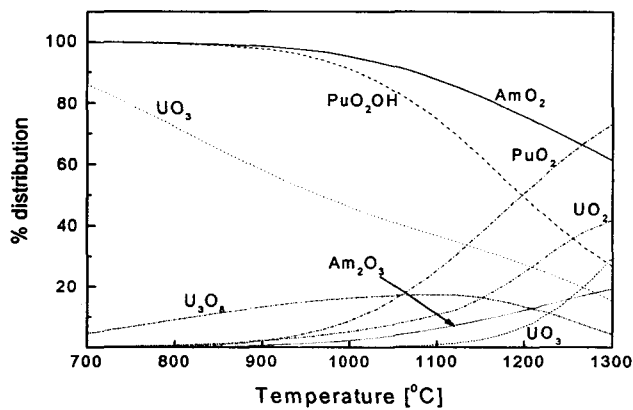


Figure 9. Equilibrium distribution of uranium and transmutation elements under the graphite incineration atmosphere.

4. Conclusions

Tested nuclear graphite waste was not easily destroyed in the oxygen-deficient condition. However, the oxidation reaction was found to be very effective in the presence of oxygen. No significant amount of the products of incomplete combustion was formed even in the limited oxygen concentration of 4% O₂. It could therefore be positively said that the gas-solid contacting oxidation would be very effective to reduce the volume of nuclear graphite waste. The influence of temperature and oxygen partial pressure was evaluated by the theoretical model analysis of thermo-gravimetric data. The activation energy and the reaction order of the graphite oxidation were evaluated as 128 kJ/mol and 1.1, respectively. Thermodynamic equilibrium model analysis shows that ²²Na, ¹³⁴Cs and ¹³⁷Cs will be partitioned in the fine fly ash particles in the graphite incineration process. It is therefore noted that an effective collection system of these semi-volatile radioactive metal species as well as that of permanent gases such as tritium and ¹⁴C should be installed in the graphite incineration process. Other radioactive elements in the graphite waste were found to be present as non-volatile species under the graphite waste incineration atmosphere. However, since volatile uranium species can be formulated at high temperatures above 1050 °C, the temperature of incinerator furnace should be minimized.

List of Symbols

B	heating rate [K s ⁻¹]	E	Activation energy [J mol ⁻¹]
K	reaction rate constants [s ⁻¹ Pa ^{-n}]	n	order of reaction [-]
w_0	initial mass of graphite [g]	P_{O_2}	oxygen partial pressure [Pa]
R	Universal gas constant [J mol ⁻¹ K ⁻¹]	r	rate of reaction [s ⁻¹]
T	Temperature [K]	X	Conversion [-]
y	Dimensionless variable in equation (8) [-]	β	Constant in Wen's model [-]

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