Analysis on Volatility of Rhenium and Iodine Trapping Filters Using a TG/DSC Apparatus

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1. Introduction

Many fission products emitting much radiation and heat are contained in the spent nuclear fuel, from which radionuclides must be eliminated at pre-treatment process in order for spent fuel to be recycled via electrorefining. Generally, volatile and semi-volatile nuclides, which are chemically trapped on ceramic filters, are volatilized as off-gases at the oxidation-reduction process carried out at more than 1000 ℃. This study is a preliminary study to draw optimal immobilising methods of technetium and iodine trapping filters generated from the volatilization of radionuclides, and the volatility at high temperature is analyzed using a simultaneous TG/DSC instrument.

2. Methods and Results

2.1 Fabrication of Specimens

The calcium based filter and AgX zeolite are selected as filter media to trap technetium and iodine, respectively, and the trapping experiments were done through the off-gas trapping system(OTS) at KAERI[1,2]. Table 1 and 2 shows the composition of each filter, respectively. We used rhenium as a technetium analogue in our experiment since technetium is an artificially fabricated element and rhenium are chemically similar with technetium[3]. To compare the volatility at high temperature according to the concentration of radionuclides, we made rhenium trapping filters with the concentration of 0.06, 0.13, 0.22, 0.49 g-Re/g-Ca, and iodine trapping filters with the concentration of 0.002, 0.01, 0.03, 0.07 g-I_2/g-AgX. Then the fabricated filters were all powdered using a pestle.

Table I: Composition of Calcium Based Filter[2]

Element	wt%	at%
O	35-45	55-60
Ca	15-25	10-15
Mg	15-20	10-15
Si	10-20	10-15
Al	5-10	10-15
others	1-2	1-2
Total	100	100

Table II: Composition of AgX Zeolite[2]

Element	wt%	at%
O	40-45	60-65
Si	20-25	15-20
Al	10-15	10-15
Na	5-10	5-10
Ag	5-10	1-2
Ca	1-2	0.5-1
Total	100	100

2.2 TG/DSC Experiment

In order to analyze the volatile characteristics at high temperature, the specimens were heated from ambient temperature to 1450 ℃ using a simultaneous TG/DSC equipment(Setsys 16/18, Setaram) at a heating rate of 10 K/min, then the curves of mass loss according to temperature were obtained. We used less than 30 mg powder in all analyses, and calibration of temperature was done by the experimental result of reference materials, Au, Al, Zn, Sn, and In. Sample pan was made of alumina, and argon gas was used as an atmosphere gas at a flow rate of 100 ml/min in order to exclude the effect of oxidation.

2.3 Results

Fig. 1 shows the TG/DSC curves of calcium based filters with various rhenium trapping concentrations. We can easily confirm that the rate of mass loss increases from 5 to 30 % as the rhenium trapping concentration grows. Additionally, the mass loss starts at about 800 ℃ to end at 1450 ℃ resulting in 100 % volatilization of trapped rhenium. According to Battles et al.[4], ReO_2 was progressively vaporized at about 790 ℃, and rhenium trapped as the form of Re_2O_7, ReO_3, ReO_2 is vaporized mainly according to the equations.

$$3ReO_3(s) \rightarrow ReO_2(s) + Re_2O_7(g), \triangle H = 54.5 \pm 0.8 \text{ kcal/mol} \tag{1}$$

$$7/2ReO_2(s) \rightarrow 3/2Re(s) + Re_2O_7(g), \triangle H = 93.5 \pm 0.7 \text{ kcal/mol} \tag{2}$$
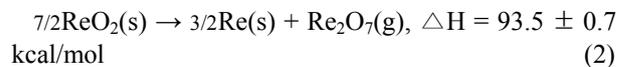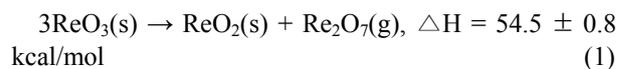
In our DSC curves, endothermic peaks are seen at about 90 ℃ and 790 ℃, and the temperature of the latter peak fits well with the vaporizing temperature presented by Battles et al. On this ground, it is inferred that the rhenium trapped in a calcium based filter is volatilized as the form of Re_2O_7. The strong peak at about 1420 ℃ seems to be due to the melting of silicon contained in the filter with melting point of 1414 ℃.
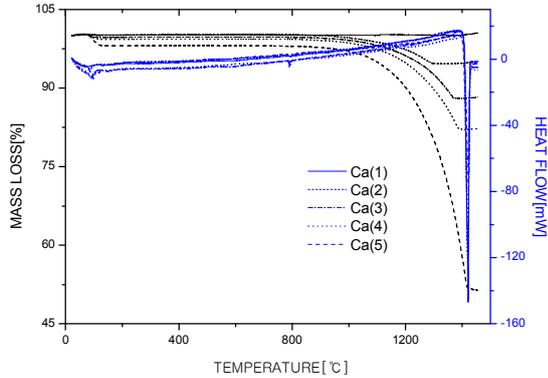
Fig. 1. TG/DSC curves for calcium based filters with various rhenium trapping concentrations.

Fig. 2 shows the TG/DSC curves of the AgX zeolites trapping iodine and the zeolite without iodine. The TG curves show that most mass loss were happened between room temperature and 400 ℃. And we can figure out that there was a broad endothermic reaction in this region of DSC curves. Based on these facts, the loss of mass below 300 ℃ is considered to mainly occur by the decomposition of oxides in the zeolite, e.g., Ag_2O whose melting point is 280 ℃. Therefore, it is not appropriate to say that the mass loss of the iodine trapping zeolite originated from the volatilization of iodine. The mass loss from detachment of iodine can be calculated from the difference of iodine trapping and non-trapping curves. Two exothermic peaks between 800 and 1000 ℃ suggest that phase transition, which makes the structure of zeolite more chemically stable, occurred twice. Endothermic peak around 1200 ℃ seems to be ascribable to the melting of Na_2O in the zeolite with melting point of 1132 ℃.
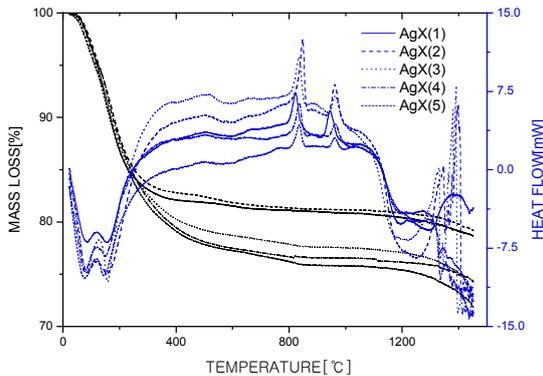
Fig. 2. TG/DSC curves for AgX zeolite without trapped iodine(AgX(1)) and AgX zeolite trapping iodine(AgX(2)).

3. Conclusions

Using conventional TG/DSC analysis, we confirmed that rhenium trapped in the calcium based filter started to volatilize at about 800 ℃, with total detachment of rhenium at 1450 ℃. In case of iodine, however, the volatility of iodine trapped in the AgX zeolite could not be validated. We are planning to study further about thermal characteristics of trapped radionuclides through TG/DSC experiments of various heating rates and isothermal cases.

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