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ARTICLE

Analysis of HONTA/SiO_2-P and TEHDGA/SiO_2-P by TG-MS and Heat-Treatment of Spent Adsorbents

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TG-DTA and GC-MS analysis of fresh TEHDGA/SiO_2-P and HONTA/SiO_2-P was performed by TG-MS. As the results, we clarified that not only CO_2 and H_2O, but also some kinds of organic compounds were included in off-gas. In addition, spent TEHDGA/SiO_2-P and HONTA/SiO_2-P used in the past hot experiment were heat-treated under the conditions based on the results of TG-MS analysis. It was confirmed that both spent adsorbents could be heat-treated with those conditions.

KEYWORDS: MA recovery, extraction chromatography, TEHDGA, HONTA, off-gas, TG-DTA, GC-MS, thermal decomposition

I. Introduction

In Japan Atomic Energy Agency (JAEA), in order to separate and recover minor actinides (MA:Am, Cm) from high-level radioactive liquid waste (HLLW) generated by MOX fuel reprocessing, we have discussed about the flow-sheet conditions using extraction chromatography.1-5) The column used for extraction chromatography is filled with an adsorbent in which extractants are impregnated into SiO_2 supports coated with styrene divinylbenzene (SDB) polymer (SiO_2-P), and in recent years, we have been conducting research and development on adsorbents impregnated with tetra2-ehylhexyl-diglycolic amide (TEHDGA) and hexa-n-octylnitrilotriacetamide (HONTA) as extractants (following, called as TEHDGA/SiO_2-P and HONTA/SiO_2-P).3-5) This column has an advantage that it can be used repeatedly, however since it is intended to treat HLLW having a high acid concentration and high radioactivity, the extractant impregnated into the adsorbent filled in the column gradually deteriorates due to acid and radiation. Therefore, it is concerned that the separation performances such as the adsorption capacity of MA and elution rate of the column are damaged depending on the number of repeated uses of the column.

Spent adsorbent in separation column must be treated in this technology, so we assumed the two methods for the treatment. Our treatment concept is shown in **Fig. 1**. One of the treatments is the regeneration of the adsorbent by Fenton reaction. In this reaction, only the extractant is decomposed, and after that, the adsorbent is regenerated to impregnate with a new extractant. On the other hand, when the adsorbent becomes non-renewable due to repeated use or deterioration by radiation, that is treated by thermal decomposition process. In this process, organic compounds included in the absorbent are decomposed completely. After decomposition, SiO_2 remains and that becomes the vitrification material. In addition, TEHDGA and HONTA which are composed only of C, H, N and O elements are expected to be decomposed to non-problematic gases, such as H_2O, CO_2, and N_2, by a thermal decomposition.1) However, data on the thermal decomposition of the adsorbent, such as generated gases and heating conditions, are limited. Therefore, in order to resolve these technical issues, we obtained some data for thermal decomposition using a thermal gravimetry-differential thermal analysis (TG-DTA) and gas chromatography-mass spectrometer (GC-MS) in this work. In addition, the both spent absorbents generated by the past hot experiment4,5) were treated in hot cell under the heating conditions based on the results obtained by these analysis.

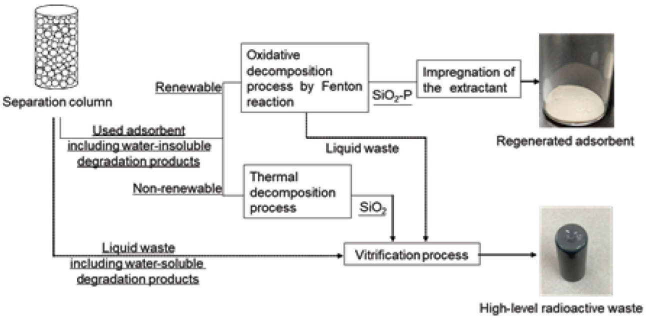

Fig. 1 Treatment concept of the spent adsorbent

II. Experiments

1. Weight Ratio of Organic Compounds in Adsorbent

Both adsorbents are included SDB polymer and extractants as organic compounds. Weight ratio of organic compounds included in TEHDGA/SiO_2-P and HONTA/SiO_2-P are shown in **Table 1.**6,7) In addition, the adsorbents used in the past hot experiment4,5) were having the same specifications in Table 1.

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Table 1 Weight ratio of organic compounds of adsorbent

Organic compound	Weight ratio
SDB polymer	15 %
Extractants (HONTA, TEHDGA)	20 %

2. Set-up of Analytical Device

Set-up of the analytical device is shown in **Fig. 2**. By connecting the off-gas system of TG-DTA (STA2500 Regulus, NETCH JAPAN) to GC-MS (JMS-Q1500GC, JEOL), this device can perform qualitative analysis of chemical substances contained in off-gas at the same time as measuring of TG-DTA. The obtained mass spectrum is compared with the data stored in the system of GC-MS to identify the generated gases (following, this device is referred to as TG-MS).

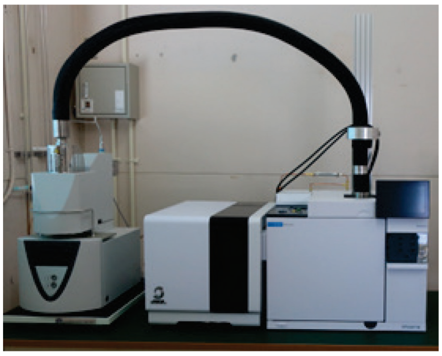

Fig. 2 Set up of TG-MS

3. TG-MS Analysis

Measurement targets and the experimental conditions of TG-MS are shown in **Table 2**. In this analysis, extractants and support were analyzed to investigate the origin of the generated substances. After that, we analyzed both adsorbents in order to confirm whether there was an interaction between extractant and support. Extractant samples were reduced the amount to prevent the overflow from measurement pan by the sudden boiling. In addition, we used platinum pan to prevent from interacting with generated chemical substances and the measurement was performed in pseudo-atmosphere with mixture of He gas and O_2 gas. He was selected as the measurement gas because of its very small interaction with the substance and small mass number, therefore it is considered to have almost no effect on the mass spectrum.

4. Heat Treatment of Spent Adsorbents in Hot Cell

As a simulation of a thermal decomposition in Fig. 1, heat treatment of HONTA/SiO_2-P and TEHDGA/SiO_2-P which were used in the past hot experiment[4,5] was performed in air atmosphere by non-airtight electric furnace without air supply system. The dimension inside the furnace is ϕ 70 × H190 mm for the heating part and the maximum temperature is 1273 K. For application to the furnace, 30 mL Al_2O_3 crucible was used in this treatment. In addition, both spent adsorbents were washed with water to reduce remaining HNO_3 and dried in advance. The drying was conducted through natural drying without controlling the atmosphere temperature, and the drying period was 1 week. The treatment conditions were determined from the results of TG-MS. In this experiment, we confirmed whether it was possible to heat-treat spent adsorbents under the conditions.

III. Results and Discussions

1. Results of TG-MS Analysis

The results of the extractants are shown in **Fig. 3** and **Fig. 4**. In Fig. 3, the weight reduction gradually began around 470 K, and a large combustion and rapid weight reduction were confirmed at around 620 K in TG-DTA. In addition, a gradual combustion peak was observed at around 820 K, and weight was finally to almost zero after 870 K. Because we also confirmed that there was no residue after measurement, it was suggested that HONTA was completely decomposed by 870 K. On the other hand, from the obtained chromatogram, a peak of m/z = 170 was observed at around 520 K, and a large peak of m/z = 18, 44 (H_2O and CO_2, respectively) was observed at around 620 K and 820 K. As the results of MS spectrum analysis, the compound with m/z = 170 was identified as formamide, N,N-dioctyl. From these results, it was suggested that HONTA starts to decompose from around 470 K, and formamide, N,N-dioctyl volatilizes at around 520 K, subsequently, the decomposition residue of HONTA is decomposed into H_2O and CO_2.

The results of TEHDGA in Fig. 4 had similar to those of HONTA. The weight reduction gradually began around 470 K in TG-DTA, and large combustion and rapid weight reduction were confirmed around 550 K. In addition, a slight combustion was confirmed at around 770 K, and weight was finally to almost zero after 800 K. As with HONTA, there was

Table 2 Measurement targets and experimental conditions of TG-MS

Targets	Amount	Temperature range	Heating rate	Gases and Flow rate
HONTA/SiO_2-P TEHDGA/SiO_2-P	~30 mg	298 ~ 1273 K	20 K/min	He:80 mL/min O_2:20 mL/min
HONTA TEHDGA	~10 mg	298 ~ 1273 K	20 K/min	He:80 mL/min O_2:20 mL/min
SiO_2-P	~30 mg	298 ~ 1273 K	20 K/min	He:80 mL/min O_2:20 mL/min

no residue after measurement, so it was suggested that TEHDGA was completely decomposed by 800 K. On the other hand, from the chromatogram, a peak of m/z = 170 and a large peak of m/z = 18, 44 were observed at around 550 K, and a peak of m/z = 44 was slightly confirmed at around 770 K. In this analysis, the compound with m/z = 170 was identified as an analogue of formamide, N,N-dioctyl. From these results, it was considered that the decomposition of TEHDGA starts at around 470 K, the compound with m/z = 170 volatilizes at around 550 K, and then the decomposition product of TEHDGA is decomposed into H_2O and CO_2 at around 770 K. From the results of both HONTA and TEHDGA, it was found that the volatile organic compounds are generated when the extractants are decomposed by the heating.

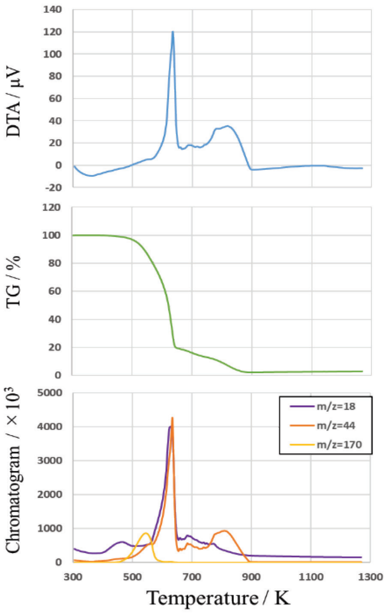

Fig. 3 The results of HONTA with TG-MS

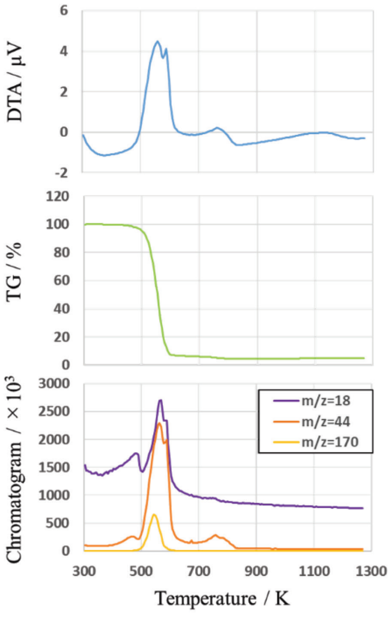

Fig. 4 The results of TEHDGA with TG-MS

The results of the SiO_2-P support are shown in **Fig. 5**. The weight reduction gradually started at around 570 K, and large combustion and rapid weight reduction were confirmed around 620 K in TG-DTA. In addition, a slight combustion was confirmed at around 820 K, and weight reduction was constant to 17% after 930 K. Because the ratio was the same as the content of SDB polymer included in SiO_2-P, it was suggested that the decomposition of SiO_2-P finished at around 930 K. On the other hand, from the chromatogram, a peak of m/z = 104 and a large peak of m/z = 18, 44 were observed near 620 K, and a peak of m/z = 44 was slightly confirmed near 820 K. As the results of MS spectrum analysis, the compound with m/z = 104 was identified as (3-methyl-1,4-diphenylbicyclo[2.2.0]hex-2-yl) methanol. From these results, it was suggested that SDB polymer contained in SiO_2-P starts to decompose at around 620 K and (3-methyl-1,4-diphenylbicyclo[2.2.0]hex-2-yl) methanol volatilizes along with H_2O and CO_2. After that, the decomposition product of SDB is decomposed into H_2O and CO_2 at around 820 K. As with both extractants, it was also found that the volatile organic compound is generated when the SDB polymer is decomposed by the heating.

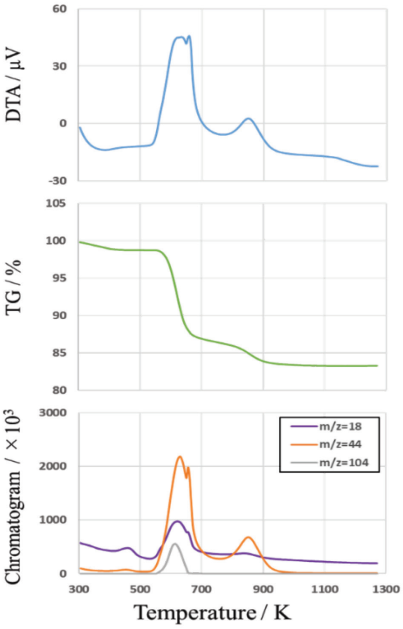

Fig. 5 The results of TEHDGA with TG-MS

The results of HONTA/SiO_2-P and TEHDGA/SiO_2-P are shown in **Fig. 6** and **Fig. 7**, respectively. The result of TG-DTA in Fig. 6 showed the three large combustion peaks at around 420 K, 620 K and 820 K. Similarly, the three large combustion peaks were confirmed at around 470 K, 620 K and 820 K in Fig. 7. The peak of 420 K in Fig. 6 was not observed in the previous measurements. In Fig. 7, the peak of 550 K in Fig. 4 caused by the combustion of TEHDGA shifted to 470 K. The weight of both adsorbents decreased with the combustions, and both weight reductions finally remained constant at 35% and 33% after 930 K, respectively. Because these ratios were approximately close to the weight ratio of the organic compounds included in both adsorbents in Table

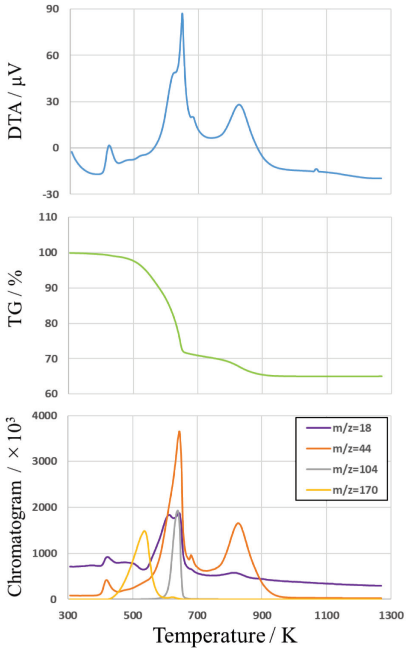

Fig. 6 The results of HONTA/SiO_2-P with TG-MS

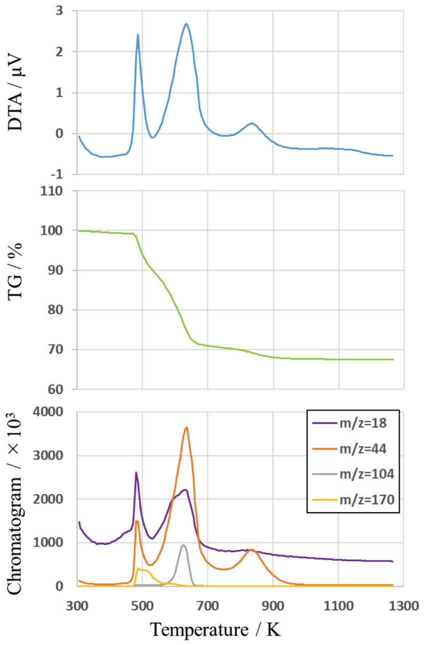

Fig. 7 The results of TEHDGA/SiO_2-P with TG-MS

1, it was suggested that the decompositions of HONTA/SiO_2-P and TEHDGA/SiO_2-P were completed by 930 K. While there was a change in the results of DTA, there was no change in the detected organic matters. Based on the results of DTA, it was considered that there was some interaction between HONTA, TEHDGA and SiO_2-P. However, because these materials were completely decomposed through the heat treatment, the observed interactions were considered to contribute little to the decomposition behavior such as the generation of organic matters and the weight reduction. As the results of investigating the safety data sheet (SDS) of the generated organic matters, because we found that the properties of the organic matters were not significantly different from those of the original compound, it was suggested that no hazardous chemical matters were generated by the thermal decomposition of these adsorbents. Therefore, in the treatment concept of spent adsorbents, we found that it was necessary to support against the volatile organic matters generated by the thermal decomposition.

2. Determination of Flow-Sheet for Heat Treatment

Flow-sheet for heat-treatment of spent adsorbents is shown in **Fig. 8**. In this treatment, we targeted that the organic compounds included in the adsorbent and combustion residues are decomposed. Therefore, the heating temperature was set to 930 K or higher, which is suggested to have finished the thermal decomposition. Completion of the treatment was determined by weight measurement. The treatment is performed in two steps, and we determined whether it has been treated or not by 2nd treatment. Furthermore, it was found that there is almost no weight reduction after 930 K from the results in Fig. 6 and Fig. 7, so the guideline for completion is that the weight reduction is less than 1%. If weight reduction exceeds 1%, repeat 2nd treatment until target value is reached. In this treatment, the generated organic matters were recovered with activated carbon. In addition, this flow-sheet was examined in advance using fresh HONTA/SiO_2-P and TEHDGA/SiO_2-P, and we confirmed to be able to heat-treat the both adsorbents.

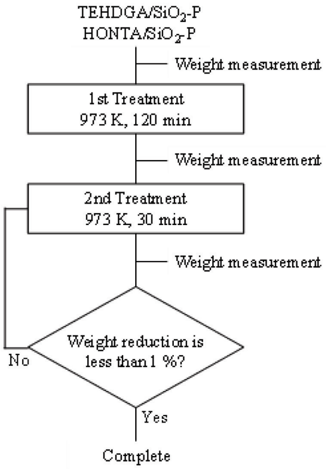

Fig. 8 Flow-sheet of heat treatment of spent adsorbent

3. Results of Heat Treatment of Spent Adsorbents

The treated amount of each spent adsorbent which were used in the past hot experiment[4,5] are shown in **Table 3** and the overview of the heat treatment in hot cell is shown in **Fig. 9**.

Table 3 Treated amount of spent adsorbents

Adsorbent	Amount
HONTA/SiO_2-P	0.77 g
TEHDGA/SiO_2-P	0.68 g

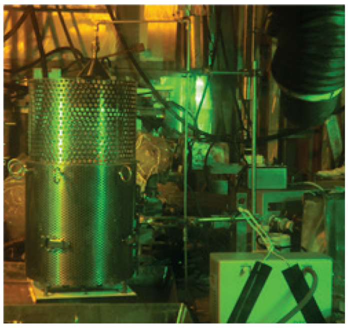

Fig. 9 Overview of heat treatment in hot cell

The results of heat treatment of spent adsorbents are shown in **Table 4**. In the treatment of HONTA/SiO_2-P, weight reduction equal to the weight ratio of organic compounds at 1st treatment. In addition, because the weight reduction of HONTA/SiO_2-P was less than 1% at 2nd treatment, it was suggested that the thermal decomposition of HONTA/SiO_2-P was finished at the first treatment. On the other hand, the weight reduction of TEHDGA/SiO_2-P exceeded the weight ratio of organic compounds. This problem is thought to be due to insufficient drying. The weight reduction after 2nd treatment also exceeded slightly more than 1%. Although the treatment was carried out under the air atmosphere, the electric furnace has no air supply system. Therefore, the supply of oxygen is not constant, it was suggested that the decomposition of TEHDGA/SiO_2-P was insufficient by a lack of oxygen. To resolve this problem, the additional treatment was carried out and we confirmed that the target value was achieved. From these results, we confirmed that both spent adsorbents could be treated with the flow-sheet determined from the results of TG-MS.

Table 4 Results of heat treatment of each spent adsorbent

Treatment	Weight reduction	
	HONTA/SiO_2-P	TEHDGA/SiO_2-P
1st	35.0 %	44.2 %
2nd-1	0.3 %	1.2 %
2nd-2	-	0.1 %

IV. Conclusion

Analysis using TG-MS was performed for extractants, support and adsorbents, and we identified the composition of off-gas of each material. As the results, not only CO_2 and H_2O, but also some kinds of organic matters were included in off-gas. Therefore, to decompose without generating these organic matters, it was found that a more advanced heat-treatment method is necessary rather than the simple heating like as the heating with an electric furnace. In addition, we also carried out the heat treatments of spent HONTA/SiO_2-P and TEHDGA/SiO_2-P were performed in hot cell. Experimental conditions were determined from the results of TG-MS analysis, and we heat-treated both spent adsorbents with these conditions.

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