Technical Note

Thermal characteristics of spent activated carbon generated from air cleaning units in korean nuclear power plants

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ABSTRACT

To identify the feasibility of disposing of spent activated carbon as a clearance level waste, we performed characterization of radioactive pollution for spent activated carbon through radioisotope analysis; results showed that the C-14 concentrations of about half of the spent activated carbon samples taken from Korean NPPs exceeded the clearance level limit. In this situation, we selected thermal treatment technology to remove C-14 and analyzed the moisture content and thermal characteristics. The results of the moisture content analysis showed that the moisture content of the spent activated carbon is in the range of 1.2–23.9 wt% depending on the operation and storage conditions. The results of TGA indicated that most of the spent activated carbon lost weight in 3 temperature ranges. Through py-GC/MS analysis based on the result of TGA, we found that activated carbon loses weight rapidly with moisture desorption reaching to 100°C and desorbs various organic and inorganic carbon compounds reaching to 200°C. The result of pyrolysis analysis showed that the experiment of C-14 desorption using thermal treatment technology requires at least 3 steps of heat treatment, including a heat treatment at high temperature over 850°C, in order to reduce the C-14 concentration below the clearance level.

1. Introduction

The air cleaning units (hereinafter ACUs) in nuclear power plants (hereinafter NPPs) are classified into exhaust ACUs and makeup ACUs according to the function. Exhaust ACUs purify radioactively contaminated air in the nuclear power plant buildings, while Makeup ACUs provide the main control room and technical support room with fresh air by cleaning up outside air contaminated with radionuclides in emergency situations such as a severe accident. These units play a very important role in protecting power plant operators and populations from radiation exposure [1]. Air cleaning facilities in NPPs are equipped with HEPA filters and granular activated carbon filters; the former removes particulate radioactive air contaminants at the front end, while the latter removes remaining pollutants such as iodine compounds at the back end. Spent activated carbon (hereinafter SAC) is generated by the replacement of filters according to performance degradation. SAC is constantly generated with the operation of NPPs; the annual amount of generation is in Korea expected to keep growing as the

replacement cycle is shortening under stricter regulation. Therefore, to save the radioactive waste disposal cost of KRW13.1 million per a 200-liter drum, the needs for an SAC treatment technology on site is increasing.

The radioactive waste classification and clearance level criteria (Nuclear Safety and Security Commission Notification No. 2014-3) limits the C-14 concentration for clearance to less than 1 Bq/g. However, the results of radioactivity analysis for the SAC from Korean NPPs showed that the C-14 concentration of about half of SAC exceeds this limit value. Although research on this topic is insufficient both in Korea and overseas, there are some Korean technology patents for the removal of C-14, which is a problematic compound in the clearance level disposal of SAC. One example of C-14 desorption techniques is a high temperature treatment technology that heats the SAC to 700–900°C using a kerosene burner and separates it into activated carbon solid and $^{14}CO_2$ gas [2]. Another is a catalyst oxidation technology that grinds the SAC into granules of 1–1.5 mm diameter and heats it to 200–500°C under vacuum condition ($10^{-2}–10^{-5}$ Torr) in a nitrogen quantiler [3]. One chemical technology is also available that converts C-14 inside the SAC into inorganic $^{14}CO_2$ gas using strong acids, strong acidizing agents (4–5% $K_2S_2O_8$) and catalysts (3–5% $AgNO_3$) [4]. A recent C-14 removal technology of the K research institute uses oxygen gas

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Table 1
Air cleaning units in Korean NPPs.

NPPs	ACUs
KORI #1,2	- Charcoal Clean Up System - Spent Fuel pit Charcoal Exhaust System - Auxiliary Building Charcoal Exhaust System - Control Access Area Charcoal Exhaust System - Reactor Building Annulus Negative Pressure Ctrl. System (only KR#2)
KORI #3,4 & HANBIT #1,2	- Containment Low Volume Purge ACU - FHB[a] Emergency Exhaust ACU - Auxiliary Building Exhaust ACU
HANBIT #3,4,5,6 & HANUL #3,4,5,6	- FHB[a] Emergency Exhaust ACU - PAB[b] Emergency Exhaust ACU - SAB[c] Exhaust ACU - HELB[d] Area Exhaust ACU - RWB[e] Emergency Exhaust ACU - ECCS[f] Emergency Exhaust ACU - CNMT Lo. Vol. Purge ACU - Post LOCA Purge ACU
SHIN-KORI #1,2 & SHIN-WOLSONG #1	- FHB[a] Emergency Exhaust ACU - ECCS[f] Emergency Exhaust ACU - CNMT Low Volume Purge ACU - Auxiliary Building Emergency Exhaust ACU - HELB[d] Area Exhaust ACU - Complex Building Carbon Adsorber Exhaust ACU
HANUL #1,2	- Fuel Building Ventilation - NAB[g] Ventilation - Peripheral Rooms Ventilation
WOLSONG #1,2,3,4	- Reactor Building Activated Carbon Filter - Spent Fuel Bay Exhaust System

[a] FHB: Fuel Handling Building.
[b] PAB: Primary Auxiliary Building.
[c] SAB: Secondary Auxiliary Building.
[d] HELB: High Energy Line Break.
[e] RWB: Radwaste Building.
[f] ECCS: Emergency Core Cooling System.
[g] NAB: Nuclear Auxiliary Building.

and maintains the ambient pressure at atmospheric level, unlike the old heating (up to 500°C) and decompressing techniques [5]. This technology uses microwaves to heat simply the absorbed organic materials to 100°C in order to vaporize them. The activated carbon waste is heated instantaneously indirectly or directly by microwaves, while the pressure is maintained at the normal atmospheric level to facilitate the carbonization of activated carbon waste absorbed with radioactive nuclides of various concentrations. Unlike the previously mentioned techniques, this technique focuses on the absorbed organic materials and carbonizes them without pre-treatment such as grinding or chemical treatments; this is done to minimize the complexity of the process. The process is a closed system that enables desorption of only the radioactive materials vaporized under decompressed condition [6]. However, the patent owners' technologies only suggest measures for the SAC treatment process; they do not provide any field-proven results obtained using the aforementioned techniques. Moreover, a feasibility study of each technology for field application revealed that there are some difficulties due to interference with other systems in the NPP and the generation of secondary waste. Therefore, to seek a method to overcome the previously mentioned difficulties, we studied the thermal characteristics of SAC engaging in analysis of the moisture content, thermal gravimetric analysis (TGA), and Pyrolysis GC/MS analysis.

Table 2
List of FAC samples.

Sample name	Manufacture company
NAC_AC	NAC Co., Ltd
DD_AC	Dae duck Co., Ltd
Camb_AC	Korea Cambridge filter Co., Ltd

2. The characteristics analysis of activated carbon

2.1. Sampling of SAC

Korean nuclear power plants are classified into 3 types of pressured light-water reactors (Westinghouse, Combustion-Engineering, Framatome) and a heavy-water reactor (CANDU-6). Table 1 shows the engineered safety feature ACUs designed to minimize the impact of design criteria accidents. ACUs are constantly in operation to remove radioactive iodides that might be present in the radiation controlled area during normal operation. All of these ACUs are equipped with activated carbon filters impregnated with triethylenediamine (hereinafter TEDA).

We took 4,000 cc representative samples of SACs that were generated from ACUs and are stored in the NPPs. To compare the characteristics with SACs, we also took fresh activated carbon (hereinafter FAC) samples from 3 domestic nuclear-grade activated carbon vendors (NAC Co., Ltd., Korea Cambridge Filter Co., Ltd., Daeduk Co., Ltd.). Most SACs are managed according to the replacement history of each building or system, while those of the Hanul 1 NPP are grouped only by year because they are mixed for storage when the SAC filters of cartridge type are broken into pieces. Systematic history tracking is necessary for efficient management of SACs which will be constantly generated in the future. A total of 37 samples from NPPs with a generation history of SAC, including three FAC samples from venders of TEDA impregnated

Table 3
List of SAC samples from ACUs in Korean NPPs.

NPPs	Sample no.	Sources
KORI NPP 1[a]	K1-1	Ann. Exh. & Aux. Bldg. Char. Exh. Sys.
	K1-2	CNMT Char. Cln. Up Sys.
	K1-3	SF Pit Char. Exh. Sys.
	K1-4	Aux. Bldg. Char. Clng. Exh. Sys.
	K1-5	Rx.Bldg.-CNMTChar.C/U Sys.
	K1-6	FHB SF Pit Area Char. Exh. Sys.
KORI NPP 2[a]	K2-1	Aux. Bldg. Normal Exh. Filtrn. Tr.
	K2-2	Fuel Bldg Emg. Exh. Tr. A/B
	K2-3	Lo.Vol.Purge Exh.ACU
SHIN-KORI NPP 1[b]	SK1-1	Comp. Bldg. Carbon Adsorber Exh. ACU
	SK1-2	HELB Area Exh. ACU
	SK1-3	Aux. Bldg. Emg. Exh. ACU
HANUL NPP 2[b]	H2-1	FHB Emg. Exh. ACU
	H2-2	Post-LOCA Purge ACU
	H2-3	HELB Area Exh. ACU
	H2-4	SAB Exh. ACU
	H2-5	Lo. Vol. Purge ACU
HANUL NPP 1[c]	H1-1[e]	Fuel Bldg. Vent. Sys.
	H1-2[f]	Nuclear Aux. Bldg. Vent. Iodine Exh. Sys.
	H1-3[f]	Peripheral Rms. Vent. Sys.
WOLSONG NPP 2[d]	W2-1	CNMT Clean Up Sys.
	W2-2-1	CNMT ATM Ctrl. Sys.
	W2-2-2	Rx.Bldg.Vent.Sys.
HANBIT NPP 1[a]	Y1-1	Aux. Bldg. Normal Exh. Filtrn. Tr.
	Y1-2	Lo. Vol. Purge Exh. AHU
	Y1-3	Fuel Bldg Emg. Exh. Tr. A
HANBIT NPP 2[b]	Y2-1	HELB Area Exh. ACU
	Y2-2	SAB Exh. ACU
	Y2-3	PAB Emg. Exh. ACU
	Y2-4	Lo. Vol. Purge ACU
HANBIT NPP 3[b]	Y3-1	SAB Exh. ACU
	Y3-2	Lo. Vol. Purge ACU
	Y3-3	RWB Emg. Exh. ACU
	Y3-4	FHB Emg. Exh. ACU

[a] NPPs type of Westinghouse.
[b] NPPs type of Combustion Engineering.
[c] NPPs type of Framatome.
[d] NPPs type of CANDU-6.
[e] Mixed samples released on 2007.
[f] Mixed samples released on 2015.

Table 4
Moisture contents of TEDA impregnated FAC and SAC.

Sample name	Moisture (wt.%), Heating time (sec)	Sample name	Moisture (wt.%), Heating time (sec)	Sample name	Moisture (wt.%), Heating time (sec)
NAC_AC[a]	3.68, 200	SK1-1	2.8, 545	W2-2-1	12.88, 485
Daeduck_AC[a]	2.33, 120	SK1-2	5.11, 345	W2-2-2	12.73, 515
Cambridge_AC[a]	9.81, 500	SK1-3	4.68, 515	Y1-1	8.13, 350
K1-1	9.22, 400	H1-1	20.7, 445	Y1-2	10.38, 420
K1-2	15.98, 600	H1-2	7.44, 485	Y1-3	23.86, 505
K1-3	9.5, 625	H1-3	20.8, 740	Y2-1	10.4, 490
K1-4	17.52, 545	H2-1	9.21, 570	Y2-2	11.86, 465
K1-5	17.72, 345	H2-2	6.24, 375	Y2-3	17.74, 450
K1-6	19.68, 505	H2-3	4.15, 420	Y2-4	14.97, 495
K2-1	4.87, 295	H2-4	4.13, 215	Y3-1	12.15, 475
K2-2	20.52, 565	H2-5	1.61, 135	Y3-2	5.8, 368
K2-3	20.05, 625	W2-1	7.02, 425	Y3-3	15.07, 470
—	—	—	—	Y3-4	17.7, 563

[a] FAC, Fresh activated carbon.

activated carbon were taken for moisture content analysis and pyrolysis analysis (Tables 2 and 3).

2.2. Analysis conditions of moisture

A&D Co., Ltd.'s MX-50 was used for moisture content measurement; this device uses halogen lamps as its heat source.

Temperature ramp rate and heating method for rapid heating or gradual heating can be easily adjusted to fit the user's needs.

First, we weighed out 1,000 mg of activated carbon sample and set the temperature ramp rate to 8°C per min until the temperature reached 200°C. The sample's weight loss was recorded every 5 sec; the measuring stopped when the moisture weight change rate of the sample reached 0.1 %/min.
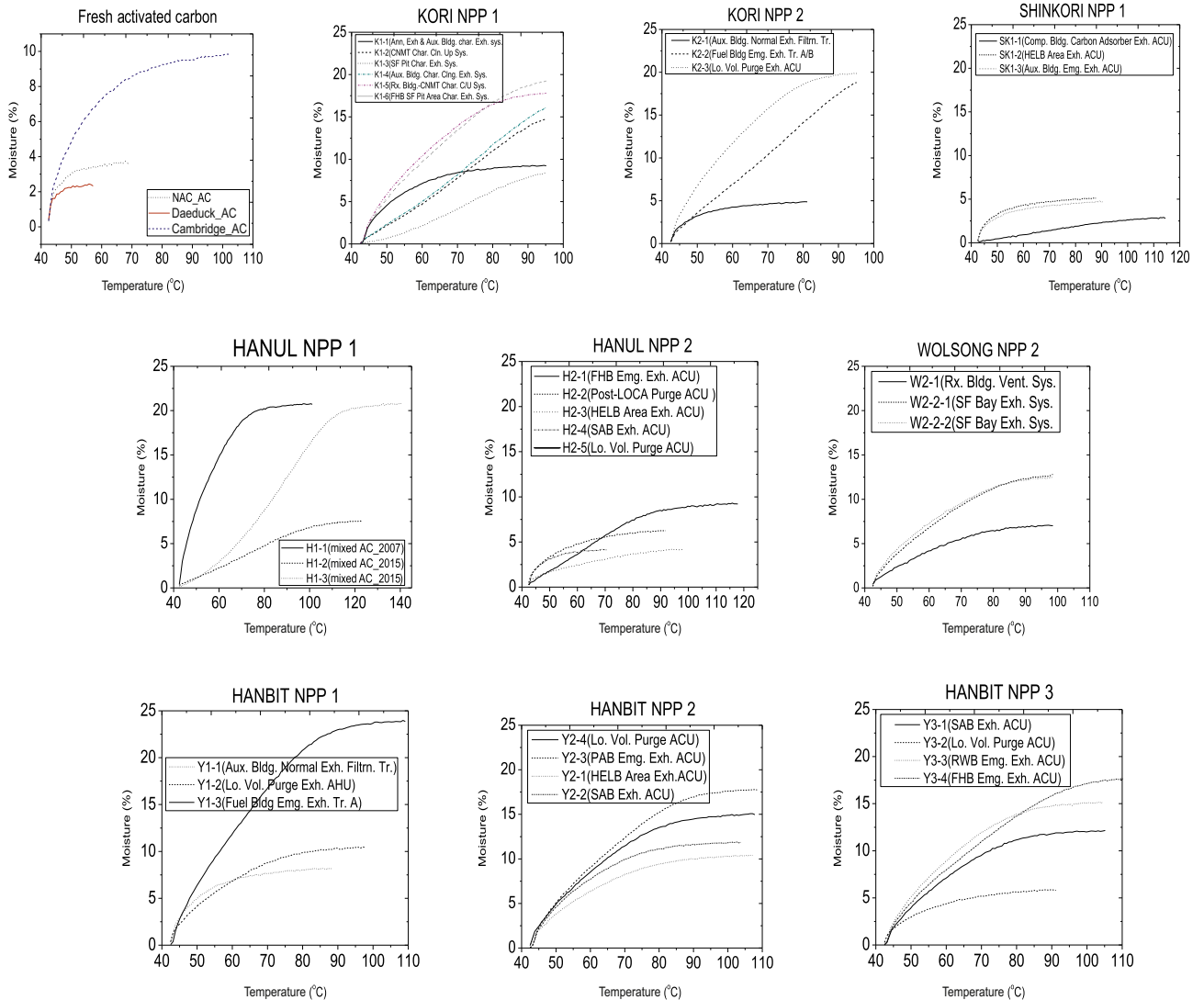

Fig. 1. Moisture content of FAC and SAC.

Table 5
Weight loss at pyrolysis temperature range.

Sample	Temp. zone 1 (°C), Weight loss (mg)	Temp. zone 2 (°C), Weight loss (mg)	Temp. zone 3 (°C), Weight loss (mg)	Temp. zone 4 (°C), Weight loss (mg)	Sample	Temp. zone 1 (°C), Weight loss (mg)	Temp. zone 2 (°C), Weight loss (mg)	Temp. zone 3 (°C), Weight loss (mg)	Temp. zone 4 (°C), Weight loss (mg)	Temp. zone 5 (°C), Weight loss (mg)	Temp. zone 6 (°C), Weight loss (mg)
H1-1	40–120, 0.2603	120–200, 0.1742	200–320, 0.137	320–1000, 0.2943	SK1-1	40–140, 0.2374	140–420, 0.6386	420–540, 0.2081	540–1000, 0.3566	–	–
H1-2	40–130, 0.3258	130–540, 0.4991	540–1000, 0.2489	–	SK1-2	40–140, 0.1529	140–500, 0.6191	500–1000, 0.2741	–	–	–
H1-3	40–150, 0.4137	150–520, 0.3681	520–1000, 0.3656	–	SK1-3	40–140, 0.2154	140–520, 0.6026	520–1000, 0.3771	–	–	–
H2-1	40–140, 0.4007	140–500, 0.3099	500–1000, 0.3166	–	W2-1	40–140, 0.2131	140–520, 0.3839	520–1000, 0.2725	–	–	–
H2-2	40–150, 0.2982	150–520, 0.3118	520–1000, 0.2591	–	W2-2-1	40–120, 0.3462	120–550, 0.5287	550–1000, 0.2581	–	–	–
H2-3	40–120, 0.3164	120–500, 0.562	500–1000, 0.3709	–	W2-2-2	40–140, 0.2851	140–560, 0.7187	560–1000, 0.2148	–	–	–
H2-4	40–120, 0.3055	120–520, 0.7643	520–1000, 0.3302	–	Y1-1	40–130, 0.343	130–540, 0.6359	540–1000, 0.3116	–	–	–
H2-5	40–120, 0.2187	120–580, 1.1803	580–900, 0.3207	900–1000, 0.1262	Y1-2	40–150, 0.3401	150–520, 0.2751	520–1000, 0.2487	–	–	–
K1-1	40–120, 0.1797	120–580, 1.1643	580–1000, 0.02	–	Y1-3	40–160, 0.3131	160–480, 0.1703	480–1000, 0.4036	–	–	–
K1-2	40–120, 0.2102	120–550, 0.4677	550–1000, 0.3376	–	Y2-1	40–140, 0.192	140–520, 0.5961	520–640, 0.0409	640–1000, 0.383	–	–
K1-3	40–160, 0.4032	160–460, 0.1787	460–1000, 0.3572	–	Y2-2	40–150, 0.2202	150–520, 0.6158	520–1000, 0.464	–	–	–
K1-4	40–140, 0.5241	140–480, 0.403	480–1000, 0.3596	–	Y2-3	40–150, 0.2028	150–520, 0.2318	520–1000, 0.2672	–	–	–
K1-5	40–120, 0.2993	120–400, 0.4401	400–580, 0.1631	580–1000, 0.2371	Y2-4	40–140, 0.1716	140–460, 0.4576	460–1000, 0.3466	–	–	–
K1-6	40–120, 0.3037	120–520, 0.2775	520–1000, 0.2142	–	Y3-1	40–130, 0.4474	~130–580, 0.7305	580–1000, 0.2597	–	–	–
K2-1	40–120, 0.2946	120–500, 0.6115	500–1000, 0.2585	–	Y3-2	40–120, 0.1314	120–520, 0.4985	520–1000, 0.2319	–	–	–
K2-2	40–160, 0.4424	160–480, 0.2552	480–1000, 0.2904	–	Y3-3	40–160, 0.3246	160–420, 0.1723	420–560, 0.0401	560–700, 0.0579	700–830, 0.0656	830–1000, 0.1334
K2-3	40–160, 0.4737	160–480, 0.2402	480–1000, 0.352	–	Y3-4	40–130, 0.4446	130–460, 0.341	460–1000, 0.1399	–	–	–

2.3. Analysis conditions of TGA

We performed thermo gravimetric analysis (TGA) to observe the desorption temperature conditions of moisture and organic and inorganic carbon compounds in the spent activated carbon. Mettler Toledo's TGA/DSC1 star system was used to measure thermo gravimetric changes while heating by 8°C/min from room temperature to 1,000°C in the nitrogen quantiler. The initial amount of the sample for TGA analysis was 5 mg.

2.4. Analysis conditions of py-GC/MS

Frontier Lab's EGA/PY-3030D pyrolyzer was used for the desorption and pyrolysis of the materials adsorbed in the activated carbon samples. Agilent Technologies 7890B-5977 was used for the analysis of gas generated by pyrolysis. The same desorption and pyrolysis conditions were set with the TGA analysis for the 4,000–5,000 mg samples, and test was performed while heating to 800°C at the ramp rate of 8°C/min. Pyrolysis range was set as the temperature range in which the sample's weight loss was observed. Gas chromatography mass spectrometry (py-GC/MS) was performed in this range.

3. Results and discussion

3.1. Results of moisture content analysis

Table 4 shows the moisture content (wt%) of each sample. The impregnated FAC samples of NAC and Daeduk contained 2~3wt% moisture, while that of Cambridge Filter showed relatively higher moisture content (9.8wt%). This difference seems to have come from differences among each company's manufacturing technology or storing method.

The relative humidity of the air flowing to activated carbon filter is controlled at less than 70% during normal operation of NPPs. However, the moisture content differs in a range from 1.61wt% up to 23.86wt% depending on the operation or storage conditions. We also found that the temperatures at the measuring points of moisture content varied from 60~130°C. This temperature difference may be attributed to the adsorption feature of moisture in activated carbon. The results of moisture content analysis of SACs are shown in Table 4 and are graphically charted by NPP in Fig. 1.

The relationship between moisture vaporization speed (kg/s) and moisture content (wt%) can be expressed as the linear equation seen below. The initial condition means the initial moisture content of the sample.

$$M(DW/DT) = -kW \qquad (1)$$

Here, M is the weight of the dry sample, while W is moisture content in wt%. If we integrate this equation to obtain the value over time, we come up with the following equation.

$$W = W_0 e^{-t/(M/k)} \qquad (2)$$

M/k here is the time constant of each sample's moisture removal process and becomes the basis to show how quickly moisture is removed. The smaller the time constant is the faster moisture is removed. The removal depends on the weight, porosity structure and distribution. Except for the samples with relatively smaller amounts of moisture, we found that moisture was removed in less than around 600 s for most of the carbon samples. The higher the moisture content was, the longer the heating time for moisture analysis was, because extra time is seemingly required to overcome the latent heat of vaporization.
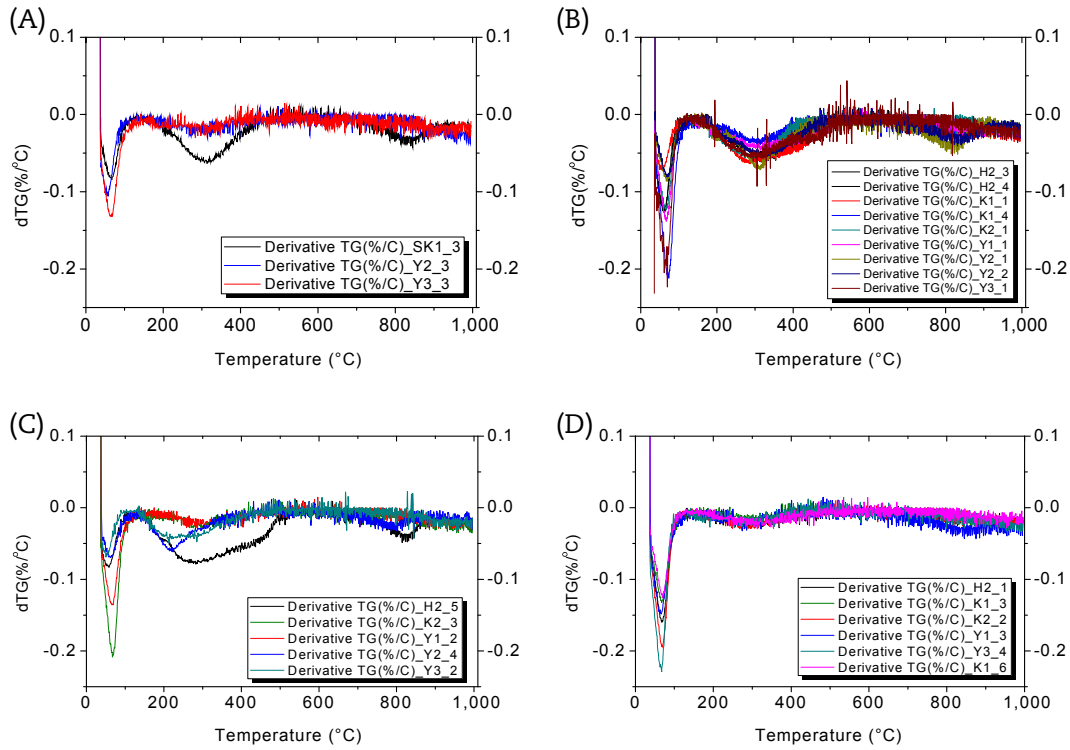
Fig. 2. TGA curve. (A) Aux. Bldg, Emrg. ACUs; (B) Aux. Bldg, Normal. ACUs; (C) Lo. Vol. purge ACUs; (D) SFP Emrg. ACUs.
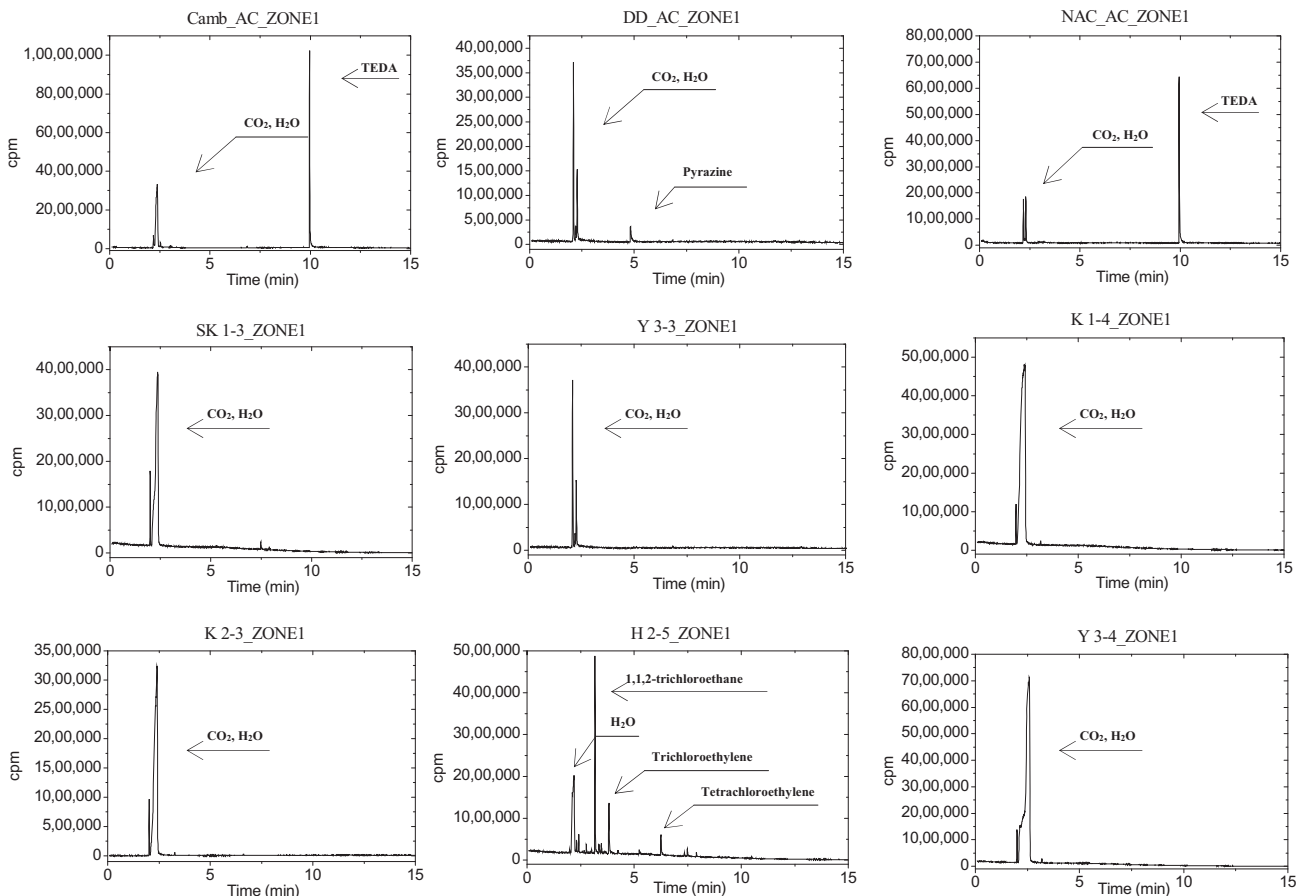

Fig. 3. py-GC/MS analysis results of FAC and SAC in zone 1.

An earlier study of the ethane gas desorption breakpoint curve at varying levels of relative humidity for a simulated activated carbon sample with 0.14 mg/g ethane content at room temperature reported that ethane desorption becomes quicker as the humidity increases [7]. An increased moisture content of a sample is likely to increase the possibility of the sample acting as an oxidizing agent, and it seems that organic gas desorption of SAC samples with relatively higher moisture content will be easier.

3.2. TGA analysis result of SAC

Table 5 shows the weight reduction by temperature range of each sample from the TGA analysis result. These results are classified by each ACU. Pyrolysis weight reduction of SACs from auxiliary building emergency ACU, the auxiliary building normal ACU, the containment building low volume purge ACU, and spent fuel storage tank emergency ACU are graphically displayed in Fig. 2. The thermal stability of each surface group in activated carbon is different because the surface groups are created at separate sites in a relation with various energies due to the interaction among oxygen, oxidized gas or oxidized solution. The carboxylic group (178–300°C) decomposes at a lower temperature than does the phenolic group (600–700°C) or the quinine group (800–900°C). Such different pyrolytic characteristics cause the need for many desorption ranges and pyrolysis ranges when an SAC sample is heat-treated in vacuum or in deactivated circumstances [8]. While most of the SACs lost weight in the 3 temperature ranges of room temperature ~200°C, 200–500°C, and around 800°C, SAC from the radwaste building emergency ACU of the

Hanbit 3 plant lost weight 6 times. All samples showed rapid weight loss at under 150°C. The reason is that moisture in activated carbon is desorbed in this range as witnessed in the moisture desorption characteristics analysis. Weight loss in other temperature ranges comes from the desorption of other carbon compounds and impregnated TEDA materials. Py-GC/MS analysis was performed for the identification of gases generated in each temperature range.

3.3. Pyrolysis-created gas analysis of FAC and SAC

The representative samples for the py-GC/MS analysis were selected reflecting the results of the TGA analysis. Figs. 3–5 show the result of py-GC/MS analysis for the representative samples. H_2O and CO_2, the main subjects of interest of this study, were released in all of three pyrolysis ranges from all of the samples; TEDA (B.P. 174°C) materials impregnated in fresh carbon were detected at around 200°C. At above 150°C, a massive desorption of carbon compounds with 5–10 carbon atoms was observed. These carbon compounds are deemed to have come from various chemical compounds that were included in a variety of chemical substances used in the radiation control area of the NPP and subsequently flowed into the ACUs. We found that various gases such as pyrazine, pyrimidine, BETX, and trichloroethane were emitted in zone 2. It seems that TEDA can be partially decomposed in this zone because pyrazine and pyrimidine are known to be formed from TEDA. And, organic compounds such as BETX, trichloroethane, trichloroethylene, and tetrachloroethylene are VOC contents of commercial paint products in Korea [9,10]. Therefore, it seems that the
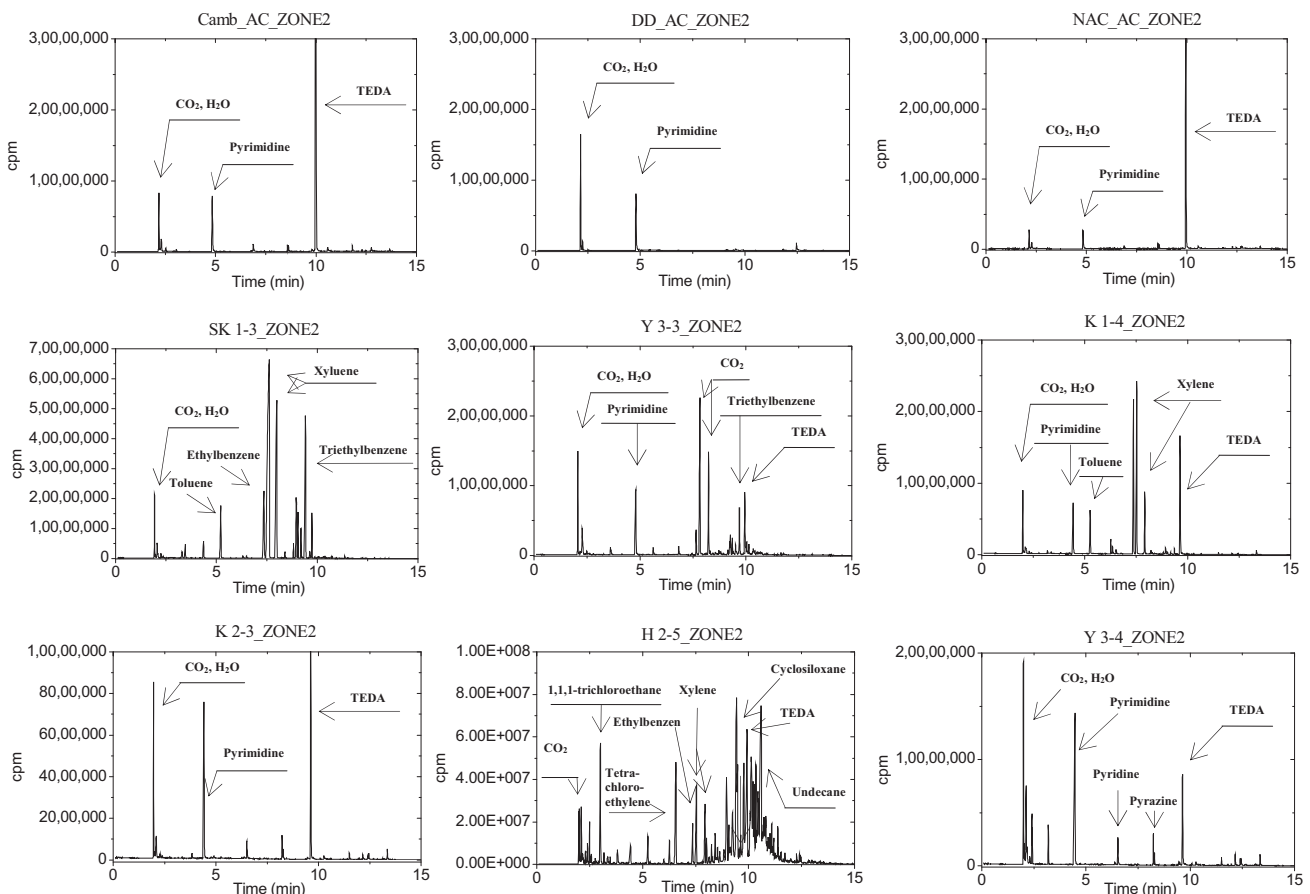

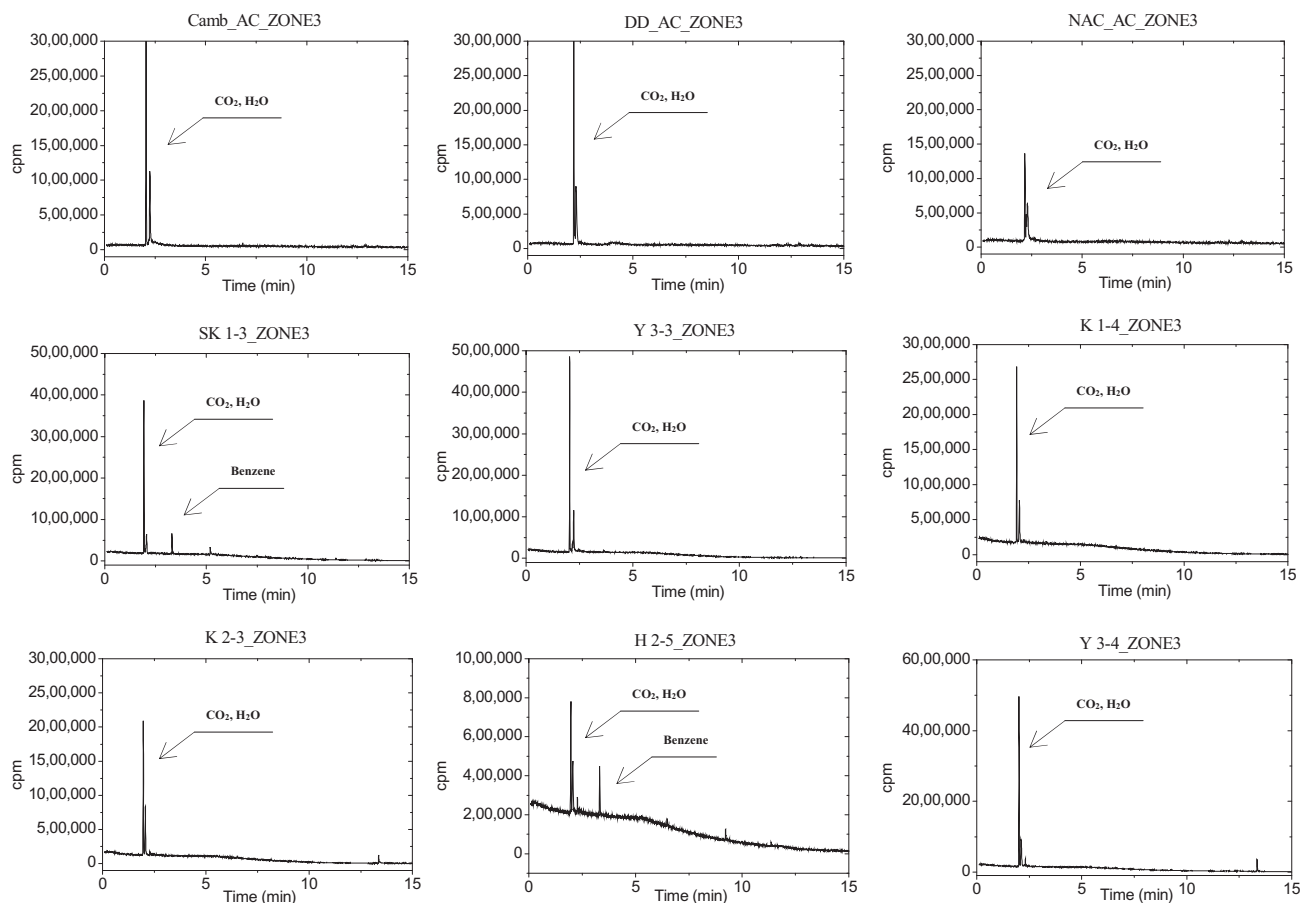**Fig. 4.** py-GC/MS analysis results of FAC and SAC in zone 2.

Fig. 5. py-GC/MS analysis results of FAC and SAC in zone 3.

detection of these contents can be attributed to paintwork in the radiation control area of NPP.

Among these, moisture and CO_2 that were desorbed at under 200°C are gaseous molecules physically adsorbed to activated carbon, while those desorbed at over 200°C are generated by the pyrolysis of chemical groups on the surface of activated carbon. Even though CH_4 was not detected in the py-GC/MS analysis, it could have reacted with O_2, which was separated from the functional groups on the surface area of activated carbon, to create CO_2 and H_2O.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{3}$$

The combustion of methane is an exothermic reaction ($\triangle H < 0$), and H_2O and CO_2 are spontaneously created because products' energy is lower than trhe reactants'. If methane reacted with a small amount of oxygen, CO_2 could be created according to the equation below.

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \tag{4}$$

The reason that CH_4, contrary to CO_2, was not detected during the pyrolytic gas analysis can be attributed to the electronic characteristics of these gas molecules. CO_2 has quadruple momentum but CH_4 doesn't, and so the probability of absorption of CH_4 to fine holes is much smaller than is that probability for CO_2. Thus, we can not exclude the possibility that CH_4 escaped to the air without being absorbed after entering the pores of activated carbon [11].

CO_2 was detected by the pyrolytic characteristics analysis; CO was not. Therefore, we can presume that the SAC had reacted with a sufficient amount of oxygen for CO to be converted to CO_2 while being stored. On the other hand, we can not exclude the possibility that the oxygen residing in the functional group of the SAC could have contributed to create CO_2 by coupling with the carbon that was desorbed during pyrolysis.

In zone 3 (around 800°C), desorption of CO_2, H_2O and benzene (only SK 10-3, H 2-5) was observed. CO_2 and H_2O observed in zone 3 have a significant meaning in the C-14 removal study. Carbon atoms can be removed from inner pores of carbons by gasification using carbon dioxide or water vapor, usually at 800–900°C [12,13]. According to the SAN MIGUEL' study, spent carbon was recovered by 60–95% for the porosity, surface area and adsorption characteristics when it was heated to 800°C under inert conditions [14]. TGA analysis also showed that the gasification reaction of absorbed organic matter occurs at around 850°C by thermal decomposition. However, it is expected that further recovery to almost 100% will be needed to satisfy the clearance level limit (1Bq/g) of C-14. Therefore, to maximize the recovery rate, it seems that we should heat SAC to over 850°C with adequate oxygen for additional desorption by partial surface combustion.

4. Conclusions

A study on the thermal characteristics such as moisture content measurement, thermo gravimetric analysis, and pyrolytic characteristics analysis was performed to facilitate a C-14 desorption

experiment using a method of thermal treatment.

The moisture in all SAC samples was almost all desorbed at temperatures under 150°C, regardless of the generic characteristics such as plants and systems; the moisture content of each sample differed from 1.6wt% to 23.9wt%. This result implies that the storage condition of SAC plays a larger role in the moisture content than does the operation condition of TEDA impregnated activated carbon. As it is assessed that the moisture content in SAC has a positive effect on the desorption efficiency of organic gas, the moisture content is very likely to act as an important variable in the desorption of C-14.

Through thermo gravimetric analysis, we observed a total of 3 times of weight loss in the specific temperature ranges (room temperature −200°C, 200−500°C, above 500°C) in most of the SAC samples from Korean NPPs. So, the contamination characteristics of ACUs in power plants are deemed to be similar. Through the py-GC/MS analysis in the 3 temperature ranges, on the basis of the results of thermo gravimetric analysis, we observed that the rapid weight losses took place due to moisture desorption under 150°C and due to the desorption of organic and inorganic carbon compounds and TEDA at temperatures under 200°C. Also, it seems that physically absorbed substances are desorbed under 200°C, while chemical groups on the surface of the activated carbon are pyrolyzed at temperatures over 200°C. The results of the thermo gravimetric analysis and the py-GC/MS analysis showed that the gasification reaction terminates at 850°C.

Therefore, the gasification temperature and adequate moisture content will become critical variables for C-14 desorption in each type of treatment for the 3 temperature ranges. Further study is necessary to determine the optimal conditions for C-14 desorption through experiments on diverse parameters such as the temperature ramp rates, the amount of moisture to be used as an oxidizing agent, the retention time of the temperature, and the flow rate of inactive gases.

Conflicts of interest

All authors have no conflicts of interest to declare.

References

[1] United States Nuclear Regulatory Commission (U. S. NRC), Design, Inspection, and Testing Criteria for Air Filtration and Adsorption Units of Post-accident Engineered-Safety Feature Atmosphere Cleanup System in Light-Water-Cooled NPPs, Regulatory Guide 1.52 Rev. 4, 2012.

[2] Mendota Co., Ltd., Processing Method of Radwaste Spent Activated Carbon, Korean, Patent 1020130072808, 25, Jun., 2013.

[3] J.G. Kim, Vacuumplant Co., Ltd., Korea Hydro Nuclear Power (KHNP) Co., Ltd., Treatment Methods and Process for Waste Activated Carbon Contaminated by Radiocarbon and Tritium Compounds, Korean, Patent 1020110034364, 13, Apr., 2011.

[4] HUVISWATER Co., Ltd., Method and Apparatus for the Decontamination of Spent Activated Carbon, Korean, Patent 1020120151155, 21, Dec., 2013.

[5] Korea Atomic Energy Research Institute (KAERI), Treatment Methods for Waste Decontaminant, Korean, Patent 1020140030542, 14, Mar., 2015.

[6] Y. Fernandez, A. Arenillas, J. Angel Menendez, Microwave Heating Applied to Pyrolysis, Instituto Nacional del carbon (CSIC), 2011 [cited 2011 Feb 14]. Available from: http://www.intechopen.com/books/advances-in-induction-and-microwave-heating-of-mineral-and-organic-materilas-microwave-heating-applied-to-pyrolysis.

[7] Korea Atomic Energy Research Institute (KAERI), Development of the Process for Decontaminating 14C & 3H in the Waste Activated Carbon from Air Cleaning System, Performing Org. Report No. KAERI/CR-316/2008, 2008.

[8] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao, Modification of the surface chemistry of activated carbons, Carbon 37 (1999).

[9] A List of VOCs Regulated, Korea Ministry of Environment Notification, No. 2015-181, 2015.

[10] S.Y. Jung, K.H. Kim, K.H. Kang, D.G. Kim, J.H. Hong, The Analysis on the VOC contents of paint products on the domestic market in Korea, J. Kor. Soc. Env. Anal. 10 (2007) 154—168.

[11] J.R. Li, R.J. Kuppler, H.C. Zhou, Selective gas adsorption and separation in metal-organic frameworks, Chem. Soc. Rev. 38 (2009) 1477—1504.

[12] H. Marsh, F. Rodriguez-Reinoso, Activated Carbon, ElsevierScience Ltd., 2006, p. 8.

[13] X. Duan, C. Srinivasakannan, J. Liang, Process optimization of thermal regeneration of spent coal based activated carbon using steam and application to methylene blue dye adsorption, J. Tai. Ins. Chem. Eng. 45 (2014) 1618—1627.

[14] G. San Miguel, S.D. Lambert, N.J.D. Graham, The regeneration of field spent granular activated carbons, J. Wat. Res. 35 (2001) 2740—2748.