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RESEARCH REACTOR CENTER

February 17, 2017

U.S. Nuclear Regulatory Commission
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Mail Station P1-37
Washington, DC 20555-0001

REFERENCE: Docket No. 50-186
University of Missouri-Columbia Research Reactor
Renewed Facility Operating License No. R-103

SUBJECT: Written communication as required by University of Missouri Research Reactor Technical Specification 6.6.c(3) regarding a deviation from Technical Specification 3.7.b

The attached documents provide the University of Missouri-Columbia Research Reactor (MURR) Licensee Event Report (LER) for an event that occurred on February 3, 2017, that resulted in a deviation from MURR Technical Specification 3.7.b.

If you have any questions regarding this report, please contact Nathan G. Hogue, the facility Reactor Health Physics Manager, at (573) 882-5358.

Sincerely,

FOR RALPH BUTLER

Ralph A. Butler, P.E.
Director

RAB:jlm

Enclosures

xc: Reactor Advisory Committee
Reactor Safety Subcommittee
Isotope Use Subcommittee
Dr. Hank Foley, Interim Chancellor
Dr. Mark McIntosh, Vice Chancellor for Research, Graduate Studies and Economic Development
Mr. Geoffrey Wertz, U.S. NRC
Mr. Johnny Eads, U.S. NRC

A020
NRR

1513 Research Park Drive Columbia, MO 65211 Phone: 573-882-4211 Fax: 573-882-6360 Web: http://web.missouri.edu/~murrwww
Fighting Cancer with Tomorrow's Technology

Licensee Event Report No. 17-03 – February 3, 2017
University of Missouri Research Reactor

Introduction

On February 3, 2017, exhaust ventilation stack effluents from an Iodine-131(I-131) process the prior day exceeded the maximum controlled instantaneous release concentration limit – for particulates and halogens with half-lives greater than 8 days – as specified in Technical Specification (TS) 3.7.b by 7% for I-131.

At approximately 00:30 on February 3, 2017, Reactor Operations observed a count rate rise on the control room off-gas stack radiation monitor strip-chart recorder that corresponded to approximately 87% of the TS effluent release limit. Throughout the day, actions were taken to manage the release including swapping charcoal filter bank trains, decreasing exhaust ventilation flow rates, attempting to identify and encapsulate potential sources within the hot cells, and eventual complete isolation of hot cell exhaust flow. By calendar day February 4, 2017, releases returned to values below the TS limit.

Description of the Iodine-131 Process Effluent Traps and Filters

The I-131 process is a dry distillation process evolving I-131 from heating of an irradiated tellurium dioxide (TeO_2) target. During the target heating process, the volatile I-131 flows from the process furnace through a quartz separator where any carryover of TeO_2 material is condensed. The exhaust stream then flows through an aqueous trapping solution containing sodium hydroxide (NaOH) followed by a multicomponent reducing diffuser trap consisting of a bubble counter trapping solution of sodium hydroxide (NaOH), sodium thiosulfate (Na_2S2O_3), and potassium iodide (KI), followed by two (2) HI-Q® silver zeolite cartridge filters in series and a final bubble counter trap (See Figure 1).

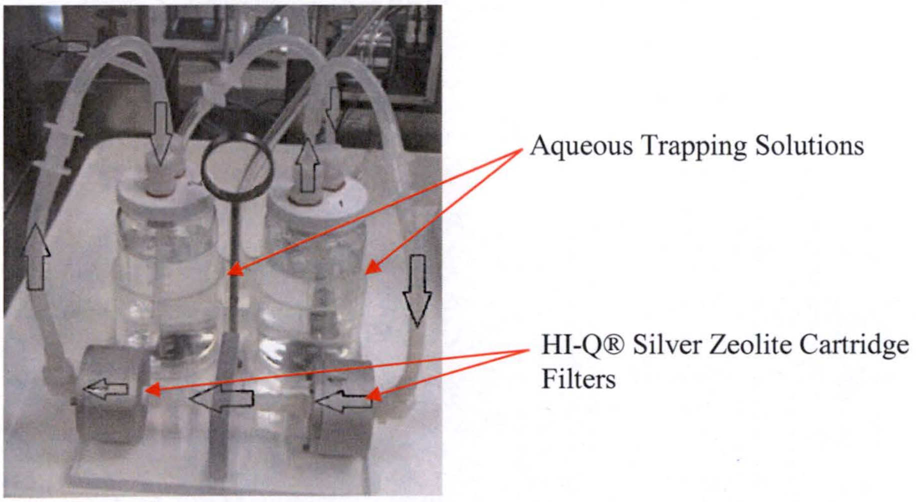

Figure 1
Reducing Diffuser Trap

The reducing diffuser traps serve dual purposes: (1) provide visual indication of adequate flow through the system, and (2) provide increased capture efficiencies for organic species of iodine, mainly methyl iodide, to facilitate ALARA effluents from the process.

The process furnace housing also has an exhaust which directs flow through a nuclear grade, activated carbon filter followed by a reducing diffuser trap prior to venting to the hot cell atmosphere.

Upon release from the reducing diffuser traps, all effluents are discharged into the hot cell where the activities are then taken up by the hot cell exhaust system. The hot cell exhaust consists of a series of four (4) parallel banks of nuclear grade, activated carbon filters impregnated with TEDA (triethylenediamine) and KI (potassium iodide). Filter Bank No. 2 in the series is monitored by a radiation detector to provide indication of filter loading during and post processing activities. Any effluents that are not captured in Filter Bank No.1 through No. 4 then pass through a HEPA filter prior to exiting the MURR Iodine Processing Suite exhaust and mixing with the facility exhaust ventilation prior to discharge through the facility exhaust stack. Airborne radiation monitors are located in-line and immediately downstream of the HEPA filter and immediately prior to discharge from the facility exhaust stack. See Figure 2 for the hot cell exhaust ventilation system schematic.

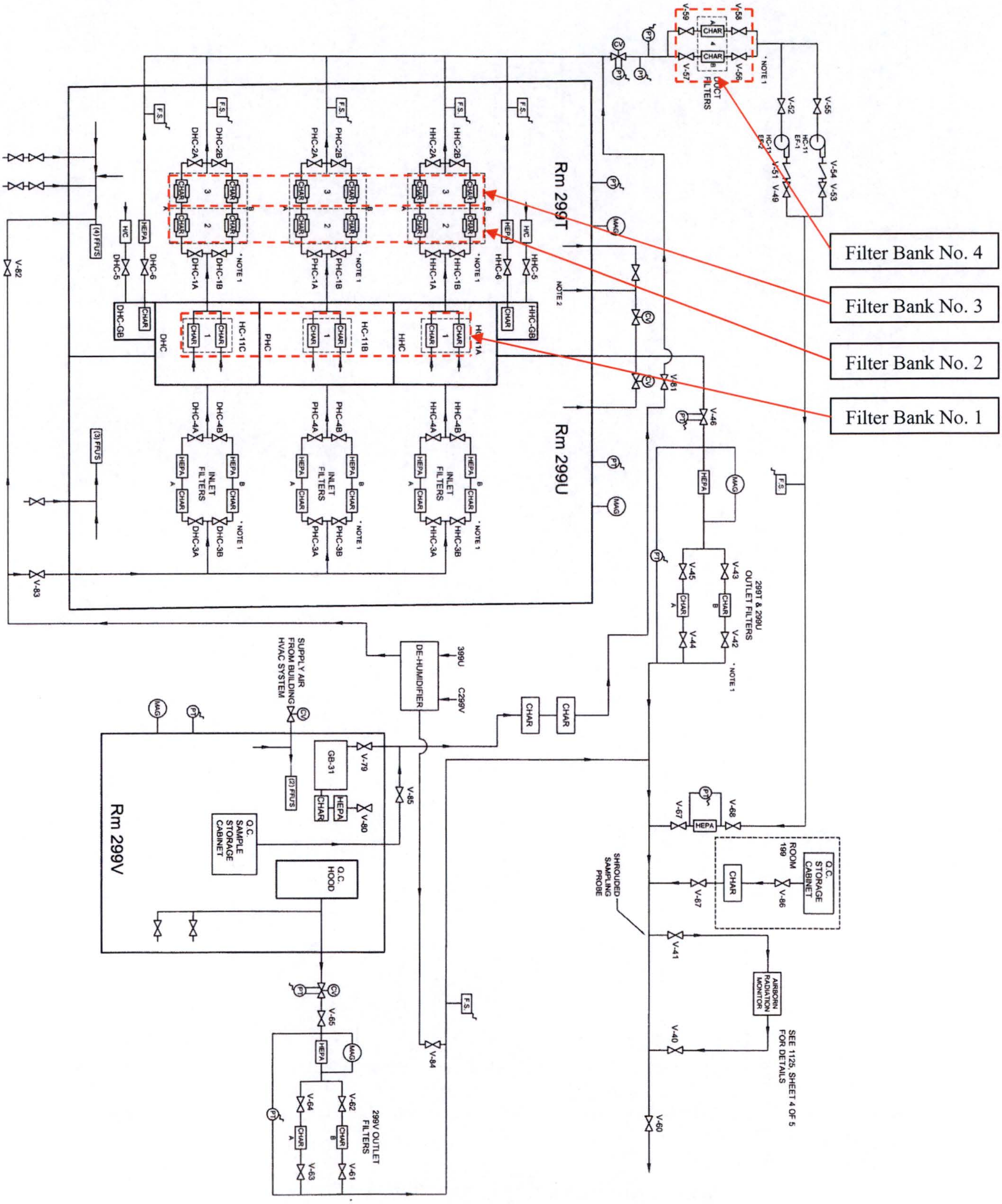

Figure 2
Iodine-131 Processing Hot Cell Ventilation Exhaust

Detailed Event Description

Sequence of Events

At approximately 00:30 on February 3, 2017, Reactor Operations observed a count rate rise on the control room off-gas stack radiation monitor strip-chart recorder that corresponded to approximately 87% of the TS effluent release limit. At approximately 03:30 the off-gas monitor filters were changed and confirmed the release. At approximately 08:30 charcoal Filter Bank No. 4 of the HC-11 exhaust ventilation train was swapped to a fresh, standby filter bank in an attempt to decrease the release rate. The release rate appeared to decrease for approximately 30 to 60 minutes but later returned to elevated values.

Action was then taken to gather and trend the data from the I-131 hot cell radiation monitors (ALMO-6). See Figure 3 for a plot of the ALMO-6 data that includes the February 2, 2017, process and post-process exposure rates on HC-11B Filter Bank No. 2. A second plot is also provided as Figure 4 for comparison of the ALMO-6 data to a typical process and post-process exposure rates from November 17, 2016.

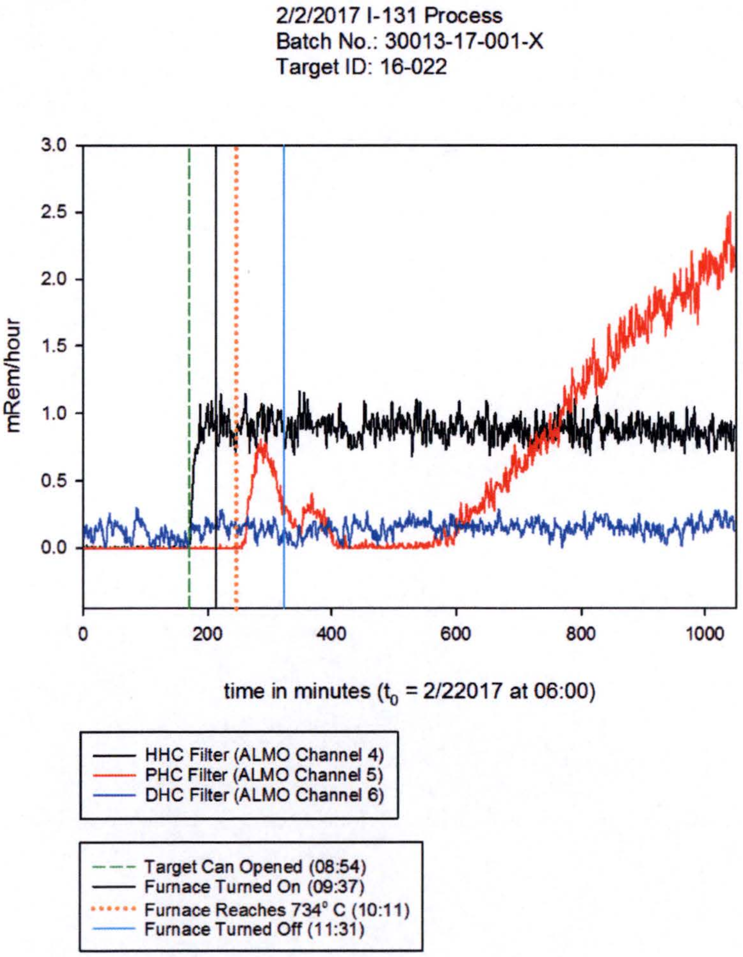

Figure 3
ALMO-6 Data from February 2, 2017 Process

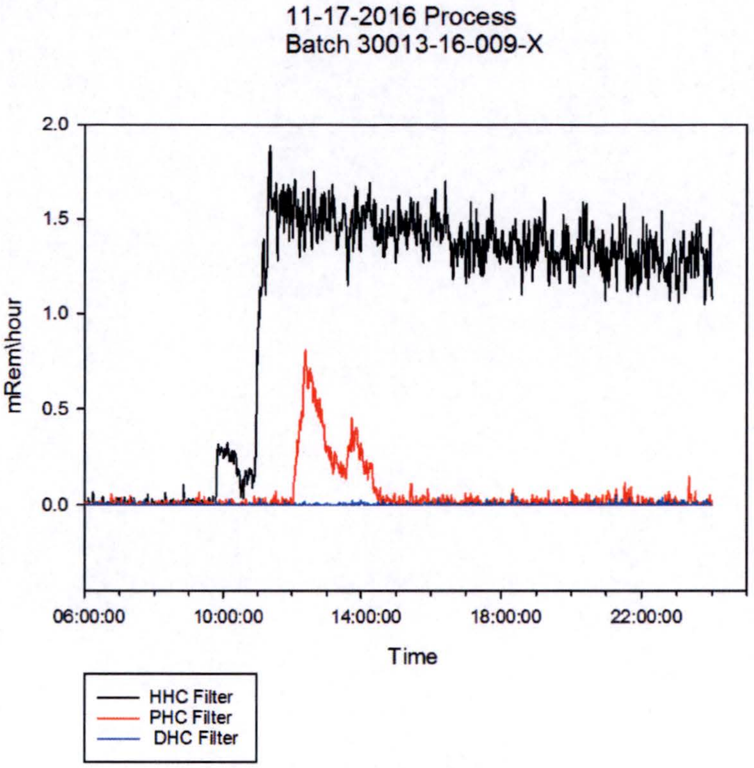

Figure 4
ALMO-6 Data from a Typical Process

After review of this data, it was clear that a markable increase in radiation exposure rates on HC-11B Filter Bank No. 2 initiated at approximately 15:30 (t=575 min) on the day of the process. At this time it became clear the origin of the release was from HC-11B, the center cell in the hot cell train where the dry distillation process occurs.

In light of this data, the principal focus turned to identifying any actively emitting sources of effluents in HC-11B, followed by swapping Filter Bank No. 2 and No. 3 to the standby trains. An inspection of the materials in HC-11B identified that the tellurium dioxide target material from the prior day's process was in its collection container in HC-11B, which is the typical storage location for the target material post processing. To confirm this was not the active source of the release, the target material was moved to HC-11A via the interstitial HC-11A/B pass-through. Also, at approximately 11:50 on February 3, 2017, the standby filters in Filter Bank No. 2 and No. 3 were placed in service in an attempt to quarantine any I-131 currently breaking through the filter beds.

At this time, Health Physics had begun an hourly regiment of removing the facility stack monitor filter for analysis and trending the release concentrations relative to the system changes being made. See Table 1 for the results of each filter change throughout the duration of the event. The average percent of the daily TS limit was derived by summing the products of the filter run time and percent TS for each filter and dividing by the sum of the filter run times for the calendar day.

Table 1
Facility Off-Gas Stack Radiation Monitor Data

I-131 Release on 3-Feb-2017				
Time Removed	**Filter No.**	**Conc. (µCi/mL)**	**Run Time (min)**	**% of TS**
3:28:00	939	1.758E-10	208	87.90
7:40:00	940	2.495E-10	252	124.75
11:55:00	941	3.225E-10	255	161.25
13:15:00	942	3.766E-10	80	188.30
14:29:00	943	1.054E-10	74	52.70
15:34:00	944	2.534E-10	65	126.70
16:48:00	945	2.734E-10	70	136.70
18:07:00	946	2.249E-10	73	112.45
19:17:00	947	1.034E-10	68	51.70
20:17:00	948	8.176E-11	60	40.88
23:57:00	949	9.658E-11	216	48.26
		%TS Average:	**107.11**	
		Total µCi Released:	**274.41**	

The 11:50 switch to the standby filters on HC-11B had minimal effect. So, it was decided to minimize the flow rate from HC-11B and in the main I-131 processing suite duct piping to increase residence time in HC-11B Filter Bank No. 2 and No. 3, and in duct piping Filter Bank No. 4. At 13:20, the I-131 processing suite booster fans were secured and the HC-11B outlet valves were throttled. Caution was taken to not reduce the flow rate below the minimum required to maintain the hot cell differential pressures negative to the surrounding areas for fear that concentrated activities may leak from the hot cells into the ambient room air. Though this action reduced the I-131 release out the facility exhaust stack in the short term, it was apparent by 15:00 that release concentrations were increasing again.

Filters 944 and 945 were removed from service at 15:34 and 16:48, respectively, and elevated release concentrations were confirmed which prompted preparations to completely isolate flow through HC-11B and submerge the container of spent tellurium dioxide target material, now in HC-11A, with activated carbon. To ensure early detection of airborne activities leaking from the isolated hot cell, four (4) additional ambient air monitors were stationed at strategic locations in conjunction with the two (2) permanently installed ambient air monitors for a total of six (6) monitoring locations.

At approximately 17:45, flow through HC-11B Filter Bank No. 2 and No. 3 were completely isolated, resulting in a flow path of air through the HC-11A/B interstitial pass-through. At approximately 20:30, activated carbon was passed into HC-11A and used to submerge the spent tellurium dioxide container. Immediately after completion of this task, all hot cell flow was isolated, and access to the I-131 processing suite was secured.

Filters 947, 948, and 949 provided indication that the releases returned to below the TS limit and by calendar day February 4, 2017, releases returned to sustained values under the TS limit. It should also be noted that all ambient air monitors deployed saw no elevation in derived air concentrations (DAC) above background, and in-vivo thyroid bioassay measurements of those individuals involved in the event corroborated that no measurable uptakes occurred. It should also be noted that there were no indications of personnel contamination germane to this process throughout the duration of this event and the days to follow.

On February 6, 2017, the next working day, an Event Review Team (ERT) meeting was convened to estimate the magnitude of release, determine if notification to the NRC would be required, and identify the event root cause. It was determined that releases for calendar day February 3, 2017, were approximately 107% of TS 3.7.b instantaneous release limit, and notification to the NRC would be made per TS 6.6.c.

Root Cause

Several potential root causes were suggested during the ERT meeting; however, additional data continues to be needed to corroborate the exact root cause. A second, third, and fourth meeting were convened to review the collected data and go through the process of elimination to identify the root cause.

At this time, there are two potential root causes continuing to be evaluated: (1) failure of the reducing diffuser traps resulting in elevated quantities of methyl iodide being released to the hot cell, and (2) charcoal filter bypass resulting in unfiltered air bypassing the exhaust filters to a degree sufficient enough to result in elevated releases.

During the evolution to submerge the spent tellurium dioxide target container at approximately 20:30 on February 3, 2017, an observation was made by the hot cell operator that the flow through the reducing diffuser traps appeared to be significantly reduced based on observation of the bubble rate through the bubble counter. Further review identified that the pumps used to force flow through the reducing diffuser traps are positive displacement pumps with no variable speed setting, and consequently, a reduced flow through the bubble counter would be indicative of a leak between the pump and bubble counter. In the event process exhaust air was not in its entirety being driven through the reducing diffuser traps, a higher than typical concentration of process effluents containing methyl iodide would be released directly to the hot cell volume and then taken up by the facility exhaust ventilation system.

As discussed previously, the purpose of the reducing diffuser trap is to capture and retain organic species of iodine, specifically methyl iodide (CH_3I-131). Historically, the reducing diffuser traps have performed extremely well for capturing and retaining effluents not captured by the product traps. Process commissioning data revealed that the product traps capture 99.8% of the iodine in the gas stream while the multicomponent reducing diffuser trap captures an additional 0.19% of the iodine in the gas stream. With the combined removal efficiencies of the product traps and reducing diffuser traps typically 0.01% of the total iodine activity or less is released into the HC-11B environment.

However, if we assume failure of the reducing diffuser trap, further attention concerning the evolution of methyl iodide from the process trap exhaust must be considered. Methyl iodide is created during the dry distillation process from elementary iodine (I_2) combining with methane (CH_4) in the air. Using the total processing activity of I-131 on February 2, 2017, of approximately 42 Curies and assuming the product trap performs normally collecting 99.8% of the total iodine activity and the reducing diffuser trap fails and provides minimal additional capture efficiency, no greater than 84 mCi of activity would be released to the cell environment. Of which, we can conservatively assume 2% is converted to methyl iodide resulting in no greater than 1.68 mCi of methyl iodide activity in the cell environment. Comparing the total release activities to that of the maximum potential methyl iodide produced provides a factor of activity available for release of approximately six (6) times greater than what was released during the event, assuming the charcoal filter banks provide little efficiency for sustained retention of methyl iodide.

A review of the literature concerning the performance of charcoal filters for capture and retention of methyl iodide further substantiates the potential root cause that the activities released were from a failure of the reducing diffuser traps. The industry often uses ASTM D3803-91(2014), "Standard Test Method for Nuclear-Grade Activated Carbon," where both methyl iodide and elementary iodine species are used to challenge the charcoal capture efficiency. This test consists of a 60-minute challenge period in which concentrations of methyl iodide or elementary iodine are fed into the system followed by a continuation of flow for an additional 60-minute elution period. At the end of the elution period, the test is complete, and analyses determine the percent efficiency and percent penetration of the charcoal being tested. Under these test conditions, nuclear grade charcoal often has an efficiency of >99% for methyl iodide and >99.9% for elementary iodine. However, the ASTM D3803-91 testing standard does not provide efficiencies for nuclear grade carbon beyond the elution test period of 60 minutes.

Furthermore, a paper entitled, "Effect of Temperature on the Adsorption and Desorption Characteristics of Methyl Iodide over TEDA-Impregnated Activated Carbon," which is provided for reference as Attachment 2, describes a series of experiments to determine how methyl iodide breaks-through (penetrates) a nuclear grade charcoal bed over time, temperature ranges, and activity concentrations. As a baseline measurement, the researcher performs a test at 30 °C on a bed depth of 3 centimeters of 6.5 wt% TEDA-impregnated activated carbon, conditions relatively comparable to those for which the I-131 processing hot cell exhaust ventilation filters are exposed. During this test, the researcher observed a relatively high efficiency and low penetration from initial feed of the activity to approximately 45 minutes after initial feed. Between minutes 45 and 300 after initial feed of activity, the percentage of breakthrough rapidly increases and eventually appears to converge at 100% breakthrough with approximately 50% breakthrough occurring at 100 minutes. Furthermore, this finding is corroborated by Flanders reference material on HEGA filters which states, "Methyl Iodide adsorbs-desorbs-adsorbs through the bed, exchanging iodine at each juncture. That is to say, methyl iodide can be radioactive-stable-radioactive-stable until it decays into harmless xenon."

Consequently, a release of methyl iodide in the I-131 processing hot cells would not be apparent until the methyl iodide activities have reached Filter Bank No. 2, where the ALMO-6 radiation monitor is located, after the release activity has traversed through 5 centimeters of bed depth on Filter Bank No. 1. Using the referenced data, the first indication of activity increase on Filter Bank No. 2 would occur at approximately 75 minutes after initial release, and 50% of the released activity would be observable on Filter Bank No. 2 at 170 minutes after initial release. These projected release times appear to be inline with the indications observed during the February 3, 2017, event.

For the potential root cause where exhaust flow bypasses the exhaust filters to a degree sufficient enough to result in elevated releases, we also assume a total failure of the reducing diffuser trap and consider two (2) of the four (4) exhaust filters are bypassing flow. In this case, we should expect to release 10 μCi of activity, which is still well below any release limits with significant margin and a factor of 27 less than the release on February 3, 2017. Therefore, filter bypass cannot be definitively ruled out, but additional investigations are warranted to better understand the event. Furthermore, the delayed increase of exposure rates on Filter Bank No. 2 on the order of 1 to 4 hours post-processing is not indicative of a bypass in flow, as the activities would be accumulated on the downstream filters at rates similar to the velocity of the air in the exhaust.

Corrective Action

As discussed above, data is continuing to be gathered to finalize a root cause and develop appropriate and robust corrective actions to prevent recurrence. However, at this time MURR intends to implement the following additional controls prior to resuming routine processing at a minimum:

1. Return the reducing diffuser traps to full service to afford the greatest potential for capture and retention of methyl iodide from the process.
2. Install additional Filter Bank No. 5 and No. 6 to provide increased bed depth such that MURR will have additional time to respond, mitigate, and contain releases from methyl iodide desorption.
3. Filter Bank No. 4 and No. 6 will be equipped with radiation monitors to provide real-time indications of adsorption and desorption of released activities.
4. Perform a sequence of lower activity runs scaling up to full process activities to ensure the effectiveness of all implemented corrective actions.

Additionally, this event has been entered into the MURR Corrective Action Program as No. 17-0021, and any additional improvements or corrective actions will be considered and documented in the CAP entry.

Safety Analysis

On calendar day February 3, 2017, it was determined that the average release concentration of I-131 discharged from the MURR exhaust ventilation stack was 2.14×10^{-10} μCi/ml or an estimated 274 μCi of total activity. Utilizing the effluent concentration limits from 10 CFR 20, Appendix B, Table 2, Column 1; we can derive a maximum dose received by any member of the public. Assuming an individual is positioned at the maximum receptor site from MURR's exhaust stack, for the duration of the release, and atmospheric conditions during the release provide the minimum potential dilution factor from the MURR stack to the receptor site, the maximum dose received by any member of the public would be 0.0005 mrem or less than 0.001% of limits specified in 10 CFR 20.1301(a)(1). This dose value is derived in Equation 1 below.

$$\begin{aligned}
\text{[Eqn. 1]} &= [(\text{discharge concentration}) / (\text{dilution factor}) / (\text{APP. B Limit})] \times (50\ \text{mrem} / 365\ \text{days}) \\
&= [(2.14 \times 10^{-10}\ \mu\text{Ci/ml}) / (292) / (2.00 \times 10^{-10}\ \mu\text{Ci/ml})] \times (50\ \text{mrem} / 365\ \text{days}) \\
&= [(0.00366)] \times (0.137) \\
&= 0.0005\ \text{mrem}
\end{aligned}$$

Furthermore, should the theoretical maximum amount of methyl iodide produced during the process be discharged from the reactor stack, 1.68 mCi, irrespective of any capture and retention efficiency from the reducing diffuser traps, the maximum hypothetical dose an individual positioned at the maximum receptor site from MURR's exhaust ventilation stack, for the duration of the release, and atmospheric conditions during the release provided the minimum potential dilution factor from the MURR exhaust stack to the receptor site, the maximum hypothetical dose received by any member of the public would have been no greater than 0.003 mrem, as calculated via the methodologies provided in Equation 1 above.

To corroborate the release resulted in no significant increase in doses to the public, MURR is expediting the analysis of 46 environmental TLD monitors positioned throughout the MURR site and surrounding areas. Environmental TLD monitors are analyzed by a third party, and results are reported to MURR after analysis. The results of this analysis are expected to be returned to MURR by the end of February 2017.

If there are any questions regarding this LER, please contact me at (573) 882-5358. I declare under penalty of perjury that the foregoing is true and correct.

State of Missouri
County of Boone
Subscribed and sworn to before me this 17 day of February, 2017
JACQUELINE L. MATYAS, Notary Public
My Commission Expires: March 26, 2019

Sincerely,

Nathan G. Hogue, CHP
Reactor Health Physics Manager

ENDORSEMENT:
Reviewed and Approved,

Ralph A. Butler, P.E.
Director

JACQUELINE L. MATYAS
My Commission Expires
March 26, 2019
Howard County
Commission #15634308

ATTACHMENT 2

Carbon Science

Vol. 2, No. 1 March 2001 pp. 9-14

Effect of Temperature on the Adsorption and Desorption Characteristics of Methyl Iodide over TEDA-Impregnated Activated Carbon

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(Received February 16, 2001; accepted March 9, 2001)

Abstract

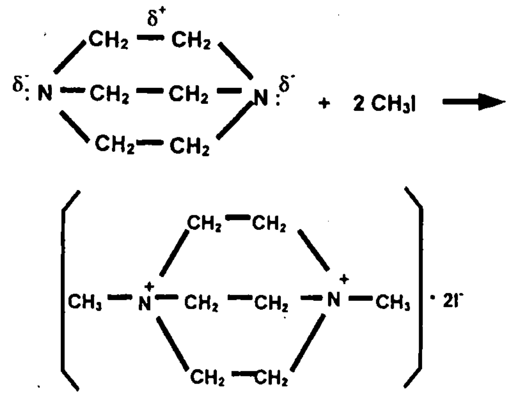
Adsorption and desorption characteristics of methyl iodide at high temperature conditions up to 250°C by TEDA-impregnated activated carbon, which is used for radioiodine retention in nuclear facility, was experimentally evaluated. In the range of temperature from 30°C to 250°C, the adsorption capacity of base activated carbon decreased sharply with increasing temperature but that of TEDA-impregnated activated carbon showed higher value even at high temperature ranges. Especially, the desorption amount of methyl iodide on TEDA-impregnated carbon represented lower value than that on unimpregnated carbon. The breakthrough curves of methyl iodide in the fixed bed packed with base carbon and TEDA-impregnated activated carbon at high temperature were compared. TEDA-impregnated activated carbon would be applicable to adsorption process up to 150°C for the removal of radioiodine in a nuclear facility.

Keywords : *TEDA-AC, High temperature, Methyl iodide, Adsorption, Desorption*

1. Introduction

During the operation of nuclear power plants or nuclear facility, various radioactive gaseous wastes are generated. Because radioiodine among these gaseous wastes has radiological harm on the human body and environment, it is significantly considered that this gas must be removed below restriction of release even in the case of normal operating and accident conditions. Therefore, numerous studies for the removal of radioiodine from the off-gas stream of nuclear facilities have been performed with formation processes and chemical structure [1-6]. Radioiodine generated from nuclear power plants are partially converted radioactive organic iodide, such as methyl iodide, by react with organic matter in process line. TEDA (TriEthyleneDiAmine) or KI-impregnated activated carbons are, in general, used to effectively remove the radioiodine under an accident of high humidity condition.

TEDA, 1,4-Diazabicyclo(2.2.2)octane(DABCO), has a molecular formula of $C_6H_{12}N_2$ with a molecular efficiency by forming charge transfer complexes with organic iodies. The impregnated TEDA on activated carbon is converted quaternary ammonium salts by react with organic iodies as following [7].



There has been some concern regarding the use of TEDA-impregnated activated carbon as an adsorbent for radioiodine removal, because of the low ignition point of TEDA and the possible release of TEDA from the charcoal in continuously flowing air streams. The ignition point of TEDA-impregnated carbon has been reported to be about 190°C [7]. It has been reported that the release of up to 1.2 μg TEDA/(g carbon, min) is observed from various TEDA at 90°C and a flow rate of 4.7 cm/s [7, 8]. Therefore, the TEDA-impregnated activated carbon cannot use in high temperature systems, such as the sintering step in DUPIC (Direct Use of Spent PWR Fuel In CANDU Reactor) process, due to the rapid drop of the removal efficiency and the ignition possi-

ATTACHMENT 2

bility of activated carbon at this condition. Extensive studies in our laboratory were focused to perform the domestic self-development of silver ion-exchanged inorganic solid adsorbent for the removal of radioiodine at high temperature. These works include the adsorption characteristics and the overall evaluation of removal efficiency of radiodine in fixed bed packed with silver ion-exchanged zeolite [9, 10].

Silver zeolite is an expensive adsorbent due to the cost of silver reagent, compared to TEDA impregnated activated carbon whose application to high temperature has some limitations. It is obvious that high temperature can be expected during design basis loss-of-coolant accident (LOCA), which can be regarded as conservatively representing the temperature in pressurized water reactor (PWR). Therefore, investigation on the retention of elemental radioiodine (^{131}I) by various activated carbons at high temperature has extensively been performed so far [11-13]. But only a few results on the adsorption of methyl iodide at high temperature condition have also been presented.

In this study, the adsorption and desorption characteristics of methyl iodide on the TEDA-impregnated activated carbon in fixed bed at high temperature up to 250°C were evaluated with respect to the variation of temperature. Based on the removal efficiency and desorption amount of methyl iodide obtained from the experimental results, the temperature limit of TEDA impregnated activated carbon in application to high temperature ranges is also suggested.

2. Experiment

2.1. Materials

Base activated carbon (AC) and TEDA-impregnated activated carbon (TEDA-AC) were used to examine the adsorption capacity of methyl iodide at various temperature. Activated carbon made from coconut shells, supplied by Samchulri Carbon Co., Korea, with a particle size 8~16 mesh was used.

TEDA-impregnated activated carbons with 6.5 wt% of TEDA were made by impregnating with chemical reagents on the base carbon according to the method presented in a patent [14]. Virgin activated carbon was dried at 110°C for 24 hours to remove moisture. The impregnation time was about 30 minutes, and the ratio of TEDA solution volume to weight of AC was 1.2 ml/g. After impregnation, TEDA-AC was dried at 70~80°C for 16 hrs. The amount of impregnant on TEDA-AC was obtained by the extraction of TEDA with acetonitrile solution and then the analysis of solution concentration using UV-Spectrophotometer. The physical property of two carbons with the aid of the BET-N_2 (Micromeritics, ASAP 2400) analysis was obtained, as listed in Table 1.

The physical properties of TEDA-AC were similar to these of the AC, except for a slight decrease on pore volume and surface area.

Table 1. Physical characteristics of Adsorbents

Characteristic	Base AC	TEDA-AC (6.5 wt%)
Mean Pore Diameter (Å)	12	13.2
Pore Volume (cm^3/g)	0.767	0.658
Micro Pore Volume (cm^3/g)	0.592	0.523
Surface area (m^2/g)	1,483	1,275

2.2. Experimental Apparatus and Methods

A schematic diagram of experimental apparatus is shown in Fig. 1. All parts of the system, such as adsorption column and gas flow lines, were made of pyrex glass to prevent the elemental iodine plate-out and trapping. Gaseous methyl iodide is produced from an evaporation of methyl iodide solution. The gas-phase concentration is adjusted by controlling the solution temperature and the nitrogen flow rate to methyl iodide generators. Dry air was used as a carrier gas at 4 l/min, a superficial velocity of 0.18 m/sec.

The temperature inside the adsorbent was controlled up to 400°C by heating the column in an electric furnace. A constant amount of the adsorbents is packed in a column with dimensions of 0.022 m I.D. and 0.6 m length, and these adsorbents were thermally equilibrated with the gaseous-phase. The effluent concentration of methyl iodide from the column was analyzed by the gas chromatography with a pulse discharged detector (PDD) and GS-Q capillary column at an oven temperature of 140°C as shown in Table 2. Both the breakthrough curve of methyl iodide adsorption and the weight change of the adsorbent were used to obtain the adsorption amount of the adsorbate. Also, desorption experiment after adsorption of methyl iodide was conducted by controlling the column temperature.

Adsorbed amount of methyl iodide by chemical reaction with only TEDA is calculated by following equation, based on the experimental data obtained from fixed bed adsorption. One mol of TEDA can be stoichiomatically adsorbed the two mole of methyl iodide.

Adsorbed amount of methyl iodide by TEDA on TEDA-AC =

$$\frac{\begin{array}{c}\text{(Total adsorption amount by TEDA AC}-\\ \text{Total adsorption amount by AC, mol/g)}\end{array}}{\text{TEDA amount on TEDA}-\text{AC(mol/g)}} \times 100$$

3. Results and Discussion

3.1. Removal Efficiency of Methyl Iodide

In order to analyze the adsorption and desorption characteristics of methyl iodide by TEDA-AC at high temperature range, adsorption behavior of methyl iodide on AC and TEDA-AC at room temperature was evaluated at first. These works were performed in a thin bed with the depth of 3 cm.

ATTACHMENT 2

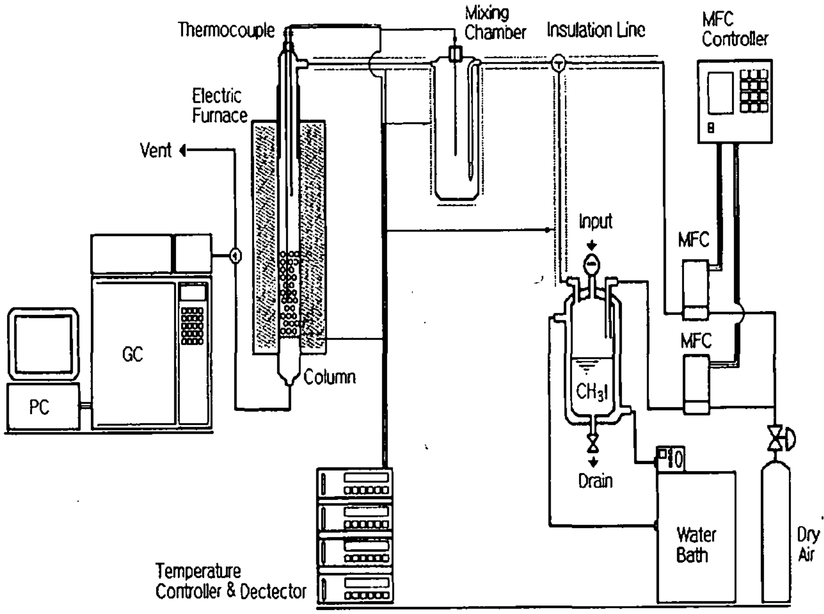


Fig. 1. Flow diagram of the experimental apparatus for methyl iodide.

Table 2. Experimental and gas chromatography conditions

Experimental parameters	Conditions	Unit
Process flow	4.0	*l*/min
Superficial velocity	0.18	m/sec
Bed depth	10	cm
Input concentration	$4 \times 10^{-6} \sim 6 \times 10^{-5}$	mol/L
Gas(CH_3I) generator temperature	30	°C
Bed temperature	30~250	°C
Relative humidity	Dry	%
GC analysis conditions		
– Capillary column	GS-Q	
– Detector	PDD	Pulse Discharged Detector
– Carrier gas(He) flow rate	6	ml/min
– Oven temperature	140	°C
– Detector temperature	160	°C
– Auto sampler volume	1.0	ml

Fig. 2 and 3 represent the breakthrough curves of methyl iodide adsorption on AC and 6.5 wt% TEDA-AC as a function of input concentration at 30°C. As the input concentration is increased, it is normal that breakthrough time becomes short. At the same input concentration in thin bed of 3 cm, adsorption capacity of AC is slightly higher than that of TEDA-AC due to the decrease of surface area as shown in Table 1. This means that adsorption capacity at room temperature depends on both the physical adsorption and chemical adsorption. However, TEDA-AC is more useful to retain the adsorbed methyl iodide, because the retention of methyl iodide by TEDA is due to chemical reaction. This result will be discussed in the next section. In general, the amount of TEDA on carbon filter installed in nuclear facility ranges from 2 wt% to 5 wt% [12]. The influence of TEDA amount on adsorption of methyl iodide at 30°C was evaluated. Fig. 4 shows that increase of TEDA amount made a short breakthrough time. Nevertheless, it is thought that the effect of TEDA inpregnation on the adsorption capacity at room temperature is minimal.

During a postulated nuclear reactor accident, the radioiodine buildup on carbon filters would be high. The highly radioactive iodine would not only provide the intensive radiation field within the carbon filter, but also it would signifi-

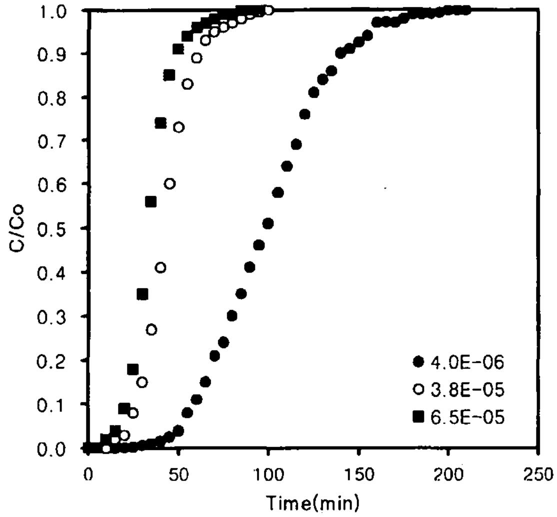


Fig. 2. Breakthrough curves of methyl iodide adsorption on AC with input concentrations (Bed Depth=3 cm, Temp.=30°C).

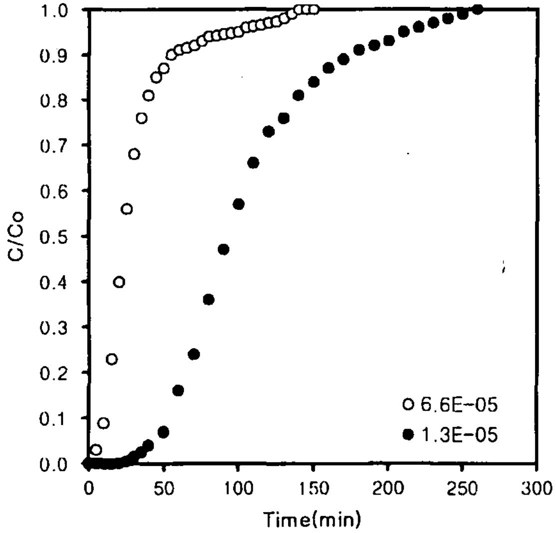


Fig. 3. Breakthrough curves of methyl iodide adsorption on 6.5 wt% TEDA-AC with input concentrations (Bed Depth=3 cm, Temp.=30°C).

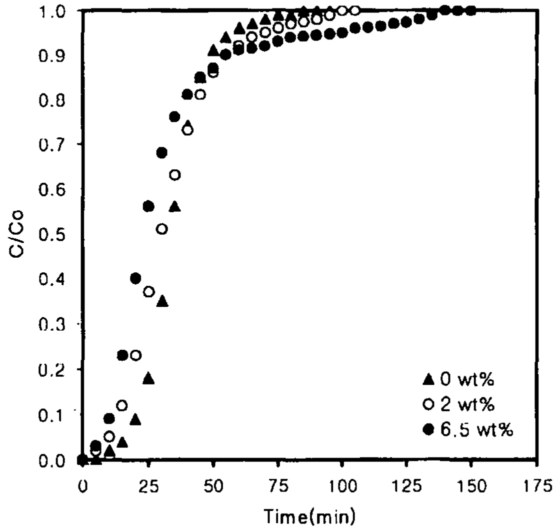


Fig. 4. Breakthrough curves of methyl iodide adsorpt6ion on various TEDA-AC at input concentration of 6.6×10^{-5} mol/l (Bed Depth=3 cm, Temp.=30°C).

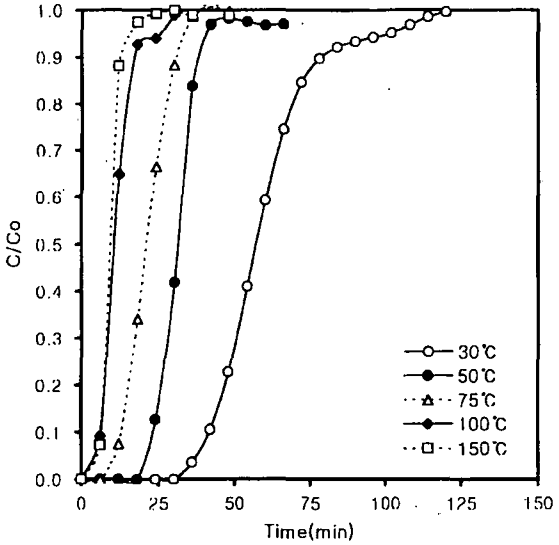


Fig. 5. Breakthrough curves of methyl iodide adsorption on AC with variation of adsorption temperature (Bed Depth=3 cm, Co=5×10^{-5} mol/l).

cantly increase the carbon temperature because of decay heat. Therefore, breakthrough curves of methyl iodide adsorption on AC and 6.5 wt% TEDA-AC at high temperature ranges up to 150 °C were obtained in thin bed of 3 cm, as shown in Fig. 5 and 6, respectively. Input concentration was about 5×10^{-5} mol/*l* in all experiments. Overall breakthrough behavior was the same; as the temperature increases, the adsorption capacity decreases. Especially, above 75°C breakthrough time sharply decreased. This result would be caused by the decrease of physisorption amount, the release of TEDA and the increase of desorption rate of adsorbed methyl iodide with increasing temperature.

The carbon filter used in a nuclear facility has general dimension, that is, bed depth is 25 cm and face velocity of air stream to carbon filter is about 25~50 cm/sec [12]. Fig. 7 represents the breakthrough curves of methyl iodide adsorption on AC and 6.5 wt% TEDA-AC at temperature of 100°C

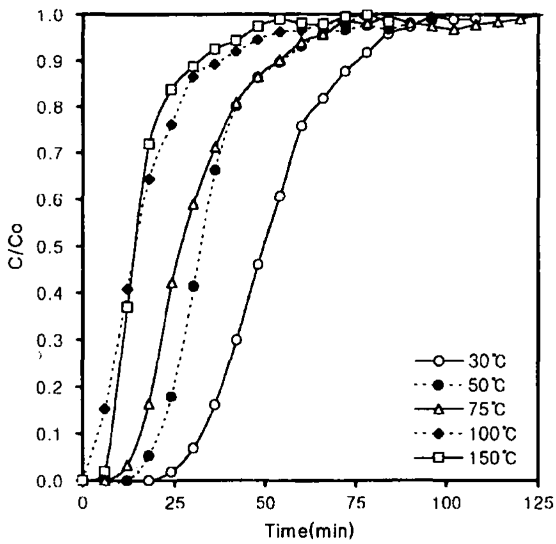


Fig. 6. Breakthrough curves of methyl iodide adsorption on 6.5 wt% TEDA-AC with variation of adsorption temperature (Bed Depth=3 cm, Co=5×10^{-5} mol/l).

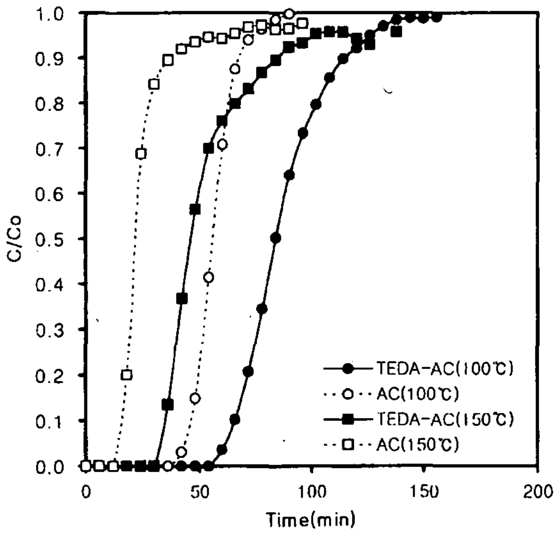


Fig. 7. Breakthrough curves of methyl iodide with temperature in deep bed packed with AC and 6.5 wt% TEDA-AC. (Bed Depth=10 cm, Co=5×10^{-5} mol/l).

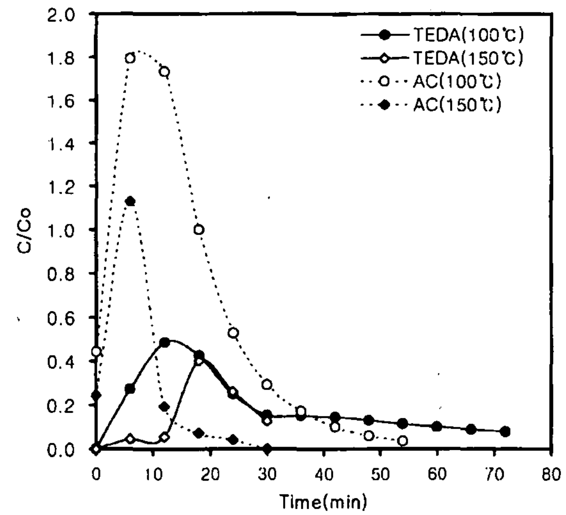


Fig. 8. Desorption curves of methyl iodide with temperature in deep bed packed with AC and 6.5 wt% TEDA-AC. (Bed Depth=10 cm, Dry Air).

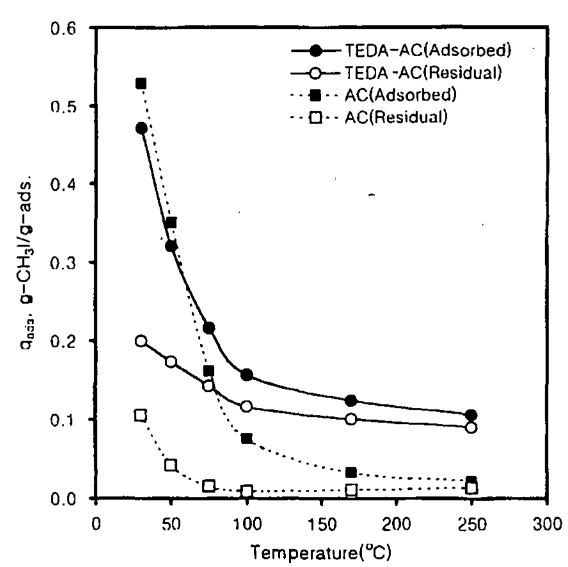


Fig. 9. Adsorption amount and residual amount after desorption with temperature on AC and 6.5 wt% TEDA-AC. (Bed Depth =3 cm, Co=5×10^{-5} mol/l).

and 150°C under the same input concentration in a deep bed of 10 cm. Adsorption capacity of TEDA-AC at 100°C and 150°C was higher than that of AC, and the increased bed temperature reduced the adsorption capacity of TEDA-AC for methyl iodide removal. A little difference on adsorption capacity at thin bed of 3 cm in the range of 100°C to 150°C was observed, as shown in Fig. 6. This is likely due to an increase of temperature inside bed by adsorption heat generated from the chemical reaction. Fig. 8 shows the concentration variation with time during desorption test for TEDA-AC and AC adsorbed methyl iodide (refer to Fig. 7). TEDA-AC had a low desorption amount at high temperature, as compared with that of AC.

3.2. Quantitative analysis of sorption amount

The adsorbed amount and the residual amount of methyl

Table 3. Adsorption amount and residual amount after desorption of methyl iodide (unit: g/g-adsorbent)

Temp. (°C)	AC		TEDA-AC	
	Adsorption	Residual	Adsorption	Residual
30	0.529	0.105	0.470	0.199
50	0.350	0.041	0.320	0.172
75	0.161	0.015	0.215	0.141
100	0.074	0.008	0.155	0.115
170	0.032	0.010	0.123	0.100
250	0.021	0.011	0.105	0.089

iodide after desorption test on each of the adsorbents in the temperature range of 30°C to 250°C are shown in Fig. 9. Quantitative data are listed in Table 3.

As mentioned before, the adsorption capacities of TEDA-AC and AC decrease with increasing temperature. TEDA-AC had a higher adsorption capacity than AC beyond 70°C, and a little difference between the adsorbed amount and the residual amount was observed. These results suggest that the adsorption capacity of AC results from almost physical adsorption, but TEDA is effective in strong fixation of methyl iodide at higher temperature by chemical reaction. Based on the previous equation, the degree of contribution on the adsorbed amount of methyl iodide by only TEDA was calculated at various temperatures. These results are 25.4% at 75°C, 51.9% at 100°C, and 73.3% at 150°C, respectively. Therefore, it would be confirmed that the impregnated TEDA contributes to the removal of methyl iodide at high temperature ranges.

Although impregnated TEDA on TEDA-AC can be released at high temperature, TEDA-methyl iodide complex due to chemical reaction was very stable. In the previous study [6], a pure TEDA begin to vaporize at 174°C, a TEDA-methyl iodide complex begin at 270°C and a TEDA-methyl iodide on TEDA-AC begin to decompose at 200°C. Based on these results, TEDA-AC would be used to remove radioiodine below 150°C. However, it is necessary to confirm the possibility of ignition by adsorption heat.

4. Conclusion

TEDA-impregnated activated carbon is generally used to remove radioiodine generated from normal operating conditions or accident conditions in a nuclear power plant. Therefore, adsorption and desorption characteristics of methyl iodide at high temperature conditions up to 250°C by TEDA-impregnated activated carbon, which represents the performance test at accident condition, was experimentally evaluated. In the range of temperature from 30°C to 250°C, the adsorption capacity of base activated carbon sharply decreased with increasing temperature but that of TEDA-impregnated activated carbon showed higher value even at high temperature ranges. It was obvious that TEDA-AC had higher adsorption capacity than AC beyond 70°C, and a little difference between the adsorbed amount and the residual amount after desorption was observed. These results suggest that the adsorption capacity of AC is largely due to physical adsorption, but TEDA is effective in strong fixation of methyl iodide at higher temperature by chemical reaction. Based on these results, TEDA-impregnated activated carbon would be applicable to temperature up to 150°C for the removal of radioiodine in nuclear facility. However, the possibility of ignition due to adsorption heat and decay heat in deep bed should be confirmed.

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