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Optimization of Off-gas Trapping Capabilities for Pyroprocessing at KAERI

KAERI Pyroprocessing 배기체공정의 최적화

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제 출 문

한국원자력연구원장 귀하

본 보고서를 사용후핵연료 고도 휘발성 산화공정 기술개발 과제에서 수행한 휘발산화공정 배기체 포집기술과 관련하여 “Optimization of Off-gas Trapping Capabilities on Pyroprocessing at KAERI”의 기술보고서로 제출 합니다.

제 목 : Optimization of Off-gas Trapping Capabilities on Pyroprocessing at KAERI

2009 년 9 월

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ABSTRACT

KAERI has been developing a voloxidation process as a head-end process of pyroprocessing technology with INL (Idaho National Laboratory). It was named as the Advanced Voloxidation Process by KAERI and INL. The Advanced Voloxidation Process can mostly remove the gaseous nuclides such as Kr, Xe, C-14, and H-3. It can also remove semi-volatile nuclides such as Cs, I, Tc, Ru, Mo, Rh, etc. Among these nuclides, Cs is a highly radioactive and decay heat eminent nuclide. I-129 and Tc-99 and C-14, etc. are long-lived fission products. The objective of this report is to develop the optimization of off-gas trapping capabilities on pyroprocessing at KAERI. Based on KAERI's experimental results and experience on the trapping characteristics in terms of chemical species, vacuum degree, and trapping temperature, INL hot experiments will be performed in off-gas treatment system (OTS) for a voloxidizer. Experiments were performed using KAERI OTS (Off-gas Trapping System) to trap the volatile. A fly ash filter was used as a trapping media for cesium, rubidium, molybdenum, and cadmium. Ca-I and Ca-II filters were used a trapping media for technetium (rhenium), molybdenum, antimony, and tellurium, respectively. As results of trapping experiments, it was found that trapping efficiency of gaseous cesium by fly ash filter at 1100 ℃ under a vacuum condition was increased by ~ 10 times, in comparison with that of 1000 ℃. Successful trapping of Mo, Te, and mixed species by using Ca- II filter under a vacuum of 7.6 torr was achieved and rhenium was well trapped under a vacuum of 76 torr. Trapping performance of molybdenum by Ca- II filter was better than that of fly ash filter. This report will be used as a useful means for determining optimization of trapping capabilities for trapping semi-volatile fission products.

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1. INTRODUCTION

The United States Department of Energy is developing a head-end fuel treatment process, known as the voloxidation process as part of the Advanced Fuel Cycle Initiative. Voloxidation, which involves oxidizing uranium oxide fuel using either air or oxygen, provides three important advantages when used as a head-end treatment process [1 - 3]. Voloxidation treatment may remove problematic constituents from the fuel prior to downstream treatment operations. Fission products such as ^{137}Cs, ^{85}Kr, ^{133}Xe, ^{99}Tc, ^{14}C, and ^{3}H (tritium) may be volatilized and removed, simplifying the process flow sheets and yielding more flexible waste treatment operations. Furthermore, the trapping media of various nuclides should be easy to be disposed of. Therefore, these gaseous fission products have to be trapped safety and kept from leakage to the environment. Cs is a major source of radiation and heat. Up-front removal reduces the need for shielding. Long-lived fission products are ^{99}Tc, ^{14}C, and ^{129}I.

It was, therefore, proposed that the two parties conduct joint experiments in the U.S. DOE laboratory with actual LWR spent fuel for the purpose of recovery and trapping of gaseous fission products (Cs, Ru, Tc, ^{14}C, I, Kr, Xe, ^{3}H, etc). In order to complete this work, literature should be reviewed, and the appropriate unit operations for each fission product should be suggested. Based on literature reviews and KAERI's experimental results on the gaseous fission products trapping, appropriate trapping method for each fission product has been selected in terms of process reliability, simplicity, decontamination factor, availability, disposal, and so on. The most promising trapping methods for each fission product were proposed to INL team.

INL team completed the design of an INL OTS (Off-gas Treatment System) to be used in HFEF of INL with co-work of KAERI. INL team accomplished manufacturing of the OTS. KAERI team also manufactured KAERI OTS in laboratory similar to INL OTS. Feedback of KAERI's cold test results to INL team will be necessary for determining hot test conditions. The data of these test results will be very useful to predict the trapping characteristics of hot test.

The objective of this report is to develop the optimization of off-gas trapping capabilities on pyroprocessing at KAERI. Based on KAERI's experimental results and experience on the trapping characteristics in terms of chemical species, vacuum degree, and trapping temperature, INL hot experiments will be performed in off-gas treatment system (OTS) for a voloxidizer. Experiments were performed using KAERI OTS (Off-gas Trapping System) to trap the volatile. A fly ash filter was used as a trapping media for cesium, rubidium, molybdenum, and cadmium. Ca-I and Ca-II filters were used a trapping media for technetium (rhenium), molybdenum, antimony, and tellurium, respectively. This report will be used as a useful means for determining optimization of trapping capabilities to remove semi-volatile fission products under air and vacuum conditions.

2. EXPERIMENTALS

(A) OTS experimental apparatus

The OTS (Off-gas Trapping System) was designed and manufactured on a lab-scale based on the estimated amount of fission products evolved from the voloxidation process of the 1 batch (200 g) of PWR spent oxide fuel (4.5 wt% U-235 enrichment, 45,000 MWD/MTU and 5-years cooling).

The OTS was incorporated into a horizontal, split-tube furnace with four separate heating zones; the first zone for oxidation of the fuel and three other zones for the trapping of volatile off-gases. The OTS installed in the KAERI laboratory is shown in Fig. 1. OTS was consisted of two sections that were voloxidizer hot zone and nuclides trapping hot zone arranged of three trapping units which were Cs trapping zone for trapping Cs, Rb, Mo, and Cd trapping zone for trapping Re(Tc), Ru, Te, Mo, Sb and I trapping zone for trapping I. The inactive surrogate chemicals were volatilized in a voloxidizer at the heating zone and then gaseous chemical species volatilized were trapped in series by each trapping unit. Fig. 2 shows the assembly of a voloxidizer and three trapping containers.

The experimental set-up included a gas delivery system to control the flow of air or oxygen and a vacuum pump capable of reducing the operating pressures to less than 100 mTorr. The structural material of the voloxidizer and cesium trapping container was inconel 601 due to the higher temperatures, and that of the others was 304 stainless steel.

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Fig. 1. Off-gas trapping system.

Fig. 2. The assembly of voloxidizer and trapping containers.

(B) Trapping test of Mo using fly ash filter (#1)

Based on the quantity of Mo contained in PWR spent oxide fuel of 200 g, MoO_3 was used as a gaseous molybdenum source. After weighting MoO_3 of 1.362 g, put it in an alumina crucible (50 ml). After loading it in the voloxidizer container, it was used as an off-gas source.

Trapping temperature condition was set at 1000 ℃ for cesium trapping zone and 800 ℃ for rhenium trapping zone in order to reach the target temperature for 1 hr and hold for 6 hrs, respectively. After reaching set temperature on cesium trapping zone and ruthenium trapping zone, voloxidizer was heated up to 500 ℃ for 1 hr and held for 3 hrs under an air (0.5 ℓ/min) condition and then heated up to 1200 ℃ for 1 hr and held for 1 hr under a vacuum of 2.6 torr. Fig. 3 shows the temperature profile for off-gas trapping test #1.

After trapping Mo under a vacuum condition, the photograph of the fly ash filters trapped Mo was shown in Fig. 4. The color of the fly ash filter surface was not changed as shown in Fig. 4. The surface of the 1st fly ash filter was analyzed by SEM and EDX procedures. The weight gain of the fly ash filter after trapping Mo was a little analyzed. However, from an identification of the SEM analysis, the image of the fly ash filter after trapping Mo was observed a rough and cracked crystal image different in the image of needle and collapsed round types of original filter as shown

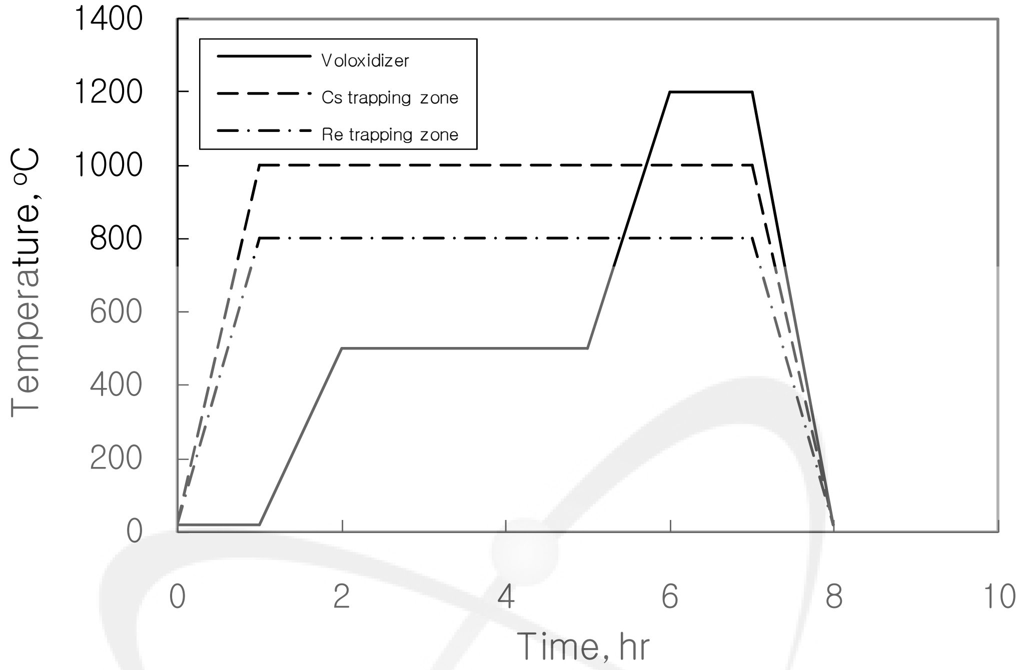


Fig. 3. Temperature profile for off-gas trapping test #1.

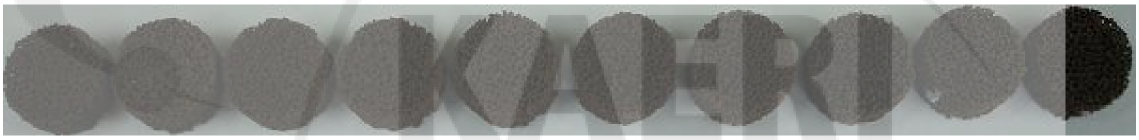
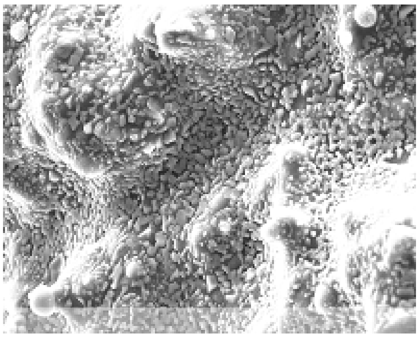


Fig. 4. Photograph of fly ash filters after trapping molybdenum under a vacuum of 2.6 torr.

in Fig. 5. SEM-EDX analysis of 1st fly ash filter indicates that Mo was well trapped on the surface of the filter as a 47 wt.% of Mo concentration. In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st fly ash filter. However, new molybdenum compound phase was not emerged as shown in Fig. 6. The result implies that the reactivity between fly ash filter and gaseous Mo under a vacuum of 2.6 torr is weak. Further detailed tests will be needed to evaluate the trapping characteristics between fly ash filter and gaseous Mo according to vacuum degree.



Element	Weight%	Atomic%
O	22.51	49.35
Al	5.60	7.29
Si	11.47	14.33
Na	0.72	1.10
Mg	0.69	1.00
Ca	8.78	7.69
Fe	3.34	2.10
Mo	46.87	17.14
Totals	100.00	100.00

Fig. 5. SEM-EDX analysis of 1'st fly ash filter after trapping gaseous molybdenum under a vacuum of 2.6 torr.

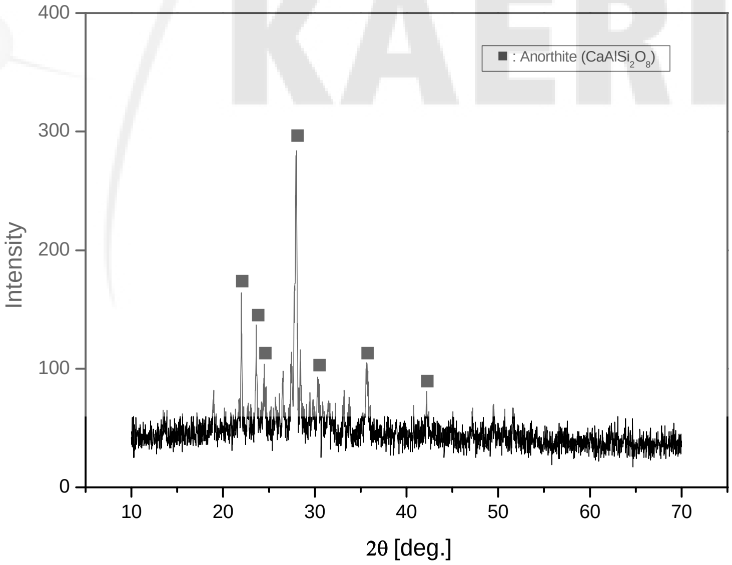


Fig. 6. XRD patterns of 1'st fly ash filter after trapping gaseous molybdenum under a vacuum of 2.6 torr.

(C) Trapping test of Cs using fly ash filter (#2)

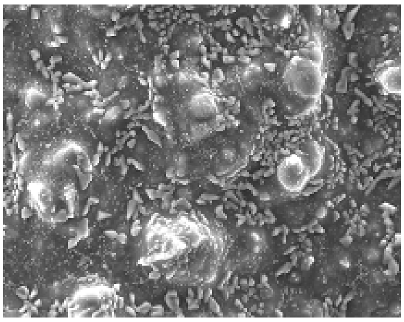
Based on the quantity of Cs contained in PWR spent oxide fuel of 200 g, $CsNO_3$ was used as a gaseous cesium source. After weighting $CsNO_3$ of 1.025g, put it in an alumina crucible (50 ml). After loading it in the voloxidizer container, it was used as an off-gas source

As shown in Fig. 3, trapping temperature condition was set at 1000 ℃ for cesium trapping zone and 800 ℃ for rhenium trapping zone in order to reach the target temperature for 1 hr and hold for 6 hrs, respectively. After reaching set temperature on cesium trapping zone and ruthenium trapping zone, voloxidizer was heated up to 500 ℃ for 1 hr and held for 3 hrs under an air (0.5 ℓ/min) condition and then heated up to 1200 ℃ for 1 hr and held for 1 hr under a vacuum of 2.7 torr .

After trapping Cs under a vacuum of 2.7 torr, the photograph of the fly ash filters trapped Cs was shown in Fig. 7. As shown in Fig. 7, the color of the 1st to 6th filter's surface was changed from brown to dark brown. Through the weight analysis before and after trapping cesium of fly ash filter, it was found that approximately 9% cesium was trapped by 1st to 6th filter. The surface of the 1st fly ash filter was analyzed by SEM and EDX procedures. From an identification of the SEM-EDX analysis as shown in Fig. 8, the surface of the fly ash filer was rough and observed pollucite ($CsAlSi_2O_6$) phase of bulky crystals. SEM-EDX analysis of 1st fly ash filter indicates that Cs was trapped on the surface of the filter as a 10 wt.% of Cs concentration.

In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st fly ash filter. However, cesium compound phase was not emerged as shown in Fig. 9. Cesium compound phase was not observed in the patterns from 1st fly ash filter due to the small amount of cesium trapped on filter.

Fig. 7. Photograph of fly ash filters after trapping gaseous cesium under a vacuum of 2.7 torr.



Element	Weight%	Atomic%
O	31.76	49.95
Al	11.34	10.57
Si	28.61	25.64
Na	1.44	1.58
Mg	1.80	1.86
Ca	9.60	6.03
Fe	5.50	2.49
Cs	9.95	1.88
Totals	100.00	100.00

Fig. 8. SEM-EDX analysis of 1'st fly ash filter after trapping gaseous cesium under a vacuum of 2.7 torr.

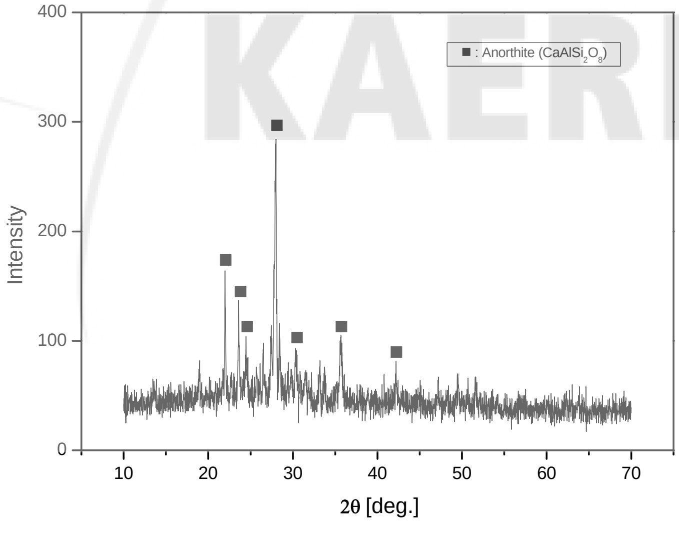


Fig. 9. XRD patterns of 1'st fly ash filter after trapping gaseous cesium under a vacuum of 2.7 torr.

(D) Trapping test of Cs using fly ash filter (#3)

Based on the quantity of Cs contained in PWR spent oxide fuel of 200 g, CsNO$_3$ was used as a gaseous cesium source. After weighting CsNO$_3$ of 1.025g, put it in an alumina crucible (50 ml). After loading it in the voloxidizer container, it was used as an off-gas source.

As shown in Fig. 10, trapping temperature condition was set at 1100 ℃ for cesium trapping zone and 800 ℃ for rhenium trapping zone in order to reach the target temperature for 1 hr and hold for 6 hrs, respectively. After reaching set temperature on cesium trapping zone and ruthenium trapping zone, voloxidizer was heated up to 500 ℃ for 1 hr and held for 3 hrs under an air (0.5 ℓ/min) condition and then heated up to 1200 ℃ for 1 hr and held for 1 hr under a vacuum of 0.2 torr.

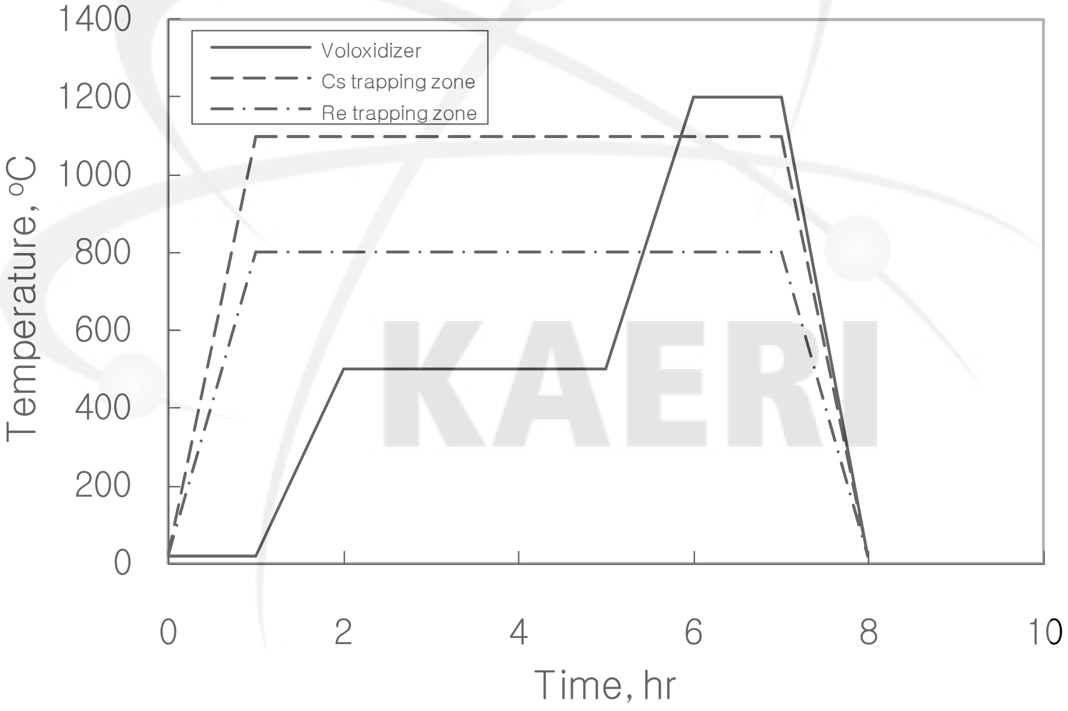


Fig. 10. Temperature profile for off-gas trapping test #3.

After trapping Cs under a vacuum condition, the photograph of the fly ash filters trapped Cs was shown in Fig. 11. As shown in Fig. 11, the color of the 1st to 9th filter’s surface was changed from brown to dark brown. Through the weight analysis before and after trapping cesium of fly ash filter, it was found that approximately

99% cesium was trapped by 1st to 9th filter. The surface of the 1st fly ash filter was analyzed by SEM and EDX procedures. SEM-EDX analysis of 1st fly ash filter indicates that Cs was trapped on the surface of the filter as a 22 wt.% of Cs concentration as shown in Fig. 12. Cesium trapping efficiency was increased according to the increase of trapping temperature compared with test (Ⅱ).

In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st fly ash filter. It was found that cesium was trapped as a pollucite phase as shown in Fig. 13.

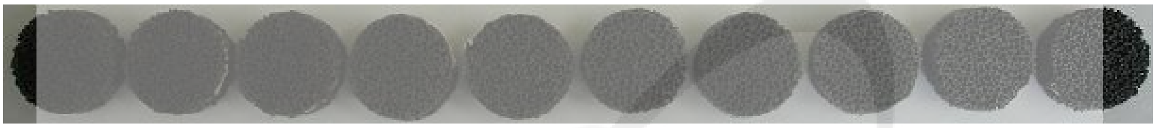
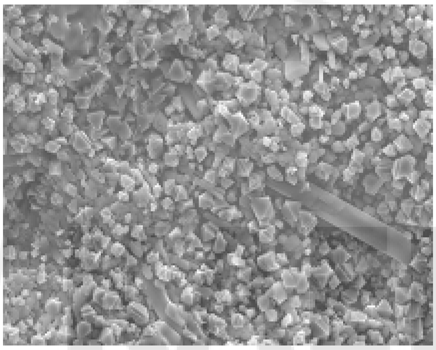


Fig. 11. Photograph of fly ash filters after trapping cesium under a vacuum of 0.2 torr.



Element	Weight%	Atomic%
O	41.24	66.89
Al	4.11	3.95
Si	12.59	11.64
Na	0.78	0.88
Mg	3.44	3.67
Ca	7.83	5.07
Fe	7.54	3.51
Cs	22.47	4.39
Totals	100.00	100.00

Fig. 12. SEM-EDX analysis of 1'st fly ash filter after trapping gaseous cesium under a vacuum of 0.2 torr.

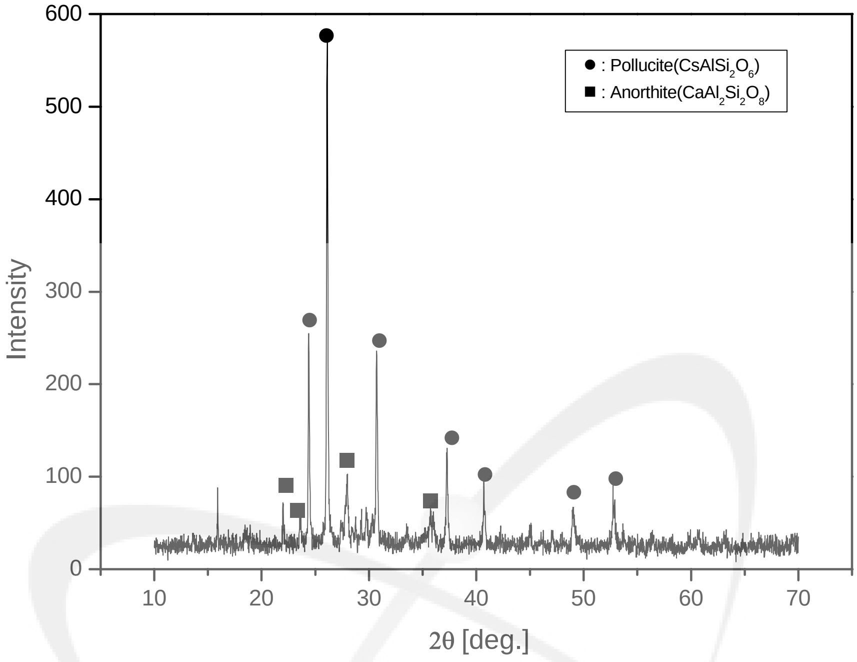


Fig. 13. XRD patterns of 1'st fly ash filter after trapping gaseous cesium under a vacuum of 0.2 torr.

(E) Trapping test of Cs using fly ash filter (#4)

Based on the quantity of Cs contained in PWR spent oxide fuel of 200 g, $CsNO_3$ was used as a gaseous cesium source. After weighting $CsNO_3$ of 1.025 g, put it in an alumina crucible (50 ml). After loading it in the voloxidizer container, it was used as an off-gas source. Temperature condition of the cesium trapping test was followed by Fig. 10. And this test was performed under a vacuum of 76 torr.

After trapping cesium, the photograph of the fly ash filters trapped cesium was shown in Fig. 14. As shown in Fig. 14, the color of the 1st to 9th filter’s surface was changed from brown to dark brown. Through the weight analysis before and after trapping cesium of fly ash filter, it was found that approximately 99% cesium was trapped by 1st to 9th filter. Cesium trapping efficiency was not changed according to the increase of vacuum degree compared with test (Ⅲ). Fig. 15 shows the change of cesium trapping quantity of fly ash filters according to vacuum degree. As shown in Fig. 15, cesium trapping quantity of fly ash filter is not affected in the range of 0.2 to 76 torts at the trapping temperature of 1100℃.

In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st fly ash filter. It was found that cesium was trapped as a poll cite phase as shown in Fig. 13.

Fig. 14. Photograph of fly ash filters after trapping cesium under a vacuum of 76 torr.

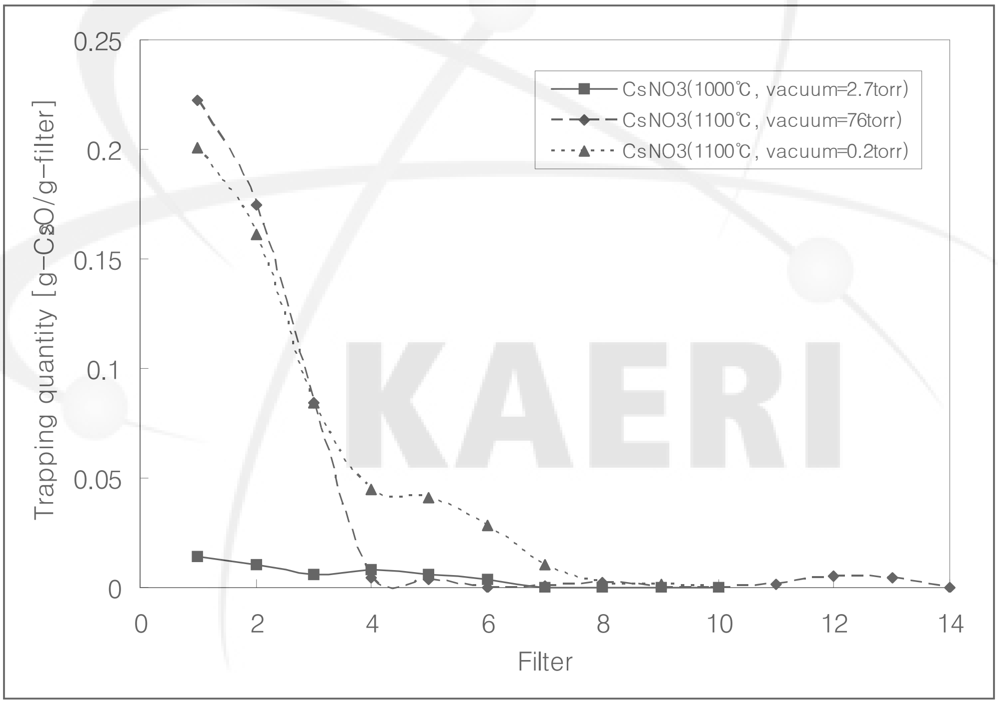


Fig. 15. Cesium trapping quantity of fly ash filters after trapping gaseous cesium according to vacuum degree.

(F) Trapping test of Cs and Mo using fly ash filter (#5)

Based on the quantity of Cs and Mo contained in PWR spent oxide fuel of 200 g, $CsNO_3$ and MoO_3 were used as a gaseous cesium and molybdenum source. After weighting these reagents, put them in an alumina crucible (50 ml). After putting it in the voloxidizer container of OTS, it was used as an off-gas source. The composition of reagents used was shown in Table 1.

As shown in Fig. 3, trapping temperature condition was set at 1000 ℃ for cesium trapping zone and 800 ℃ for rhenium trapping zone in order to reach the target temperature for 1 hr and hold for 6 hrs, respectively. After reaching set temperature on cesium trapping zone and ruthenium trapping zone, voloxidizer was heated up to 500 ℃ for 1 hr and held for 3 hrs under an air (0.5 ℓ/min) condition and then heated up to 1200 ℃ for 1 hr and held for 1 hr under a vacuum of 0.13 torr.

Table 1. Composition of reagents used for test (#5)

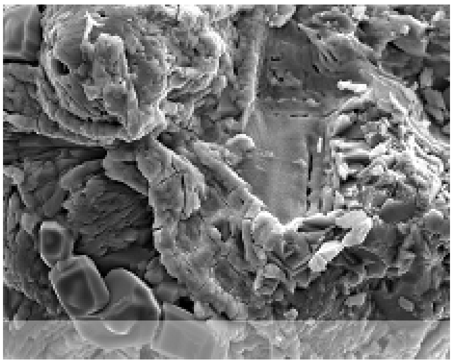
Regents	Weight, g	Remarks
MoO_3	1.362	Mo : 0.908
$CsNO_3$	1.025	Cs : 0.699

After trapping cesium and molybdenum under a vacuum condition, the photograph of the fly ash filters trapped cesium and molybdenum was shown in Fig. 16. The color of the fly ash filter surface was changed from brown to light brown. Through the weight analysis before and after trapping cesium and molybdenum of fly ash filter, it was found that approximately 56% of Cs and Mo were trapped by 1st to 10th filter.

The surface of the 1st fly ash filter was analyzed by SEM and EDX procedures. SEM-EDX analysis of 1st fly ash filter indicates that Cs and Mo were well trapped on the surface of the filter as a 21 wt.% of Cs concentration and 58 wt.% of Mo concentration as shown in Fig. 17.

In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st fly ash filter. The filter was identified as a mixture of pollucite and powellite ($CaMoO_4$) phases as shown in Fig. 18.

Fig. 16. Photograph of fly ash filters after trapping cesium and molybdenum under a vacuum of 0.13 torr.



Element	Weight%	Atomic%
O	14.70	48.59
Al	2.04	4.00
Si	1.88	3.54
Na	0.41	0.94
Mg	0.09	0.19
Ca	1.38	1.83
Fe	0.79	0.75
Mo	57.62	31.77
Cs	21.10	8.40
Totals	100.00	100.00

Fig. 17. SEM-EDX analysis of 1'st fly ash filter after trapping gaseous cesium and molybdenum under a vacuum of 0.13 torr.

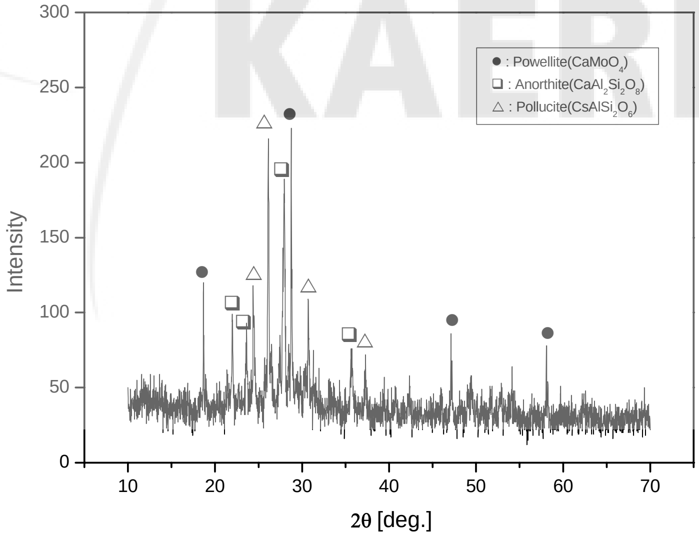


Fig. 18. XRD patterns of 1'st fly ash filter after trapping gaseous cesium and molybdenum under a vacuum of 0.13 torr.

(G) Trapping test of Ru using Ca-I filter (#6)

Based on the quantity of Ru contained in PWR spent oxide fuel of 200 g, RuO_2 was used as a gaseous ruthenium source. After weighting RuO_2 of 0.783 g, put it in an alumina crucible (50 ml). After loading it in the voloxidizer container, it was used as an off-gas source.

As shown in Fig. 19, trapping temperature condition was set at 800 ℃ for cesium trapping zone and 600 ℃ for rhenium trapping zone in order to reach the target temperature for 1 hr and hold for 5.5 hrs, respectively. After reaching set temperature on cesium trapping zone and ruthenium trapping zone, voloxidizer was heated up to 1200 ℃ for 1.5 hrs and held for 4 hrs under a vacuum of 7.6 torr.

The gaseous ruthenium volatilized in voloxidizer might be condensed because the distance between voloxidizer and rhenium trapping zone is long. Calcium filters were stacked in the cesium trapping zone in order to prevent the condensation in the trapping line.

After trapping Ru under a vacuum condition, the photograph of the Ca-I filters trapped Ru was shown in Fig. 20. As shown in Fig. 20, the color of the 1st filter's surface was changed from white to dark brown. As shown in Fig. 21, SEM-EDX

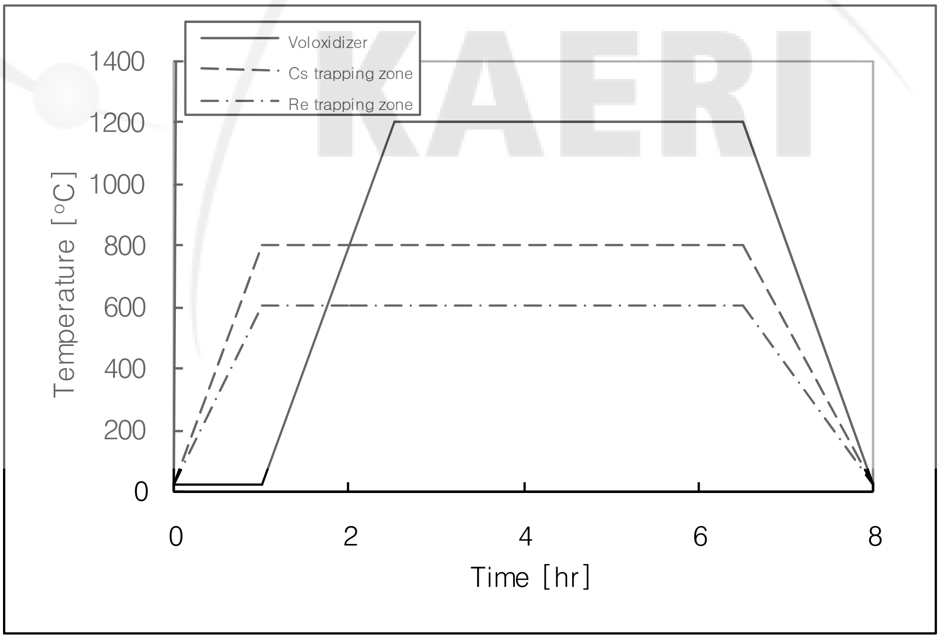


Fig. 19. Temperature profile for off-gas trapping test #6.

analysis of 1st fly ash filter indicates that Ru was trapped on the surface of the Ca-I filter as a Ru of 45 wt.%.

In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st Ca-I filter. However, ruthenium compound phase was not emerged as shown in Fig. 22. Ruthenium compound phase was not observed in the patterns from 1st Ca-I filter due to the small amount of cesium trapped on filter.

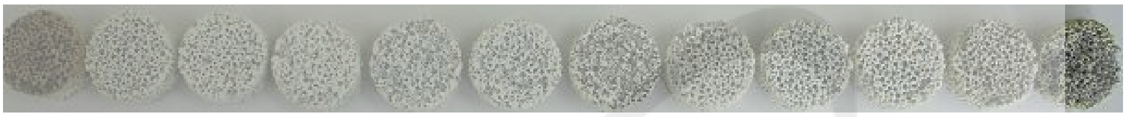
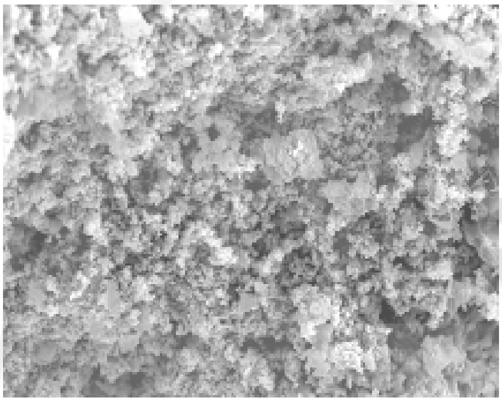


Fig. 20. Photograph of Ca-I filters after trapping ruthenium under a vacuum of 7.6 torr.



Element	Weight%	Atomic%
O	27.92	60.67
Al	0.36	0.47
Si	0.53	0.65
Na	0.00	0.00
Mg	0.00	0.00
Ca	26.10	22.63
Fe	0.25	0.16
Ru	44.85	15.43
Totals	100.00	100.00

Fig. 21. SEM-EDX analysis of 1'st Ca-I filter after trapping gaseous ruthenium under a vacuum of 7.6 torr.

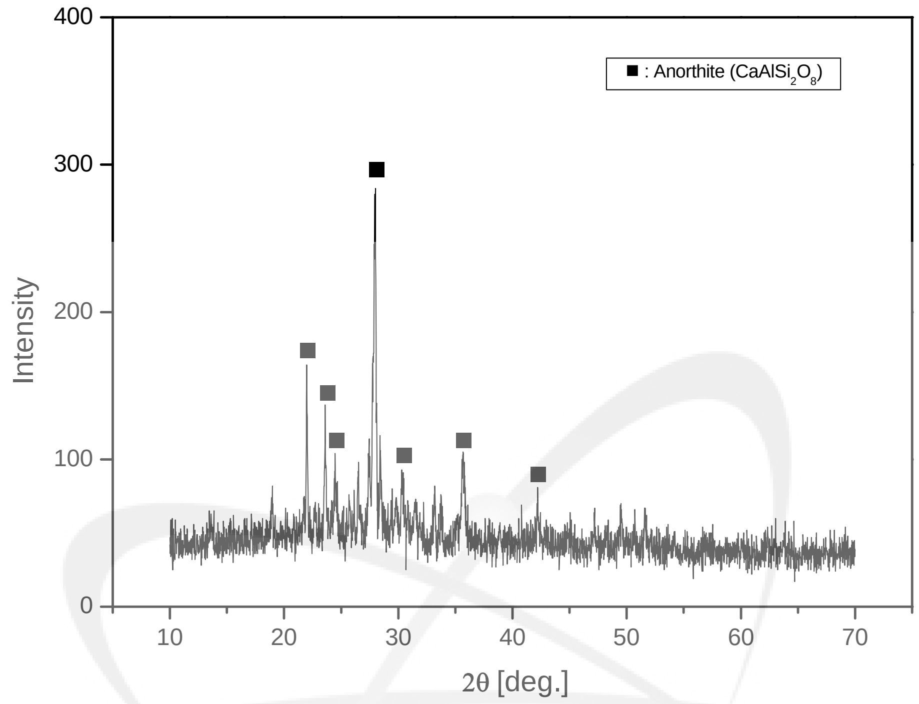


Fig. 22. XRD patterns of 1'st Ca-I filter after trapping gaseous ruthenium under a vacuum of 7.6 torr.

(H) Trapping test of Re using Ca-I filter (#7)

Based on the quantity of technetium contained in PWR spent oxide fuel of 200 g, Re was used as a surrogate of Tc. After weighting Re of 0.206 g, it put in an alumina crucible (50 ml), and then loaded the alumina crucible into a voloxidizer.

As shown in Fig. 23, trapping temperature condition was set at 800 ℃ for cesium trapping zone and 600 ℃ for ruthenium trapping zone in order to reach the target temperature for 1 hr and hold for 4 hrs, respectively. After reaching set temperature on cesium trapping zone and ruthenium trapping zone, voloxidizer was heated up to 560 ℃ for 1 hr and held for 3 hrs under a vacuum of 76 torr. The gaseous rhenium volatilized in voloxidizer might be condensed because the distance between voloxidizer and ruthenium trapping zone is long. Ca-I filters were stacked in the cesium trapping zone in order to prevent the condensation in the trapping line.

After trapping Re under a vacuum condition, the photograph of the Ca-I filters trapped Re was shown in Fig. 24. As shown in Fig. 24, the color of the 1st to 9th filter's surface was changed from white to yellow. As shown in Fig. 25, SEM-EDX analysis of 1st Ca-I filter indicates that Re was trapped on the surface of the filter as a Re of 10 wt.%. In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st calcium filter. It was found that rhenium was trapped as a calcium rhenium oxide hydrate ($Ca(ReO_4)_2 . 2H_2O$) phase as shown in Fig. 26.

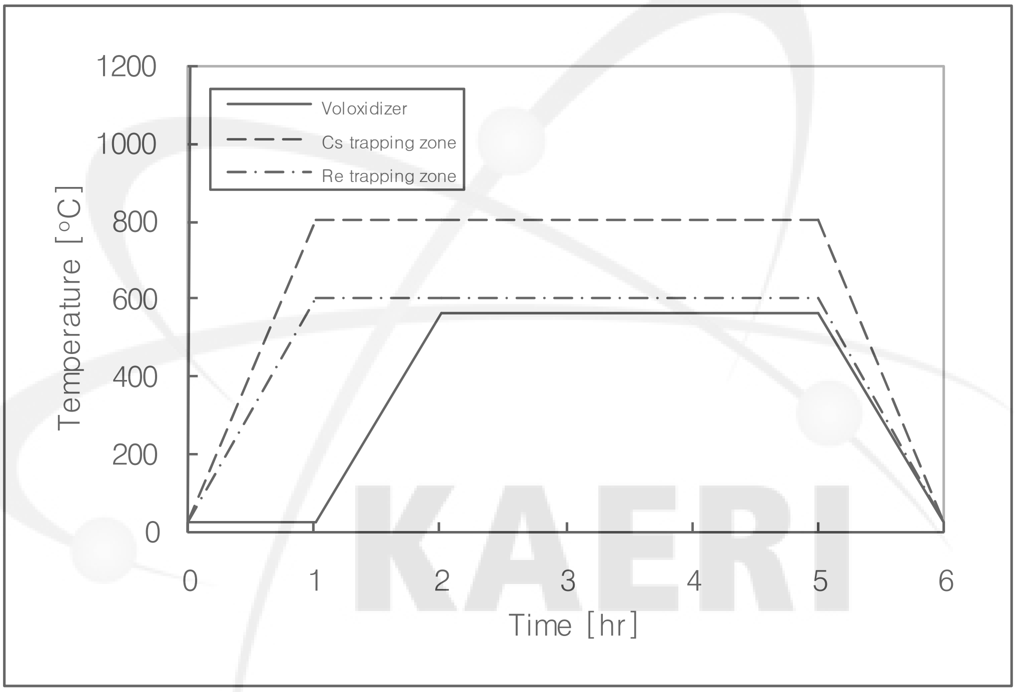


Fig. 23. Temperature profile for off-gas trapping test #7.

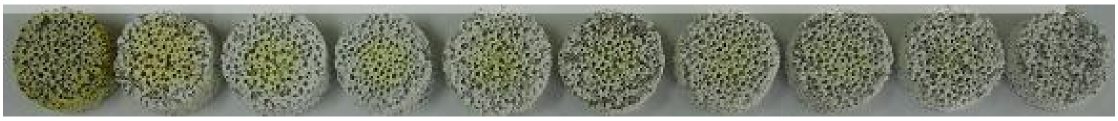
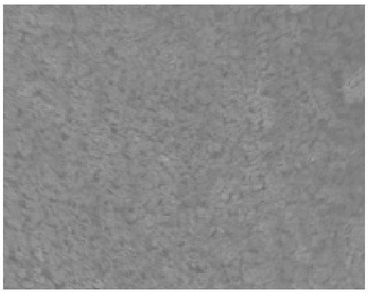


Fig. 24. Photograph of Ca-I filters after trapping rhenium under a vacuum of 76 torr.



Element	Weight%	Atomic%
O	34.21	48.83
Al	0.00	0.00
Si	0.00	0.00
Na	0.00	0.00
Mg	0.00	0.00
Ca	26.32	15.00
Fe	29.04	34.90
Re	10.43	1.28
Totals	100.00	100.00

Fig. 25. SEM-EDX analysis of 1'st Ca-I filter after trapping gaseous rhenium under a vacuum of 76 torr.

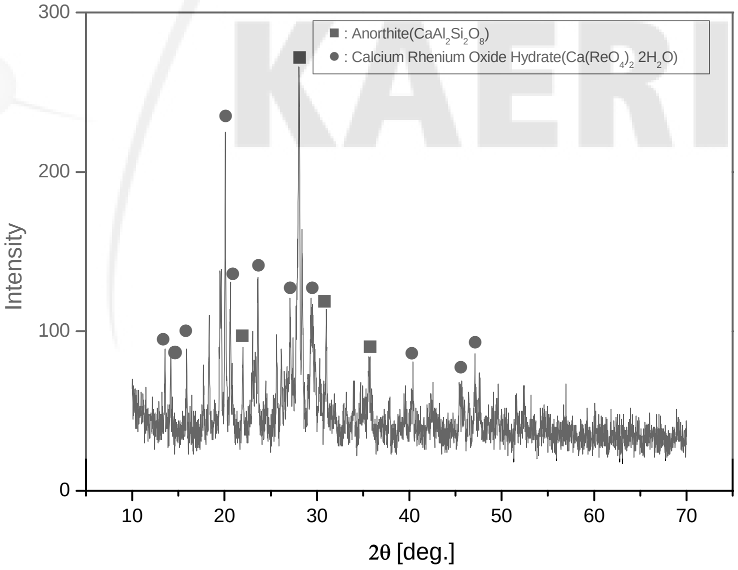


Fig. 26. XRD patterns of 1'st Ca-I filter after trapping gaseous rhenium under a vacuum of 76 torr.

(I) Trapping test of Mo using Ca-II filter (#8)

Based on the quantity of Mo contained in PWR spent oxide fuel of 200 g, MoO_3 was used as a gaseous molybdenum source. After weighting MoO_3 of 1.362 g, put it in an alumina crucible (50 ml), and then loaded the alumina crucible into a voloxidizer. The molybdenum volatilized in voloxidizer might be condensed due to the long distance of voloxidizer and rhenium trapping zone. Ca-II filters were stacked in trapping container at the cesium trapping zone in order to prevent the condensation in the trapping line. Ten Ca-II filters were used as a trapping media for removing gaseous molybdenum.

Trapping temperature condition was set at 800 ℃ for the cesium trapping zone and 600 ℃ for the rhenium trapping zone in order to reach the target temperature for 1 hr and hold for 6 hrs, respectively. After reaching set temperature on the cesium and rhenium trapping zones, voloxidizer was heated up to 500 ℃ for 1 hr and held for 3 hrs under an air (0.5 ℓ/min) condition and then heated up to 1200 ℃ for 1 hr and held for 1 hr under a vacuum condition of 7.6 torr. Fig. 27 shows the temperature profile for off-gas trapping test #8.

Volatilization rate of MoO_3 was 99.9 %. Fig. 28 shows the photograph of Ca-II filters after trapping molybdenum. The color of the of 1st and 2nd Ca-II filters was changed from white to light ocher as shown in Fig. 28. Shown in Fig. 29 is the weight change data for the filters from test#8. A positive weight gain indicated from 1st filter to 5th filter, and a negative weight loss indicated from 6th filter to 10th filter as shown in Fig. 29. A majority of the total molybdenum was trapped on the 1st and 2nd filter. The trapping quantity of the 1st and 2nd filter was 0.73, 0.11 g-MoO_3/g-filter, respectively.

In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st Ca-II filter after trapping molybdenum. The filter was identified as a powellite ($CaMoO_4$) phase as shown in Fig. 29. The result implies that the reactivity between Ca-II filter and gaseous molybdenum under a vacuum of 7.6 torr is strong. Further tests will be needed to evaluate the trapping characteristics between Ca-II filter and gaseous molybdenum according to vacuum degree.

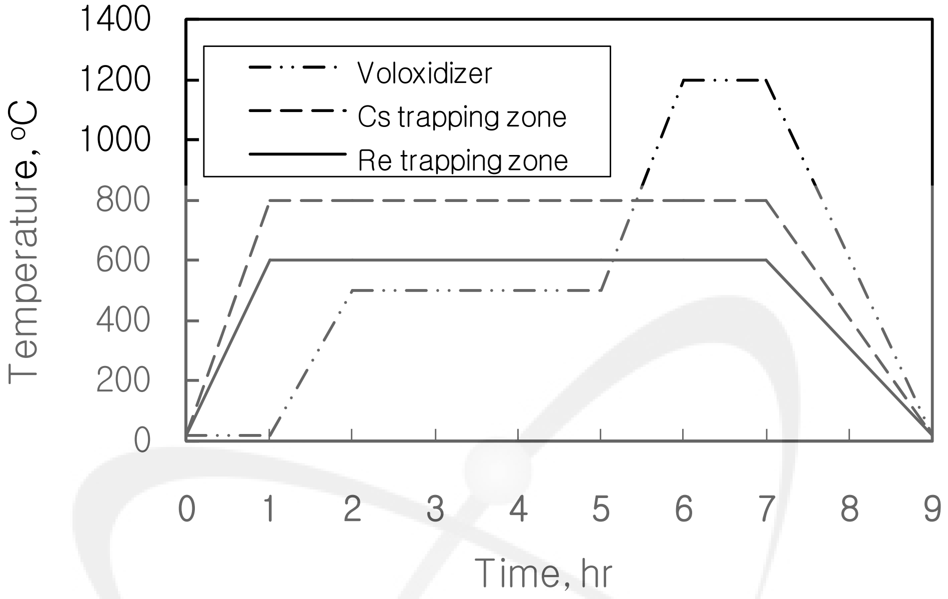


Fig. 27. Temperature profile for off-gas trapping test #8.

Fig. 28. Photograph of Ca-II filters after trapping molybdenum under a vacuum of 7.6 torr.

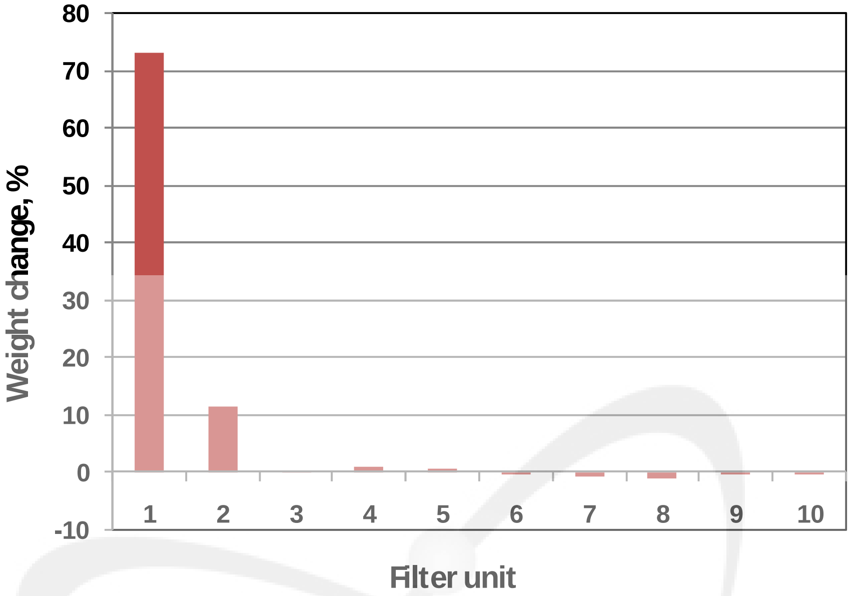


Fig. 29. Weight measurements of filters sampled for test #8.

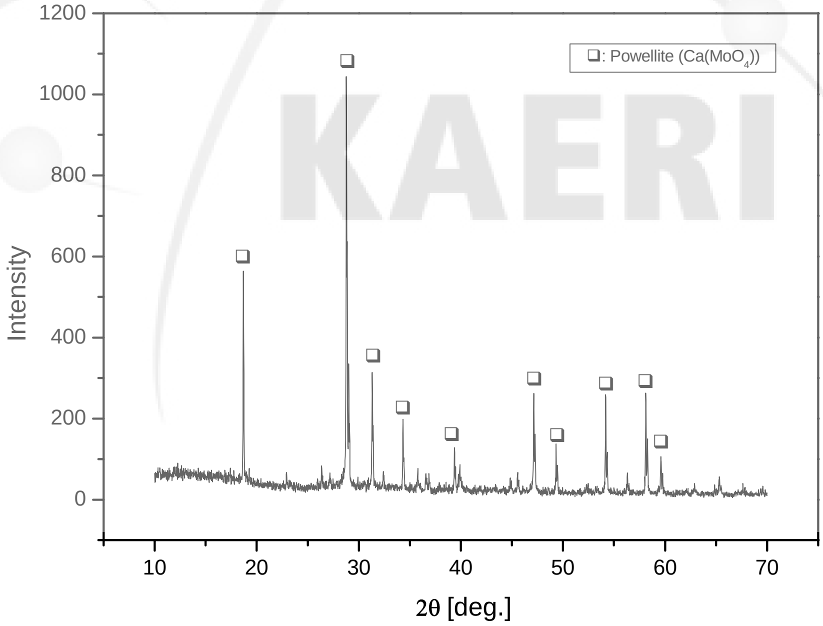


Fig. 30. XRD patterns of 1'st Ca-II filter after trapping gaseous molybdenum under a vacuum of 7.6 torr.

(J) Trapping test of Re using Ca-II filter (#9)

Based on the quantity of technetium contained in PWR spent oxide fuel of 200 g, Re was used as a surrogate of Tc. After weighting Re of 0.206 g, put it in an alumina crucible (50 ml), and then loaded the alumina crucible into a voloxidizer. The rhenium volatilized in voloxidizer might be condensed due to the long distance of voloxidizer and rhenium trapping zone. Ca-II filters were enclosed in trapping container at the cesium trapping zone in order to prevent the condensation in the trapping line. Ten Ca-II filters were used as a trapping media for removing gaseous rhenium. Temperature conditions of the rhenium trapping test was followed by Fig. 27. And this test was performed under a vacuum of 7.6 torr.

Volatilization rate of Re was 99.9 %. Fig. 31 shows the appearance of Ca-II filters after trapping rhenium. The color of the of 1st to 6th Ca-II filters was changed from white to dark yellow as shown in Fig. 31. Shown in Fig. 32 is the weight change data for the filters from test #9. A positive weight gain indicated up to 9th filter, and a negative weight loss indicated at the five filters. Low rhenium trapping quantity of Ca-II filter might be due to the decrease of contact time between Ca-II filter and gaseous rhenium under a vacuum of 7.6 torr.

In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st Ca-II filter after trapping rhenium. It was found that rhenium was trapped as a calcium rhenium oxide hydrate ($Ca(ReO_4)_2 . 2H_2O$) phase as shown in Fig. 33.

Fig.31. Photograph of Ca-II filters after trapping rhenium under a vacuum of 7.6 torr.

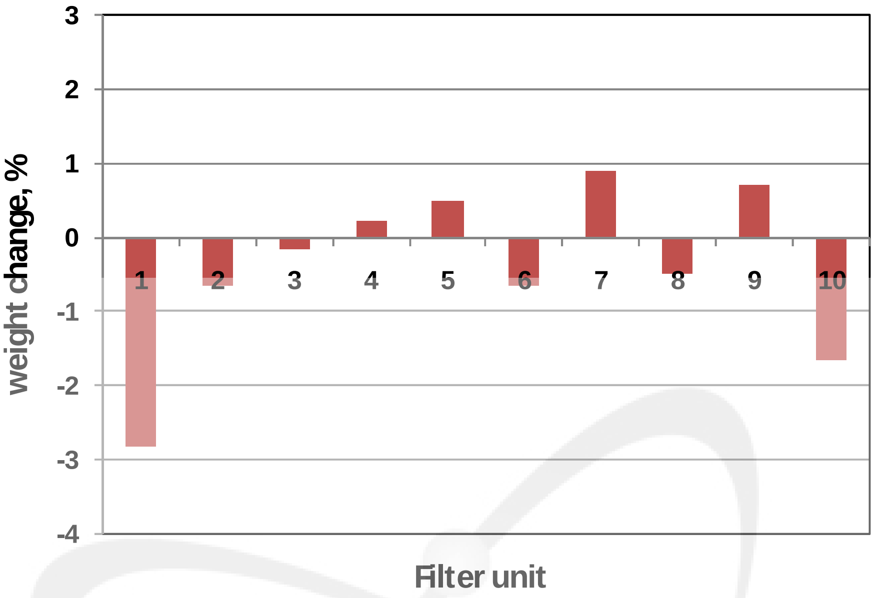


Fig. 32. Weight measurements of filters sampled for test #9.

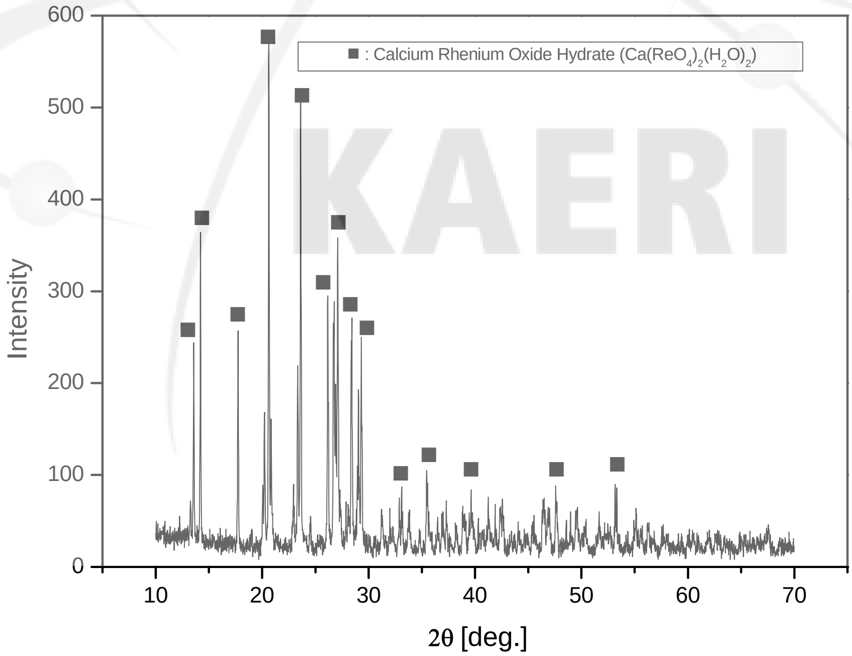


Fig. 33. XRD patterns of 1'st Ca-II filter after trapping gaseous rhenium under a vacuum of 7.6 torr.

(K) Trapping test of Re using Ca-II filter (#10)

All experimental conditions of trapping test (#10) were followed by trapping test (#9) except for the vacuum of 76 torr. Volatilization rate of Re was 99.9 %. Fig. 34 shows the appearance of Ca-II filters after trapping rhenium. The color of the of 1st to 3th Ca-II filters was changed from white to dark gray as shown in Fig. 34. Shown in Fig. 35 is the weight change data for the filters from test #10. A majority of the total rhenium was trapped on the 1st and 2nd filter. The trapping quantity of the 1st and 2nd filter was 0.16, 0.20 g-Re/g-filter, respectively.

In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st Ca-II filter after trapping rhenium. It was found that rhenium was trapped as a calcium rhenium oxide hydrate $(Ca(ReO_4)_2 . 2H_2O)$ phase as shown in Fig. 33. Further tests will be needed to evaluate the trapping characteristics between Ca-II filter and gaseous rhenium depending on vacuum degree.

Fig.34. Photograph of Ca-II filters after trapping rhenium under a vacuum of 76 torr.

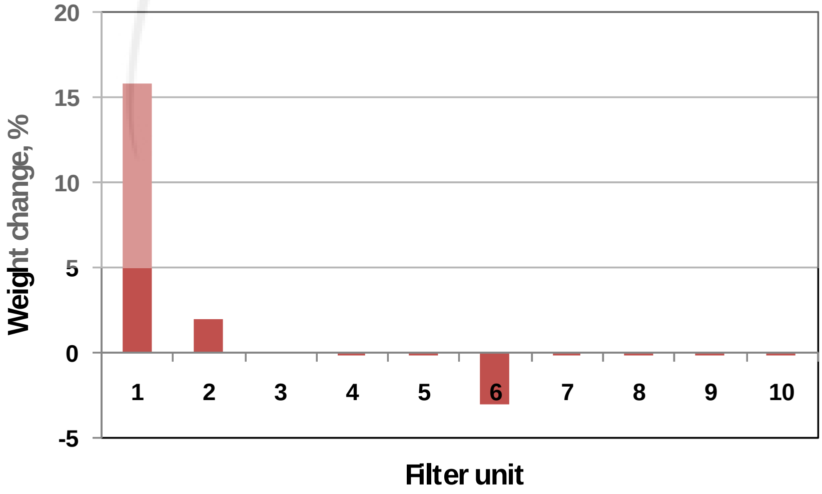


Fig. 35. Weight measurements of filters sampled for test #10.

(L) Trapping test of Sb using Ca-II filter (#11)

Based on the quantity of antimony contained in PWR spent oxide fuel of 200 g, Sb_2O_3 was used as a gaseous antimony source. After weighting Sb_2O_3 of 0.642 g. put it in an alumina crucible (50 ml), and then loaded the alumina crucible into a voloxidizer. Gaseous antimony volatilized in voloxidizer might be condensed due to the long distance of voloxidizer and rhenium trapping zone. Ca-II filters were enclosed in trapping container at the cesium trapping zone in order to prevent the condensation in the trapping line. Ten Ca-II filters were used as a trapping media for removing gaseous antimony.

Trapping temperature condition was set at 800 ℃ for the cesium trapping zone and 600 ℃ for the rhenium trapping zone in order to reach the target temperature for 1 hr and hold for 6.5 hrs, respectively. After reaching set temperature on the cesium and rhenium trapping zones, voloxidizer was heated up to 1200 ℃ for 1.5 hrs and held for 5 hrs. Vacuum pump run at a 7.6 torr condition when the voloxidation temperature was reached up to 500 ℃. Fig. 36 shows the temperature profile for off-gas trapping test #11.

Volatilization rate of Sb_2O_3 was 98.3 %. Fig. 37 shows the appearance of Ca-II filters after trapping antimony. The color of the of 1st to 6nd Ca-II filters was changed from white to light yellow as shown in Fig. 35. Shown in Fig. 38 is the weight change data for the filters from test #11. positive weight gain indicated up to 7th filter, and a negative weight loss indicated at the three filters as shown in Fig. 36. Low antimony trapping quantity of Ca-II filter might be due to the decrease of contact time between Ca-II filter and gaseous antimony under a vacuum of 7.6 torr.

In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st Ca-II filter after trapping antimony. It was found that antimony was trapped as $CaSb2O_6$, $MgSb2O_6$, and $CaSb2O_7$ phases as shown in Fig. 39. Further tests will be needed to evaluate the trapping characteristics between Ca-II filter and gaseous antimony depending on vacuum degree.

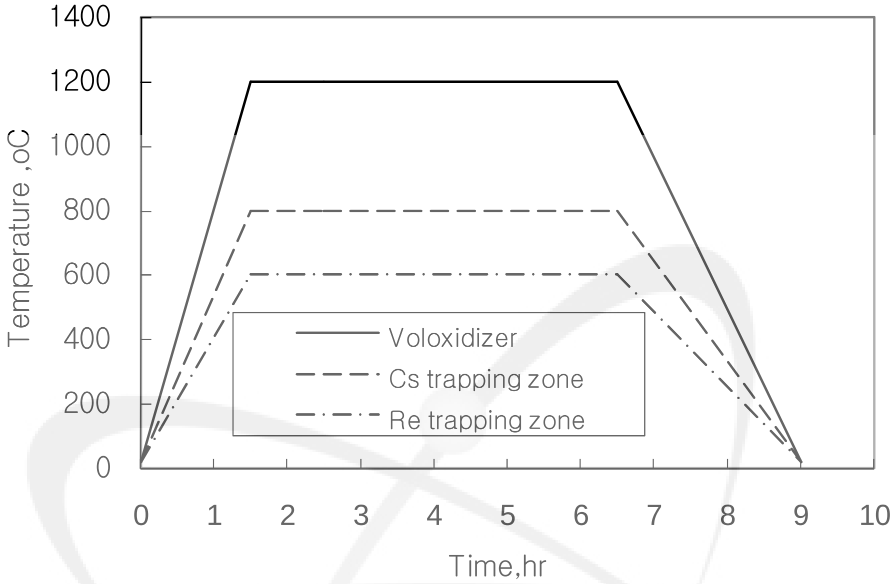


Fig. 36. Temperature profile for off-gas trapping test #11.

Fig. 37. Photograph of Ca-II filters after trapping antimony under a vacuum of 7.6 torr.

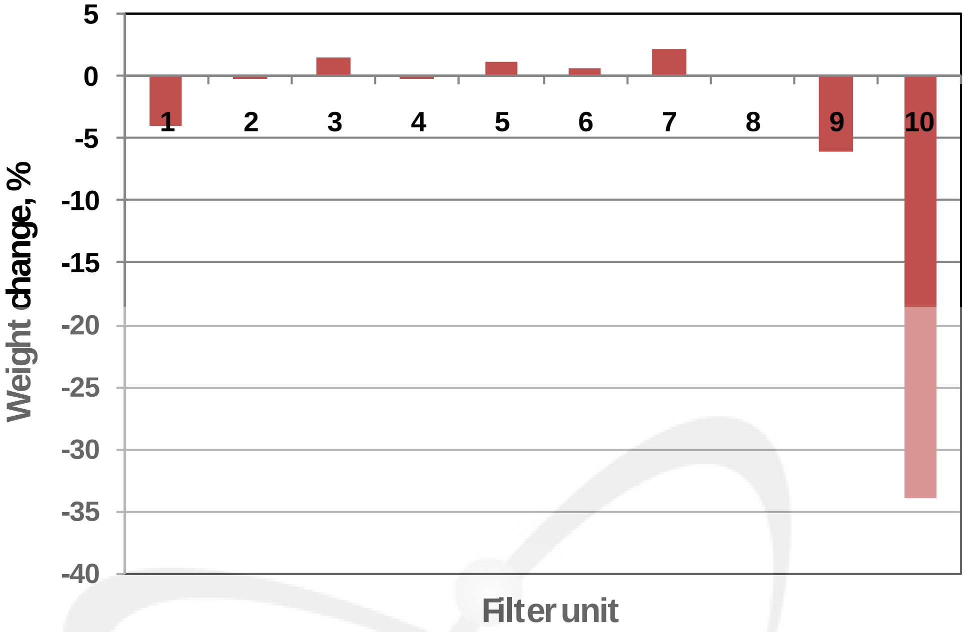


Fig. 38. Weight measurements of filters sampled for test # 11.

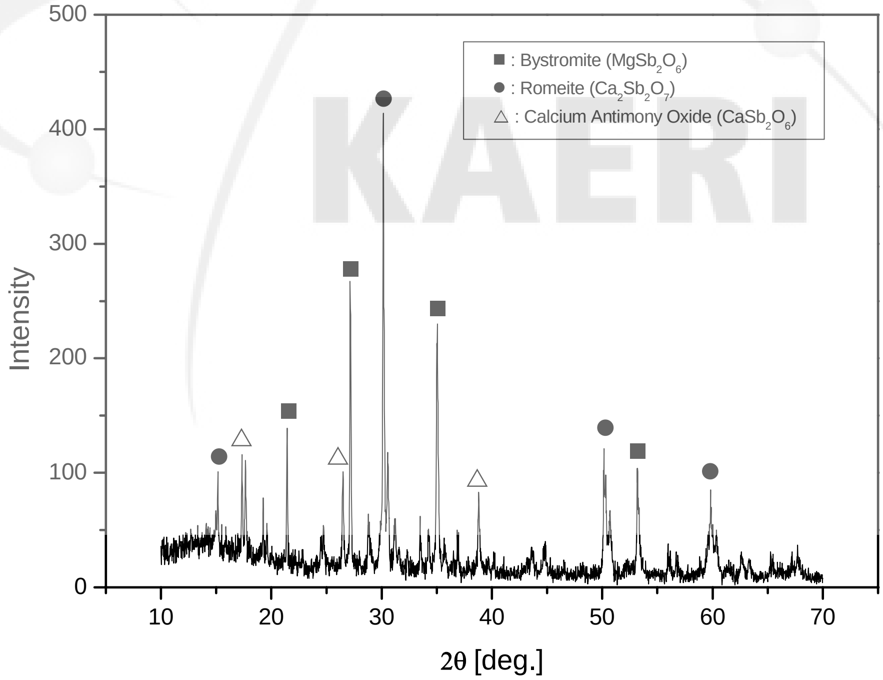


Fig. 39. XRD patterns of 1'st Ca-II filter after trapping gaseous antimony under a vacuum of 7.6 torr.

(M) Trapping test of Te using Ca-II filter (#12)

Based on the quantity of Te contained in PWR spent oxide fuel of 200 g, TeO_2 was used as a gaseous tellurium source. After weighting 0.206 of the Te reagent, put it in an alumina crucible (50 ml), and then loaded the alumina crucible into a voloxidizer. The tellurium volatilized in voloxidizer might be condensed due to the long distance of voloxidizer and trapping zone. Ca-II filters were enclosed in trapping basket at the cesium trapping zone in order to prevent the condensation in the trapping line. Ten Ca-II filters were used as a trapping media for removing gaseous tellurium. Temperature condition of the tellurium trapping test was followed by Fig. 36. And this test was performed under a vacuum of 7.6 torr.

Volatilization rate of TeO_2 was 95.1 %. Fig. 40 shows the appearance of Ca-II filters after trapping tellurium. The color of 1st to 5th Ca-II filters was changed from white to light green as shown in Fig. 40. Shown in Fig. 41 is the weight change data for the filters from test #12. A positive weight gain indicated from 1st filter to 5th filter. A majority of the total tellurium was trapped on the 1st filter. The tellurium trapping quantity of the 1st filter was 0.11 g-TeO_2/g-filter.

In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st Ca-II filter after trapping tellurium. The filter was identified as $Ca3TeO_6$ and $CaTeO_6$ phases. The result implies that the reactivity between Ca-II filter and gaseous tellurium under a vacuum of 7.6 torr is strong. Further tests will be needed to evaluate the trapping characteristics between Ca-II filter and gaseous tellurium depending on vacuum degree.

(N) Trapping test of mixed species using Ca-II filter (#13)

Based on the quantity of Mo, Tc, Sb, and Te contained in PWR spent oxide fuel of 200 g, Mo, Re, Sb, and Te were used as a gaseous mixed species source. After weighting the target reagents, these reagents put in an alumina crucible (50 ml). After putting it in the voloxidizer container of OTS, it was used as off-gases source. The composition of reagents used was shown in Table 2. Temperature condition of the mixed species (Mo, Re, Sb, and Te) trapping test was followed by Fig. 36. And this test was performed under a vacuum of 7.6 torr.

Volatilization rate of mixed species was 99.0 %. Fig. 42 shows the appearance of Ca-II filters after trapping mixed species. The color of the of 1st to 3rd Ca-II filters was changed from white to dark gray as shown in Fig. 42. Shown in Fig. 43 is the weight change data for the filters from test #13. A positive weight gain indicated from 1st filter to 4th filter. A majority of the mixed species was trapped on the 1st filter. The mixed species trapping quantity of the 1st filter was 0.80 g-mixed species/g-filter.

In addition, XRD pattern analysis was performed to identify the crystal structure and microstructure for the surface of the 1st Ca-II filter after trapping mixed species. The filter was identified as $CaMoO_4$, $CaTeO_6$, $CaSb2O_6$, $MgSb2O_6$, and $Ca(ReO_4)_2 \cdot 2H_2O$ phases. The result implies that the reactivity between Ca-II filter and gaseous mixed species under a vacuum of 7.6 torr is strong. Further tests will be needed to evaluate the trapping characteristics between Ca-II filter and mixed species according to vacuum degree.

Fig. 40. Photograph of Ca-II filters after trapping tellurium.

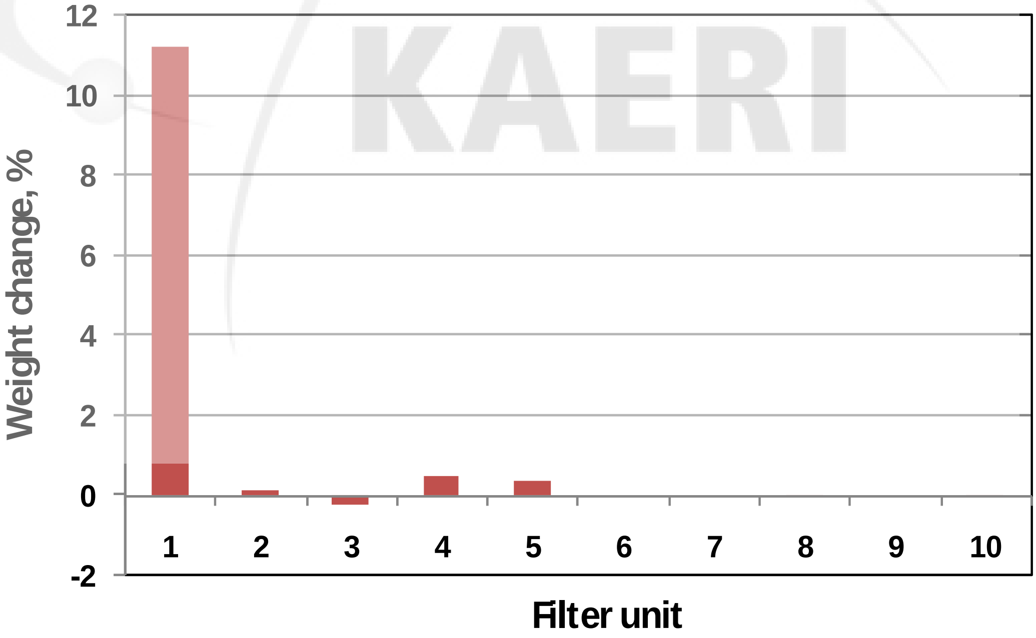


Fig. 41. Weight measurements of filters sampled for test # 12.

Table 2. Composition of reagents used for test #13

Reagents	Weight, g
MoO_3	1.362
Re	0.206
$Sb2O_3$	0.642
TeO_2	0.16

Fig. 42. Photograph of Ca-II filters after trapping molybdenum, rhenium, antimony, and tellurium under a vacuum of 7.6 torr.

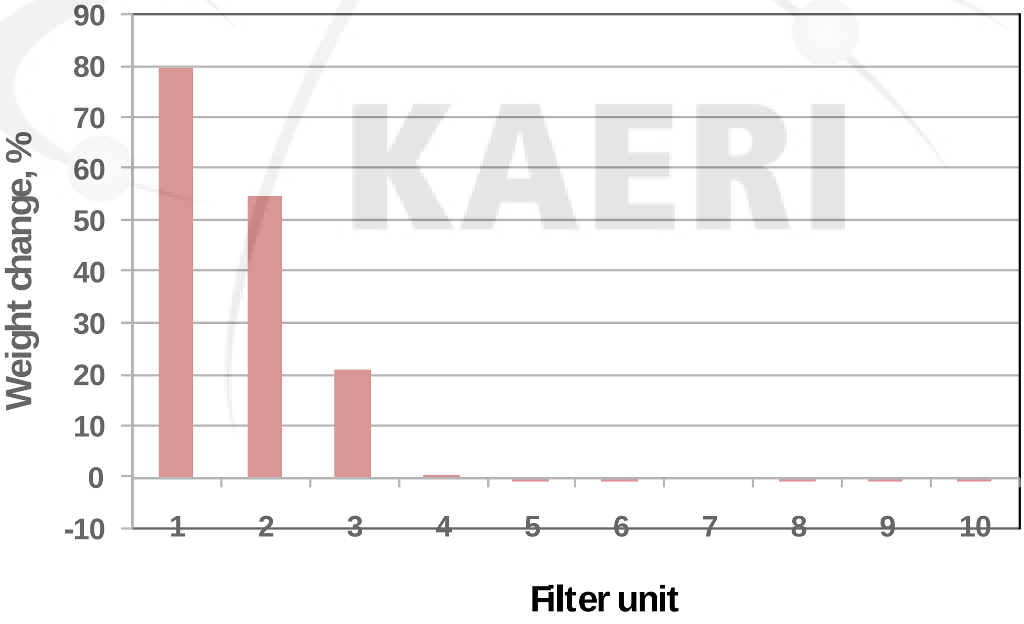


Fig. 43. Weight measurements of filters sampled for test # 13.

(O) Summary of inactive tests at KAERI

Table 3. Summary of inactive experiments at KAERI

Test #	Reagent	Filter	Voloxidation condition	Trapping temp.	Trapping efficiency
1	MoO_3	Fly ash filter 10 units	Air,0.5ℓ/min(500℃ for 3hrs) →Vacuum(2.6torr, 1200℃ for 1hr)	1000℃	-
2	$CsNO_3$	Fly ash filter 10 units	Air,0.5ℓ/min(500℃ for 3hrs) →Vacuum(2.7torr, 1200℃ for 1hr)	1000℃	9%
3	$CsNO_3$	Fly ash filter 10 units	Air,0.5ℓ/min(500℃ for 3hrs) →Vacuum(0.2torr, 1200℃,1hr)	1100℃	99%
4	$CsNO_3$	Fly ash filter 14 units	Air,0.5ℓ/min(500℃ for 3hrs) →Vacuum(76torr,1200℃ for 1hr)	1100℃	99%
5	MoO_3 + $CsNO_3$	Fly ash filter 10 units	Air,0.5ℓ/min(500℃ for 3hrs) →Vacuum(0.13torr,1200℃ for 1hr)	1000℃	56%
6	RuO_2	Ca-I filter 12 units	Vacuum(7.6torr,1200℃ for 4hrs)	800℃	-
7	Re	Ca-I filter 10 units	Vacuum(76torr,560℃ for 3hrs)	800℃	-
8	MoO_3	Ca-II filter 10 units	Air,0.5ℓ/min (500℃ for 3hrs) →Vacuum, 7.6torr (1200℃ for 1hr)	800℃	99%
9	Re	Ca-II filter 10 units	Air,0.5ℓ/min (500℃ for 3hrs) →Vacuum, 7.6torr (1200℃ for 1hr)	800℃	-
10	Re	Ca-II filter 10 units	Air,0.5ℓ/min (500℃ for 3hrs) →Vacuum, 76torr (1200℃ for 1hr)	800℃	99%
11	Sb_2O_3	Ca-II filter 10 units	Air,0.5ℓ/min (500℃ for 25min) →Vacuum, 7.6torr (1200℃ for 5hr)	800℃	-
12	TeO_2	Ca-II filter 10 units	Air,0.5ℓ/min (500℃ for 25min) →Vacuum, 7.6torr (1200℃ for 5hr)	800℃	99%
13	MoO_3 +Re + Sb_2O_3 + Te O_2	Ca-II filter 10 units	Air,0.5ℓ/min (500℃ for 25min) →Vacuum, 7.6torr (1200℃ for 5hr)	800℃	99%

3. CONCLUSIONS

Experimental results obtained from this study show that trapping efficiency of gaseous cesium by fly ash filter at 1100 ℃ under a vacuum condition was increased by ~ 10 times, in comparison with that of 1100 ℃. Trapping efficiency by fly ash filter at 1100 ℃ under a vacuum condition was increased by ~ 10 times, in comparison with that of 1100 ℃. As results of trapping experiments, it was found that successful trapping of Mo, Te, and mixed species by using Ca- II filter under a vacuum of 7.6 torr was achieved and rhenium was well trapped under a vacuum of 76 torr. Trapping performance of molybdenum by Ca- II filter was better than that of fly ash filter. These results indicate great promise for the use of fly ash filter and Ca-II filter as potential filters for the trapping gaseous cesium, technetium, molybdenum, tellurium, and their mixed species under a vacuum condition. It is expected that this work will be very useful for providing information on determining optimization of trapping capabilities for trapping semi-volatile fission products.

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BIBLIOGRAPHIC INFORMATION SHEET

Performing Org. Report No.		Sponsoring Org. Report No.	Standard Report No.		INIS Subject Code
KAERI/TR-3884 /2009					
Title / Subtitle	Optimization of Off-gas Trapping Capabilities on Pyroprocessing at KAERI				
Main Author and Department	Jin Myeong Shin (Recycled Nuclear Fuel Development Division)				
Researcher and Department	J.J. Park, J. W. Lee, J, W, Lee (Recycled Nuclear Fuel Development Division)				
Publication Place	Daejon	Publisher	KAERI	Publication Date	2009. 9.
Page	p.41	Ill. & Tab.	Yes(V), No ( )	Size	A4.
Note	The objective of this report is to develop the optimization of off-gas trapping capabilities on pyroprocessing at KAERI. Based on KAERI's experimental results and experience on the trapping characteristics in terms of chemical species, vacuum degree, and trapping temperature, INL hot experiments will be performed in off-gas treatment system (OTS) for a voloxidizer. Experiments were performed using KAERI OTS (Off-gas Trapping System) to trap the volatile. A fly ash filter was used as a trapping media for cesium, rubidium, molybdenum, and cadmium. Ca-I and Ca-II filters were used a trapping media for technetium (rhenium), molybdenum, antimony, and tellurium, respectively. As results of trapping experiments, it was found that trapping efficiency of gaseous cesium by fly ash filter at 1100 ℃ under a vacuum condition was increased by ~ 10 times, in comparison with that of 1000 ℃. Successful trapping of Mo, Te, and mixed species by using Ca- II filter under a vacuum of 7.6 torr was achieved and rhenium was well trapped under a vacuum of 76 torr. Trapping performance of molybdenum by Ca- II filter was better than that of fly ash filter. This report will be used as a useful means for determining optimization of trapping capabilities for trapping semi-volatile fission products.				
Classified	Open(V), Restricted( ), -___ Class Document		Report Type	Technical Report	
Sponsoring Org.			Contract No.		
Abstract (15-20 Lines)					
Subject Keywords (About 10 words)	Advanced voloxidation process, Gaseous fission products, Trapping, Fly ash filter, Calcium filter, Off-gases				

서지정보양식

수행기관보고서번호	위탁기관보고서번호	표준보고서번호	INIS 주제코드
KAERI/TR-3884/2009			

제목 / 부제	KAERI Pyprocessing 배기체공정의 최적화
주저자 및 부서명	신 진명 (재순환핵연료기술개발부)
공동저자 및 부서명	박 장진, 이 재원, 이 정원 (재순환핵연료기술개발부)

출 판 지	대전	발행기관	한국원자력연구소	발행년월	2009. 9
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참고사항					

비밀여부	공개(V), 대외비( ), -__급비밀	보고서종류	기술보고서
연구위탁기관		계약 번호	

초록 (15-20 줄내외)

본 연구의 목적은 KAERI 파이로 공정의 휘발성 산화공정 중에 발생하는 배기체를 포집할 최적 조업변수를 도출하는 것이다. 본 보고서는 비방사능 물질을 이용하여 단일 및 혼합 핵종, 진공도 및 포집온도별 배기체의 포집특성과 관련하여 수행한 내용을 기술하였다. 세슘, 루비듐, 카드늄 및 몰리브데늄의 포집매질로서 석탄회필터와 테크네튬, 루테늄, 몰리브데늄, 안티몬 및 텔루륨의 포집매질로서 Ca-I 및 II 를 이용하여 포집실험을 수행하였다. 진공조건하 석탄회필터를 이용하여 포집온도 1100℃에서 기체상 세슘을 포집한 결과 포집온도 1000℃와 비교하여 포집효율이 약 10 배 증가하였다. Ca-II 필터를 이용하여 7.6 torr 의 진공조건하에서 기체상 몰리브데늄과 텔루륨을 포집한 결과 제거효율 99% 이상의 우수한 포집성능을 나타내었다. 또한 Ca-II 필터를 이용하여 76 torr 의 진공조건하에서 기체상 레늄을 포집한 결과 제거효율 99% 이상의 우수한 포집성능을 나타내었다.

주제명키워드 (10 단어내외)	고도휘발산화공정, 가스상 핵분열 생성물, 포집, 석탄회 필터, 칼슘 필터, 배기체