TRAPPING CHARACTERISTICS FOR GASEOUS CESIUM GENERATED FROM DIFFERENT CESIUM COMPOUNDS BY FLY ASH FILTER

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Abstract

The purpose of this study is to evaluate the applicability of the fly ash ceramic foam filter to trap gaseous cesium generated during the OREOX and sintering processes of DUPIC green pellets. The trapping experiments of gaseous cesium generated from different cesium compounds using fly ash filters were carried out in a two-zone furnace under air and hydrogen (Ar/4% H_2) conditions. XRD and SEM analyses were used to analyze reaction products of different cesium compounds with fly ash filters. To manufacture ceramic foam filters, fly ash with a Si/Al mole ratio of 2.1 and polyvinyl alcohol as binder were used. Reaction products formed by the trapping reaction of different cesium compounds with fly ash filters were investigated. The major reaction products of gaseous cesium generated from cesium silicate and CsI by fly ash filters indicated that pollucite ($CsAlSi_2O_6$) phase was formed under air and hydrogen conditions when the carrier gas velocity was 2 cm/sec. The minimum reaction temperature of fly ash filter with gaseous cesium was determined as about 600°C. Finally, off-gas treatment system of sintering process in a hot cell of IMEF was explained as an application example of fly ash filter for trapping gaseous cesium.

1. INTRODUCTION

Semi-volatile gaseous radioactive wastes, such as cesium and ruthenium, can be released from the Oxidation and Reduction of Oxide fuel (OREOX) process for manufacturing the Direct Use of PWR Spent Fuel in CANDU (DUPIC) nuclear fuels [1]. They are also expected to be released at high temperature during vitrification processes and imaginary fire accidents during their storage. Among semi-volatile gaseous radioactive wastes, cesium is one of the most hazardous and leachable radioactive fission products. Among well-known cesium aluminosilicates such as cesium nepheline ($CsAlSiO_4$), pollucite ($CsAlSi_2O_6$) and $CsAlSi_5O_{12}$, pollucite has been recommended as a preferable phase for fixing cesium because of its low leach rate, low solubility and good thermal stability and leach resistance [2, 3].

Fly ash is a finely divided particle between 1 and 150 μm entrained in flue gas, which is produced at a ratio of 15- 45% of the raw coal as a by-product when fine coal powder is burned. The remaining amount of fly ash is stored in an ash pond after changing it into slurry form in most coal-fired power plants. It is known that fly ash is a serious pollutant of ground water and soil due to the leaching of potentially toxic substances from an ecological and an economical point of view. Currently, small amounts of fly ash are utilized, mainly as a raw material in the cement industry and a composite material of concrete [4, 5].

It was recently suggested by Park, et al., that fly ash could be used as the raw material for trapping gaseous cesium because of Si/Al mole ratio corresponding approximately to that of pollucite [6]. The cesium loading quantity was determined from their research. Thermal stability of fly ash after trapping cesium was also studied [7]. Cesium compounds such as Cs_2O, CsI, Cs and CsOH are expected to be generated during the OREOX and sintering processes of DUPIC fuel fabrication. Therefore, a fly ash filter should trap these cesium compounds, which is supposed to be used in the off-gas treatment systems of DUPIC fuel fabrication process. To apply for these off-gas treatment systems, it is necessary to understand trapping characteristics of gaseous cesium generated from different cesium compounds by a fly ash filter.

Experiments are performed to evaluate trapping characteristics of gaseous cesium with fly ash filters in a two-zone furnace of 50 mm I.D. alumina tube under air and hydrogen conditions. X ray Diffractometry Analyzer (XRD) and Scanning Electron Microscope (SEM) were used to analyze each reaction product from different cesium compounds with fly ash filters. Finally, the off-gas treatment system for sintering process of DUPIC fuel in a hot cell of IMEF (Irradiated Material Examination Facility) at KAERI was commented briefly.

2. EXPERIMENTAL

Fly ash from Boryung coal fired power plant was used. The chemical composition is shown in Table I. To manufacture the fly ash filter, fly ash and binding material were mixed together to make an uniform slip solution. This slip solution was impregnated with a polyurethane sponge. Drying and sintering processes were followed. The fly ash filter has an inner diameter of 44 mm, thickness of 9mm, average weight of 11.5g. The weight ranges from 10.1 g to 13.4g. The pore density of fly ash filter manufactured ranged from about 20 to 33 pores per linear centimeter. The color of fly ash filter was brown. Various cesium compounds such as cesium silicate, CsI and CsOH were used as the source material of gaseous cesium. Cesium silicate glass was prepared mixing $CsNO_3$ and SiO_2 quantitatively to be the composition of $Cs_2SiO_3(Cs_2O \cdot SiO_2)$. The mixture was reached at 1100°C for 30 minutes, cooled, and powdered for the experiment.

TABLE 1. CHEMICAL COMPOSITION OF FLY ASH

Constituents	wt %
SiO_2	62.04
Al_2O_3	25.02
Fe_2O_3	5.88
CaO	1.39
MgO	0.68
Na_2O	0.36
K_2O	2.10
TiO_2	0.09
Others	2.44
Total	100.0

The trapping experiments were run using different cesium compounds as a source of volatile cesium, with trapping temperatures from 500°C to 1000°C for 6 hours at 2 cm/sec of carrier gas under air and hydrogen (Ar/4% H_2) conditions. The two-zone furnace of 5.0cm I.D. alumina tube is shown in Fig. 1. In the first hot zone, cesium compounds were used to generate a controlled source of gaseous cesium, which was scheduled to pass through the fly ash filters mounted in the second hot zone.

The XRD (Siemens, D-5000) technique was applied to analyze phases of the reaction products. The X ray that was used was a Cu Kα ray and the scanning rate was 2° /min. The angle, 2θ, was within the range of 15° to 60°. SEM (Scanning Electron Microscope, Jeol, JSM-5200) was also used to observe reaction products of fly ash filter with cesium compounds.

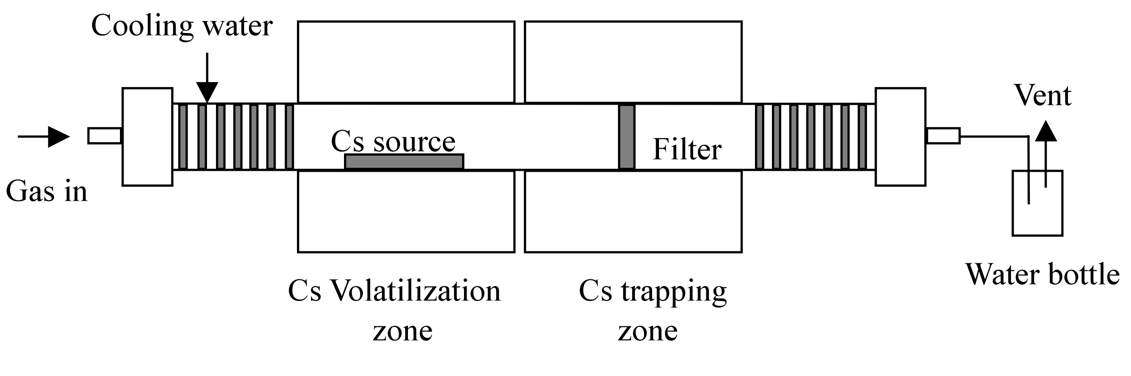

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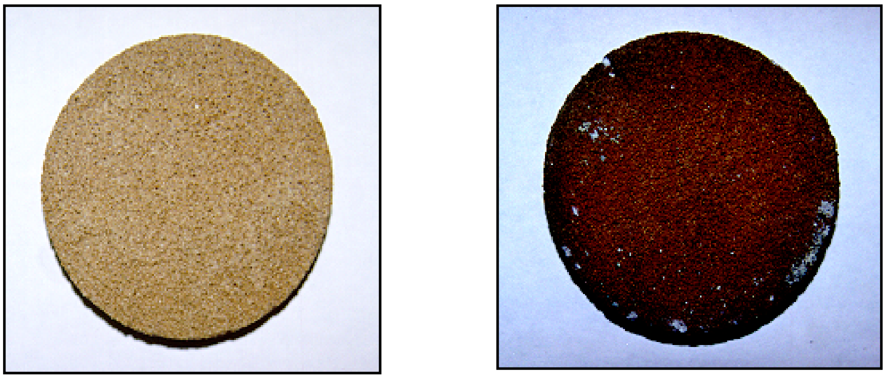
FIG.1. Schematic diagram of the experimental apparatus for trapping Cs.

3. RESULTS AND DISCUSSION

3.1. Observation of fly ash filter and reaction products

When cesium silicate glass was used as a source of gaseous cesium, the color of the fly ash filter changed from brown to dark brown with temperature increasing under air condition. It changed from gray to black with temperature increasing under hydrogen condition. When cesium iodide and cesium hydroxide were used as a source material, the same color change was observed. In case of cesium hydroxide, however, it changed from gray to dark blue with temperature increasing under reduction atmosphere. The typical photographs before and after trapping gaseous cesium generated from CsOH at 800^{o}C under the hydrogen condition were shown in Fig. 2.

Micrographs of fly ash filters before and after trapping gaseous cesium generated from CsOH at 800^{o}C under the hydrogen condition are shown in Fig 3. Unreacted fly ash filter has smooth and flat surface, but its shape is completely different from that of original fly ash particle having spherical shape. Meanwhile, microscopic observation of fly ash filter after trapping gaseous cesium as shown in Fig. 3, indicates that it has new rough surface, which are determined to have pollucite and Cs-nepheline phases by XRD analysis.

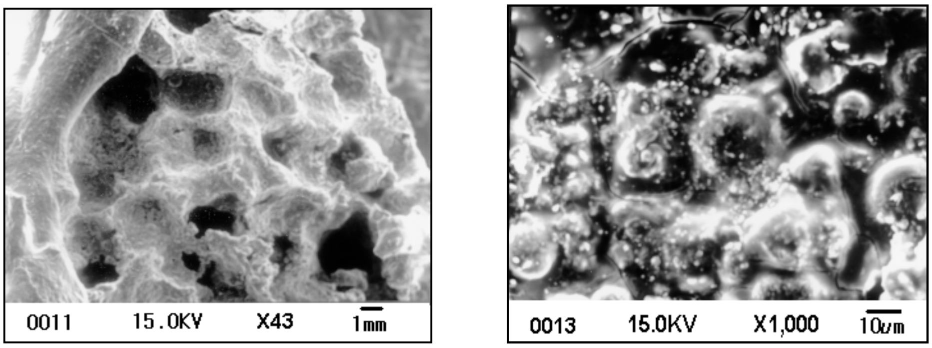


(Before) **(After)**

FIG.2. Photographs of fly ash filters before and after trapping gaseous cesium.

3.2. Phase analysis

The result of phase change with cesium compounds and trapping temperature was shown in Tables II, III and IV. As indicated in Table II, pollucite was formed in the fly ash filters over 600^{o}C under both air and hydrogen (Ar/4% H_2) conditions as a result of trapping gaseous cesium generated from cesium silicate. It was confirmed that fly ash filter could be used to trap gaseous cesium generated from cesium silicate. As shown in Table III, same result was obtained when cesium iodide was used as a source material. The typical XRD result of fly ash filter after trapping gaseous cesium from cesium iodide 800^{o}C under air condition was shown in Fig. 4. This result corresponds to the result of Park, et al., who performed similar experiment using cesium iodide and fly ash powder [6]. For the fly ash filter after trapping gaseous cesium generated from cesium hydroxide, pollucite was formed from 600^{o}C to 700^{o}C under both air and hydrogen conditions as shown in Table IV. Meanwhile, Cs-nepheline and pollucite phase were formed from 800^{o}C to 1000^{o}C under both oxidation and reduction conditions as shown in Table IV. It was indicated that Cs-nepheline as well as pollucite were formed from 800^{o}C to 1000^{o}C. The reason for this might be due to the increase of cesium loading quantity, which should be controlled for the optimum trapping of gaseous cesium with fly ash filter.



(Fly ash filter) (Fly ash filter reacted)

F IG. 3. SEM micrograph of the fly ash filters before and after trappping gaseous cesium generated from CsOH at 800^{o}C under the hydrogen condition.

3.3. Application of fly ash filter for sintering process of DUPIC fuel

Fly ash filters will be used for trapping gaseous cesium generated during OREOX and sintering processes of DUPIC green pellets. In order to show an example of fly ash filter to be applied for DUPIC manufacturing process, the off-gas treatment system for sintering process in IMEF was shown in Fig. 5. As shown in Fig. 5, it consists of Cs trapping unit, TGT (Thermal Gradient Tube) and HEPA filter, etc. More than 90% of cesium is expected to be volatilized in sintering process, which will be implemented at 1650^{o}C under hydrogen (Ar+4% H_2) condition during 8 hours. Cs trapping unit of 80 mm in I. D. and 250 mm in height will be performed to trap gaseous cesium at about 800^{o}C. Fly ash will be mounted to in the Cs trapping unit as a form of disk of 80 mm in diameter and 7 mm in thickness. To prevent the condensation of gaseous cesium in a connection tube between cesium trapping unit and sintering furnace, a connection tube was designed to be heated at 500^{o}C.

Cesium compounds such as CsOH and CsI, etc., are expected to be generated during the sintering process of DUPIC fuel fabrication process. Therefore, gaseous cesium compound of CsOH and CsI should be trapped on a fly ash filter as forms of pollucite and Cs-nepheline during sintering process under hydrogen condition, which could be understood from Tables III and IV. Although the minimum reaction temperature between fly ash filter and gaseous cesium generated from CsI and CsOH was determined as about 600^{o}C, real reaction temperature to be used is considered to be at 800^{o}C because of reaction rate and reactor volume.

TABLE II. XRD ANALYSES OF TRAPPING EXPERIMENTS FOR GASEOUS CESIUM GENERATED FROM CESIUM SILICATE GLASS

Trapping Temperature	Cesium silicate glass	
	Air condition	Hydrogen condition
500^{o}C	Cristobalite, Quartz, Mullite	Cristobalite, Quartz, Mullite
600^{o}C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite
700^{o}C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite
800^{o}C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite
900^{o}C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite
1000^{o}C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite

TABLE III. XRD ANALYSES OF TRAPPING EXPERIMENTS FOR GASEOUS CESIUM GENERATED FROM CESIUM IODIDE

Trapping Temperature	CsI	
	Air condition	Hydrogen condition
500°C	Cristobalite Quartz, Mullite	Cristobalite Quartz, Mullite
600°C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite
700°C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite
800°C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite
900°C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite
1000°C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite

TABLE IV. XRD ANALYSES OF TRAPPING EXPERIMENTS FOR GASEOUS CESIUM GENERATED FROM CESIUM HYDROXIDE

Trapping Temperature	CsOH	
	Air condition	Hydrogen condition
500°C	Cristobalite, Quartz, Mullite	Cristobalite, Quartz, Mullite
600°C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite
700°C	Pollucite, Cristobalite Quartz, Mullite	Pollucite, Cristobalite Quartz, Mullite
800°C	Pollucite, Cs-nepheline Cristobalite, Quartz, Mullite	Pollucite, Cs-nepheline Cristobalite, Quartz, Mullite
900°C	Pollucite, Cs-nepheline Cristobalite, Quartz, Mullite	Pollucite, Cs-nepheline Cristobalite, Quartz, Mullite
1000°C	Pollucite, Cs-nepheline Cristobalite, Quartz, Mullite	Pollucite, Cs-nepheline Cristobalite, Quartz, Mullite

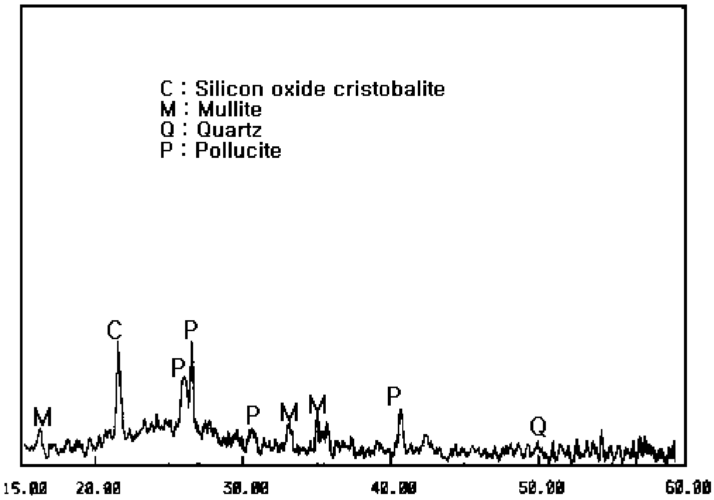


FIG.4. X ray diffraction pattern of the fly ash filter reacted with gaseous cesium generated from CsI at 800℃ under the air condition.

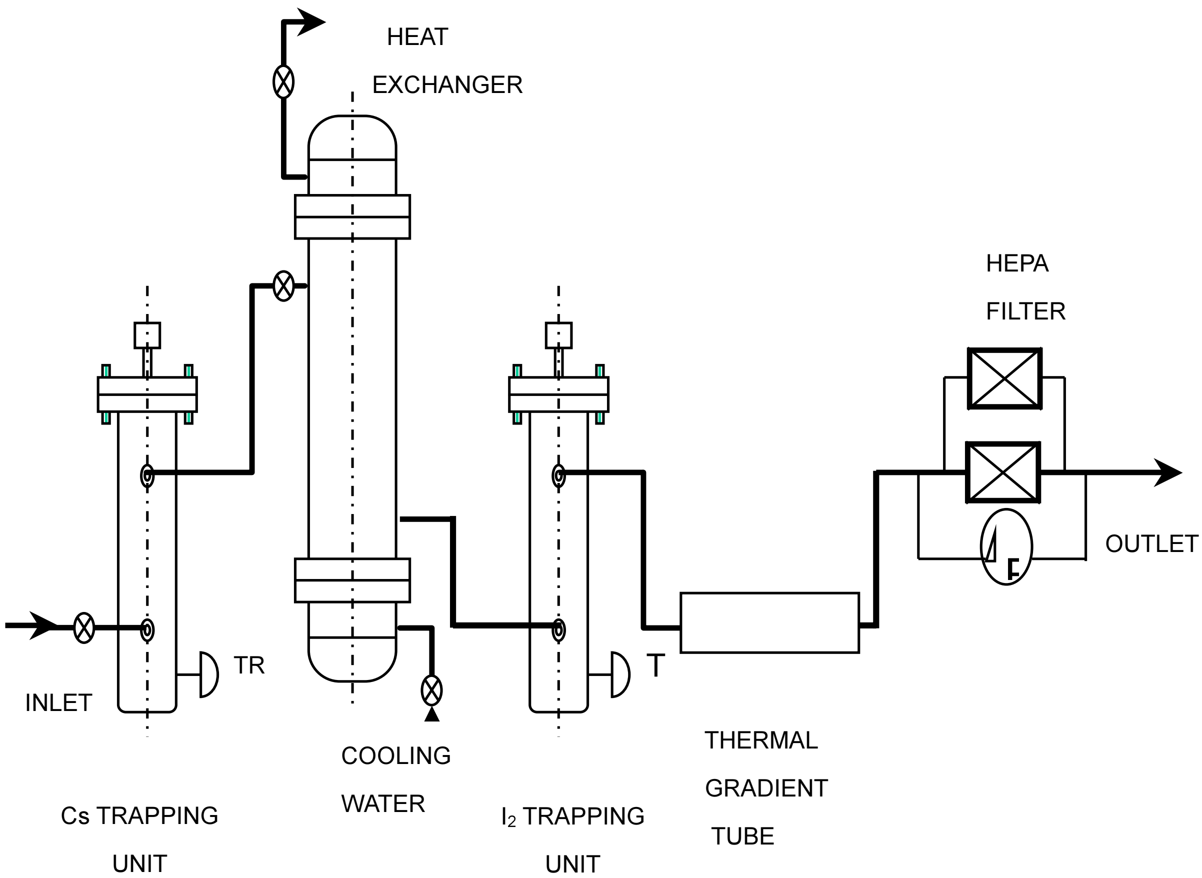


FIG.5. Flow diagram of off gas treatment system for sintering process of DUPIC fuel in IMEF.

4. CONCLUSION

The two-zone furnace experiments were performed to evaluate and determine trapping characteristics and minimum reaction temperature of gaseous cesium generated from different cesium compounds with fly ash filter. The trapping results of gaseous cesium generated from cesium silicate, CsI and CsOH by fly ash filters indicated that pollucite ($CsAlSi_2O_6$) and Cs-nepheline ($CsAlSiO_4$) were mainly formed. The minimum reaction temperature between fly ash filter and gaseous cesium generated from cesium silicate, CsI and CsOH was determined as about 600 ^oC.

ACKNOWLEDGEMENT

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