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Trapping Characteristics of Cesium in Off-Gas Stream Using Fly Ash Filter

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Abstract—The cesium trapping characteristics with changing reaction temperature, carrier gas and gas velocity by the fly ash filter were analyzed. The SEM (Scanning electron microscope) on the pore structure of the fly ash filter showed that pores up to 0.1 mm in diameter were widely interconnected with each other throughout the whole structure of the filter. According to the XRD (X-ray diffraction) analysis for the cesium compound trapped on the fly ash filter, the thermally stable pollucite phase was formed. The cesium trapping quantity of the fly ash filter was increased with increasing reaction temperature, whereas it was decreased with increasing gas velocity. SEM showed that the fly ash filter after trapping gaseous cesium had mullite phase of needle-like crystals and pollucite phase of bulky crystals with rough surface.

Key words: Fly Ash Filter, Cesium, Pollucite, Trapping, DUPIC Nuclear Fuels

INTRODUCTION

A new fuel cycle, called Direct Use of PWR Spent Fuel in CANDU reactor (DUPIC), has received renewed interest recently as PWR to CANDU synergistic fuel recycling option [Yang et al., 1998]. The DUPIC fuel fabrication process consists of rod-cut, decladding, repeated OREOX (Oxidation and REduction of OXide fuel), pelletizing and sintering processes. The schematic diagram of the DUPIC fuel fabrication process is shown in Fig. 1. During the rod-cut process, tritium can be generated. In addition to the rod-cut process, during the OREOX and sintering processes, volatile fission gases (tritium, carbon-14, krypton, iodine etc.) and semi-volatile fission gases (cesium, ruthenium etc.) might be released. Among semi-volatile gaseous radioactive wastes, cesium is one of the most hazardous and leachable radioactive fission products.

Aluminosilicates have been studied from various aspects of preparation, leachability and thermal stability as a trapping material for cesium. 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 and good thermal stability [Denis et al., 1979]. According to Mukerji and Kayal [1975a, b], TG, DTA and XRD analysis techniques showed that clay materials such as metakaolin ($Al_2O_3 \cdot 2SiO_2$), bentonite ($Al_2O_3 \cdot 4SiO_2 \cdot 6H_2O$) and pyrophyllite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$) could be used for trapping gaseous cesium.

Fly ash consists of finely divided particles between 1 and 150 μm entrained in flue gas, which is produced at a ratio of 15-45% of the raw coal as by-product when the fine coal powder is burned. The remaining amount of fly ash is stored in an ash pond after being changed into a 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 composite material of concrete [Lin, 1992].

Recent papers have reported [Park et al., 1996, 1997] on the use of fly ash to trap gaseous cesium, which includes the analysis of optimum loading quantity of gaseous cesium with fly ash and the analysis of thermal stability of cesium trapped on a fly ash. The Si/Al mole ratio of fly ash corresponding approximately to that of pollucite ($CsAlSi_2O_6$) indicates the feasibility of this fly ash in trapping gaseous cesium generated from DUPIC fuel fabrication process. To apply fly ash for off-gas treatment system of gaseous cesium, it should be manufactured as a disk form. Also, it is necessary to obtain the information on the operating conditions of cesium trapping unit using the fly ash filters.

In this work, therefore, experiments were performed to evaluate the trapping characteristics with changing trapping temperature, carrier gas and gas velocity by the fly ash filter in a two-zone furnace. Reaction products formed by the reaction of gaseous cesium compounds with the fly ash filters were investigated by using SEM and XRD analyses.

EXPERIMENTAL

Fly ash from a Boryung coal fired power plant was used. The chemical compositions are shown in Table 1. To manufacture a ceramic foam filter, fly ash and polyvinyl alcohol as a binding material were mixed together to make a uniform slip solution. This slip solution was impregnated with a polyurethane sponge and surplus slip was removed from the sponge. And then it was dried at 95°C and sintered at 1,200°C. The heating rate was constantly maintained at 5°C/min and sintering time was 120 min. The fly ash filter has an inner diameter of 44 mm, thickness of 10 mm and average weight of about 7 g. The number of pores for the fly ash filter ranged from

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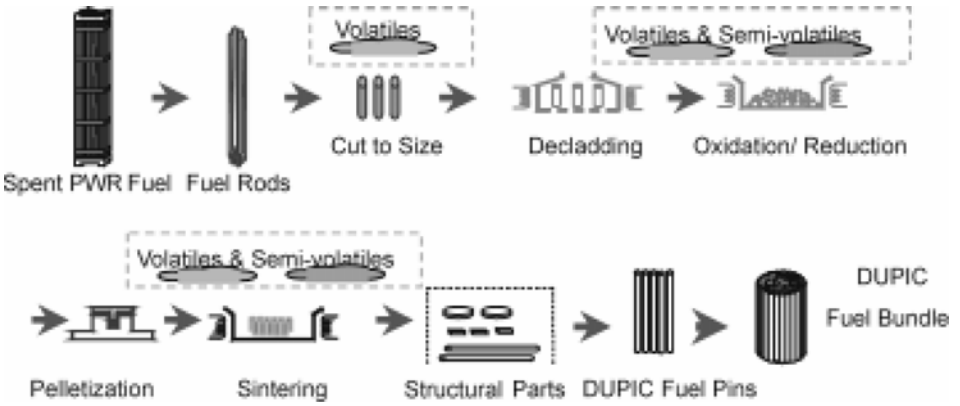


Fig. 1. DUPIC fuel fabrication process.

Table 1. Chemical compositions 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

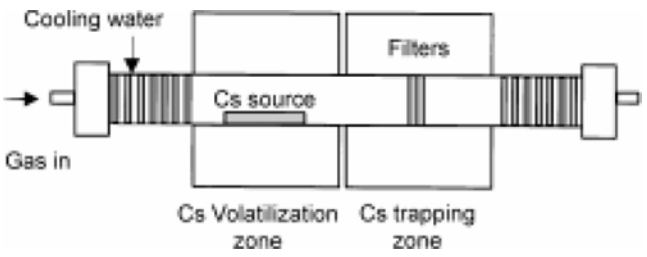


Fig. 2. Schematic diagram of the experimental apparatus for trapping gaseous cesium.

about 13 to 40 pores per linear centimeter. Two-zone furnace of 5.0 cm I.D. alumina tube is shown in Fig. 2. In the first hot zone, cesium silicate was 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. Filters were tightly packed in an alumina tube of furnace by using an alumina mat. The experiments were conducted under air and hydrogen (Ar/4% H_2) conditions because gaseous cesium was considered to be released during the OREOX process in manufacturing DUPIC fuel.

In order to determine minimum trapping temperature, trapping experiments were conducted by heating the trapping zone from 500 °C to 1,000 °C for 18 hours, and then cooling it down to the room temperature. Source temperature of cesium silicate was constantly maintained at 1,000 °C. The air velocity was controlled as 5 cm/sec at the trapping zone. XRD (Siemens, D5000) technique was applied for analyzing reaction products on the fly ash filters. The X-ray used was Cu Kα ray, and the scanning rate was 2°/min. The angle, 2θ, was within the angle of 15° to 60°. SEM (Jeol, JSM-5200) was also used to observe reaction products of the fly ash filter with cesium silicate.

In order to understand the effect of gas velocity on the cesium-trapping quantity of the fly ash filter, the air velocity was varied between 2 and 20 cm/sec. The trapping temperature was constantly maintained at 1,000 °C and trapping time was 18 hours under the air condition. Cesium trapping quantity was calculated by measuring the weight change of the filter before and after trapping gaseous cesium.

RESULTS AND DISCUSSION

When gaseous cesium reacted with the fly ash filter under the air and hydrogen conditions, the colors of the fly ash filter changed from brown to dark brown and from gray to black with increasing temperature, respectively. The typical photographs of the fly ash filters under the air and hydrogen conditions are shown in Fig. 3. It may show that the trapping characteristics of gaseous cesium by the fly ash filter could be changed with the trapping temperature and carrier gas.

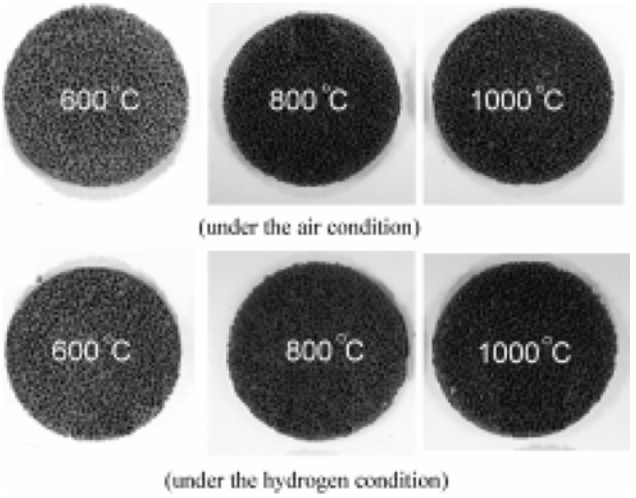
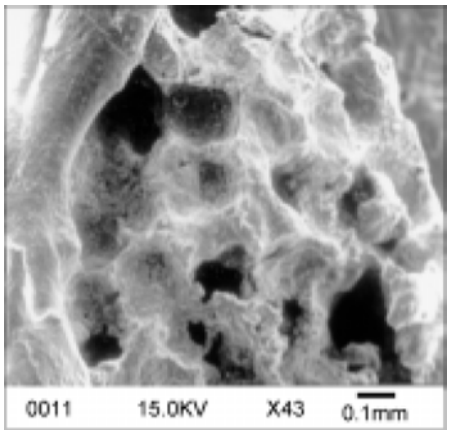
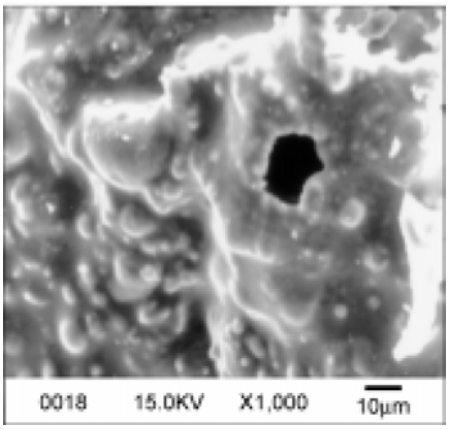


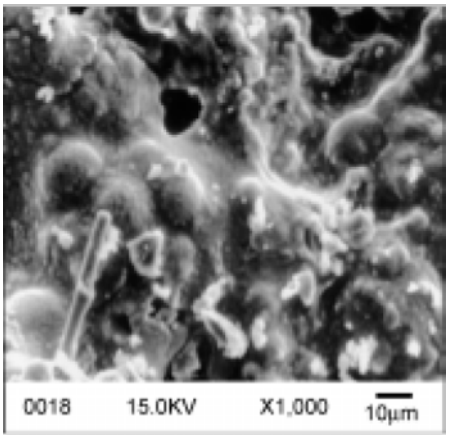
Fig. 3. Photographs of the fly ash filters after trapping gaseous cesium under the air and hydrogen conditions.



(a)



(b)



(c)

Fig. 4. SEM photographs of the fly ash filter before and after reaction at 1,000 °C under the air condition.
(a) filter, ×43, (b) filter, ×1,000, (c) reacted filter, ×1,000

Fig. 4(a) shows SEM photographs of the fly ash filter at 43X magnification. The structure of the fly ash filter indicates that pores up to 0.1 mm in diameter are widely interconnected with each other throughout the whole structure of the filter. The microscopic observation of the fly ash filter is completely different from that of the fly ash particles having spherical shapes [Flagan and Friedlander, 1988]. Microscopic observation of the fly ash filter after trapping gaseous cesium, as shown in Fig. 4(c), taken at 1,000X magnification, indicates that it has pollucite phase of bulky crystals with rough

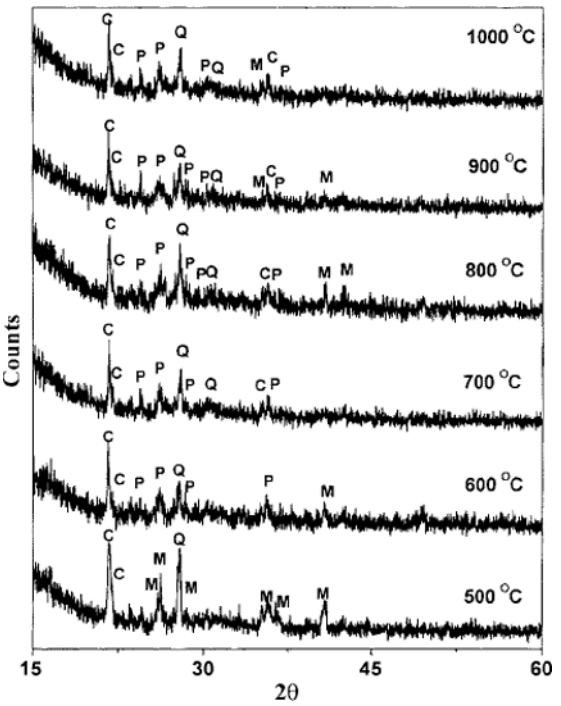


Fig. 5. XRD patterns for the fly ash filters reacted with gaseous cesium under the air condition at different temperatures.
C: Cristobalite, Q: Quartz, M: Mullite, P: Pollucite

surface and mullite phase of needle-like crystals, whose shapes are different from those of the fly ash filter [Fig. 4(b)].

After the reaction of the fly ash filter with gaseous cesium at over 600 °C of trapping temperature under the air conditions, the reacted surface of the fly ash filter gave XRD peaks that indicates cristobalite, quartz, mullite and pollucite phases as shown in Fig. 5. At 500 °C of trapping temperature, only cristobalite, quartz and mullite phases were formed under the air condition as shown in Fig. 5. That is, pollucite phase was not formed at 500 °C. It might indicate that the minimum trapping temperature of gaseous cesium by the fly ash filter is about 600 °C under the air condition.

On the other hand, Fig. 6 shows XRD patterns of the fly ash filters reacted under the hydrogen condition at different temperatures. The reacted surfaces of the fly ash filter from over 600 °C of trapping temperature under hydrogen condition gave XRD peaks that indicate cristobalite, quartz, mullite and pollucite phases as shown in Fig. 6. At 500 °C of trapping temperature, cristobalite, quartz and mullite phases were formed under the hydrogen condition as shown in Fig. 6. That is, the pollucite phase was not formed at 500 °C. It might indicate that the minimum trapping temperature of gaseous cesium by the fly ash filter is also about 600 °C under the hydrogen condition.

The cesium trapping quantity of the fly ash filter was increased with increasing trapping temperature under the air condition as shown in Fig. 7. This might be that the reaction rate was increased with increasing reaction temperature. Fig. 8 shows that the cesium trapping quantity of the fly ash filter was decreased with increasing gas velocity. This might be that the contact time between the fly ash filter and gaseous cesium was decreased with increasing gas velocity.

According to Park et al. [1997], cesium trapping experiments

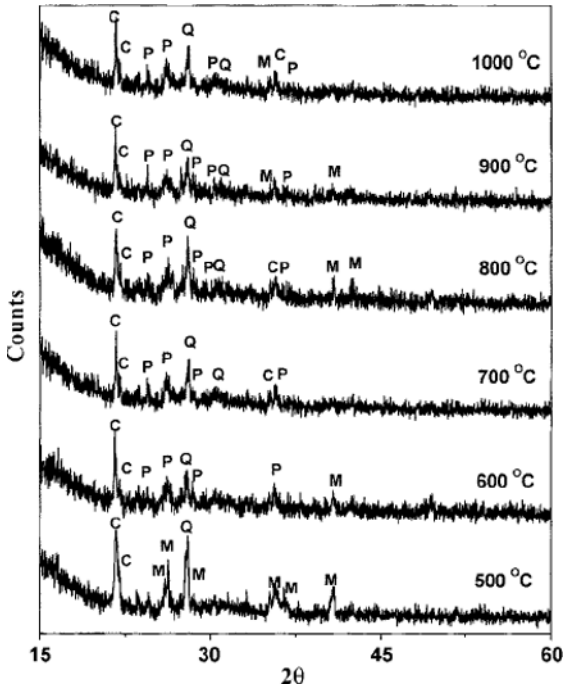


Fig. 6. XRD patterns for the fly ash filters reacted with gaseous cesium under the hydrogen condition at different temperatures.
C: Cristobalite, Q: Quartz, M: Mullite, P: Pollucite

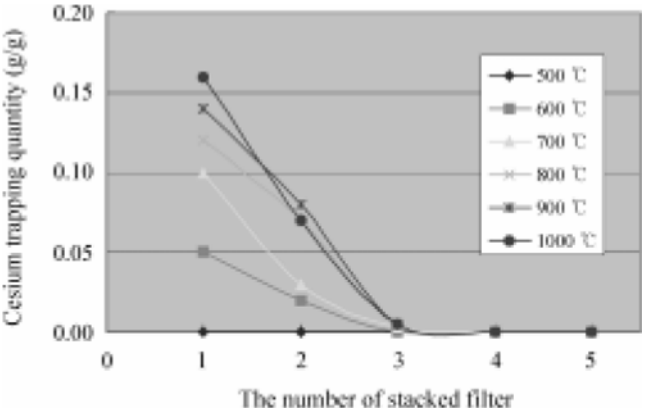


Fig. 7. Effect of trapping temperature on cesium trapping quantity under the air condition.

showed that cesium nepheline ($CsAlSiO_4$) phase began to emerge in addition to pollucite phase when the cesium trapping quantity was greater than 0.31 g-Cs_2O/g-fly ash. Cesium nepheline phase was increased with increasing cesium trapping quantity. Anyway, from the above experiment results, it may be suggested that the fly ash filter can act as a good filter in cesium-trapping quantity of less than 0.31 g-Cs_2O/g-fly ash under the air and hydrogen conditions by trapping and fixing gaseous cesium as a form of thermally stable pollucite phase.

CONCLUSIONS

The results of trapping experiments for gaseous cesium generated from cesium silicate by the fly ash filter are as follows:

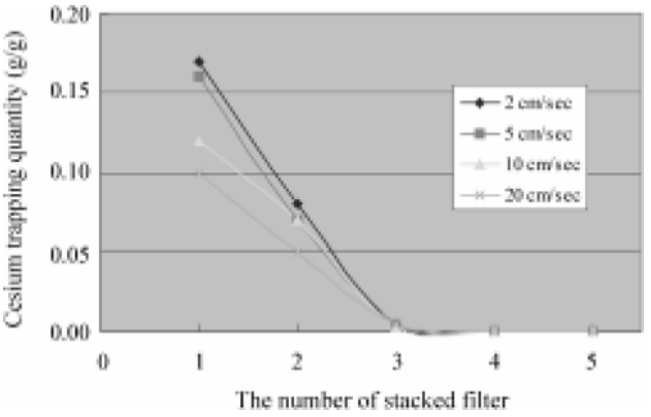


Fig. 8. Effect of gas velocity on cesium trapping quantity under the air condition.

1. When gaseous cesium reacted with the fly ash filter under the air and hydrogen conditions, the colors of the fly ash filter changed from brown to dark brown and from gray to black with increasing temperature, respectively.
2. Pollucite phase was formed by trapping gaseous cesium generated from cesium silicate with the fly ash filter at over 600°C of trapping temperature under both the air and hydrogen atmospheres.
3. The cesium trapping quantity of the fly ash filter was increased with increasing trapping temperature.

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