

High-Temperature Cesium Capture Using Activated Kaolinite in the Presence of Chlorine and Volatile Heavy Metals

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Abstract

This study investigated the use of porous activated kaolin particles in the size range of 300-400 μm as high-temperature sorbents for cesium capture in the presence of chlorine and/or in the presence of cadmium and lead. Packed bed sorption tests by passing CsCl-carrying flue gas through the packed bed of activated porous kaolin particles were first performed at the temperature range of 973-1173 K and a CsCl partial pressure range of 7.4-11.1 Pa. The observed structural change of the sorbent mineral at the stage of sorption revealed the characteristics of an irreversible chemical reaction as a major cesium capturing mechanism. In the fully saturated kaolin sorbent, $\text{Cs}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ is present as a sorption reaction product, together with much smaller amount of water-soluble cesium species. The increase in sorbent bed temperature resulted in an increase in the rate of sorption, but it had no effect on maximum cesium uptake. In the presence of other condensable gas-phase metal chlorides such as cadmium and lead, cesium was preferentially adsorbed onto tested activated kaolinite, but a half of cesium appeared to be physically-sorbed cesium species, CsCl.

1. Introduction

Cesium is one of the important fission products included in the high-level nuclear-fuel processing waste. Cesium volatilizes easily during waste thermal treatment process such as vitrification melter [1-2]. The high-volatility of cesium in the form of Cs_2O and CsOH from both calcine and from glass is notable. On calcination and vitrification cesium volatilities commonly range around 1% through values as high as 13% [3]. A number of radionuclide partitioning study for waste thermal plant show that cesium is the most troublesome radionuclide due to its high volatility [4-6]. Therefore, the emission of volatile radioactive cesium species has been identified as one of the greatest health risks associated with radwaste thermal plants [7].

Volatilized cesium species condense into particulate matters in the downstream of a vitrification melter or a combustion chamber. In most systems, volatilized semi-volatile metals including cesium ultimately end up as submicron particles that are difficult to control. The developing technologies of concern, from the point of view of controlling semi-volatile metals are those that prevent the formation of fine particles from their volatilized species [8].

One promising technology is the high-temperature capture of vapor-phase metals before their condensation into fine particles. A number of literature reports throughout the past decade have indicated that many volatile metals such as arsenic, selenium, cadmium and lead could be reactively scavenged by fly ash and earth elements such as calcium, aluminum and silicon, etc [9-10].

This study investigated the high-temperature capture of cesium species using activated kaolin, with particular emphasis on the interaction between activated kaolin and gaseous reactant CsCl. The structural change of the sorbent material at different stages of sorption was investigated by powdered XRD (X-ray diffraction) and the microscopy of the sorbent samples. Through the evaluation of experimental sorption data, the effect of CsCl vapor diffusion into the sorbent pore was determined. The effect of other condensable metal chlorides on cesium capture is investigated in the second part of this study.

2. Experimental Methods

2.1. Materials and Experimental System

The principle of the experiment is to pass a simulated flue gas, which includes vapor-phase cesium compounds, through a high-temperature bed of activated kaolin particles. The experimental system, as shown in Fig. 1, mainly consists of a flue gas supplying system, a sorption reactor assembly, and a vapor collection train. The flue gas supplying system included a thermo-gravimetric furnace (MAC-500, from LECO Inc.) and a gas mixer. The details of the thermo-gravimetric furnace system, which vaporizes cesium chloride with a continuous monitored vaporization rate, are described in the previous works [10]. The sorbent bed reactor assembly consists of a 1373 K ceramic tube furnace and a stainless steel sorbent bed holder assembly. The ceramic tube furnace is a 2-inch ID custom-fabricated single-zone furnace. The sorbent bed holder with a 1-inch ID and a 1.5-inch length is made of a stainless steel tube and 300-mesh stainless steel screens. The flue gas exhaust tube of the sorbent bed reactor assembly is connected with a metal vapor scrubbing train.

The sorbent used in this study was the natural mineral from Dae-Myoung Mining Co. located in Kyungnam Province in Korea. The mineral composition of raw kaolin, determined by quantitative XRD software (SIROQUANT), was 58.5% kaolin (halloysite and kaolinite), 27.9% alkali feldspar, 13.0% muscovite, 0.6% montmorillonite, and a traceable amount of quartz. This raw kaolin was activated at 1173 K for 2 hours in air. Activated kaolin particles in the 300-400 μm size range, which is the largest size range of activated particles, were selected for the sorbent bed material to reduce the pressure drop across the packed bed. Selected sorbent particles were stored in a heated oven at 423 K until used. The approximate chemical composition of activated kaolin, observed by EPMA (Electron Probe Microanalysis) (JEOL, JXA 8600), was 32.8% Al_2O_3 , 50.9% SiO_2 , 14.8% CaO , and 1.5% Fe_2O_3 . The apparent density and the BET surface area of activated kaolin in the size range of 300-400 μm were 0.82 g/cc and 15.5 m^2/g , respectively. The cesium source, which was volatilized in the thermo-gravimetric furnace, was powdered high-purity CsCl (Aldrich Co., >99.9%).

2.2 Experimental Procedure

In the first part study, the experiments were performed with a CsCl vapor-carrier gas of 20 LPM (liter per minute). The major composition of the simulated flue gas entering the sorption bed, which included CsCl vapor, was 12% O_2 , 5% CO_2 and 1% H_2O by volume, with the remainder consisting of nitrogen. The concentration of CsCl vapor in the simulated flue gas was controlled from the knowledge of the averaged vaporization rate, which was determined

from the weight loss of the sample CsCl in the vaporizing furnace per experimental duration and gas flow rate. The second part study was performed with the flue gas including CdCl₂, PbCl₂ and CsCl. Simulated flue gas was passed through heated packed bed of sorbents. Residual metal vapors in the flue gas passing through the sorbent bed were collected by a glass fiber filter with pore diameter of 0.45 μm and four chilled impingers. The first and the fourth impingers were empty and other two impingers contain an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide. After each experiment, metal-captured sorbed sorbent and glass fiber filter were digested in acid mixtures of HF-HCl-HNO₃(3:1:1). All solutions including impinger solutions were then analyzed using atomic adsorption spectroscopy (AAS). A mass balance closure criterion of ±10% was chosen as a quality assurance objective and those tests not meeting the criterion were repeated.

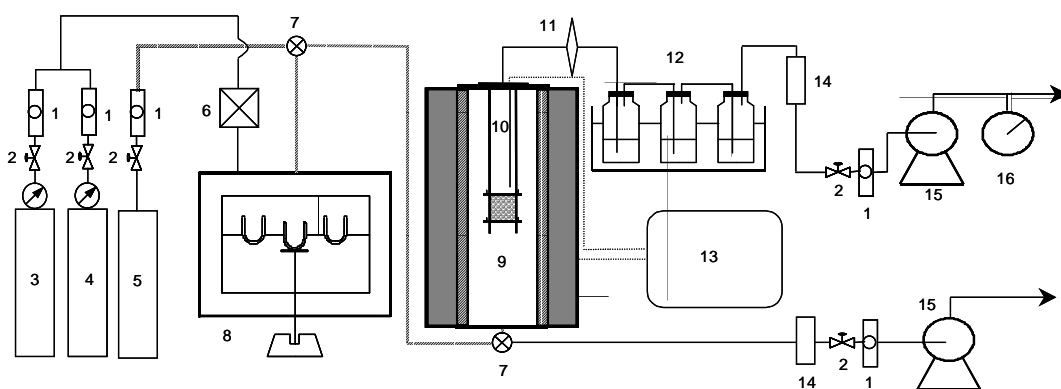


Fig. 1. Schematic diagram of experimental system.

- | | |
|-------------------------------|----------------------------------|
| 1. Flow meter | 9. High temperature sorption bed |
| 2. Needle valve | 10. Thermocouple |
| 3. N ₂ | 11. Filter |
| 4. O ₂ | 12. Impingers |
| 5. Steam generator | 13. Controller |
| 6. Gas mixer | 14. Silicagel bed |
| 7. Valve | 15. Vacuum pump |
| 8. Thermo gravimetric furnace | 16. Dry gasmeter |

3. Results and Discussion

3.1 Sorption Mechanism

The structural and morphological change of the sorbent samples at the stage of cesium sorption was observed by the powdered XRD analysis and the SEM (scanning electron microscopy) analysis of the raw, activated and cesium-sorbed kaolinite sorbents. SEM photographs of the activated kaolinite particles are shown in Figs. 2a-b. It can be seen in Fig. 2a that the activated kaolin includes fine metakaolinite grains in the size range of about 2-3 μm, relatively coarse feldspar and muscovite grains. Fig. 2b illustrates that the activated kaolin particles are an agglomerate of numerous fine metakaolinite grains and thus have a highly porous structure. The results of a BET analysis of activated kaolin agreed with the microscopic observation. The measured BET surface area of activated kaolin was 15.5 m²/g.

No micro pores were found by BET analysis and the averaged pore diameter is 200.5 Å. These results show that the macro pores of activated kaolin were well developed by agglomeration of fine metakaolinite particles but metakaolinite particles themselves have no porous structures. A SEM photograph of the cesium-sorbed kaolin is shown in Fig. 2c. Adsorbed cesium was evenly distributed with the surface and inside the metakaolinite grains in the activated kaolin particles, but no cesium species was distributed on the other minerals included in the activated kaolinite such as feldspar and muscovite.

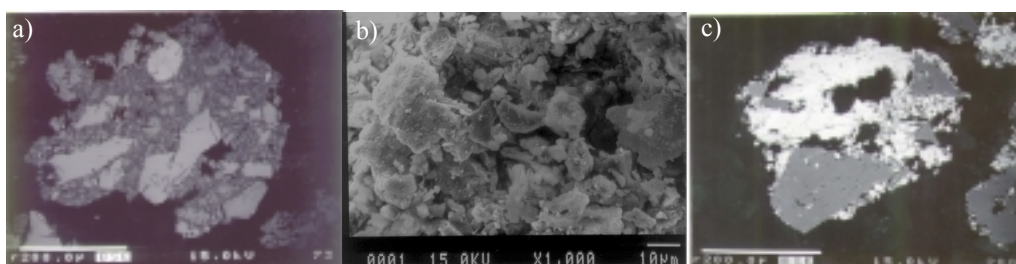
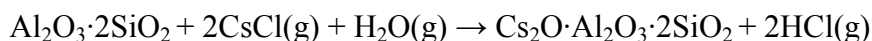


Fig. 2. SEM microphotographs: (a) cross-sectional view of activated kaolin particle, (b) surface view of activated kaolin, and (c) fully saturated cesium-sorbed kaolin particle

Through the powdered XRD analysis, the changes in the mineral composition of the sorbent samples by calcination and by cesium sorption are illustrated in Figs. 3a-c. As shown in Fig. 3a, the raw kaolin supplied from Dae-Myung Mining Co. is composed of several aluminum silicate minerals. Calcination of this raw kaolin causes the dehydration reaction of minerals and a lattice rearrangement, including the conversion of kaolinite group minerals ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$) such as halloysite and kaolinite into metakaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) (10). The XRD patterns of activated kaolin of this study are shown in Fig. 3b. The peaks assigned to halloysite and kaolinite in the natural kaolin disappeared by calcination. Although metakaolinite was not identified in the XRD patterns due to its amorphous characteristics, it must be present as a calcination product of kaolinite group minerals such as halloysite and kaolinite. The presence of metakaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is expected by comparison of XRD patterns of pre- and post-sorption kaolin samples. $\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, which is the product of reaction between metakaolinite and CsCl in the presence of water vapor, is assigned to the XRD patterns of partly converted sorbent (see Fig. 3c). Therefore, the following reaction scheme for cesium capture can be suggested in this study.



$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ in above reaction scheme is metakaolinite, which is dehydration product of kaolinite and halloysite in raw kaolin. The results of the long-time sorption tests at 973 K, 1073 K and 1173 K are shown in Fig. 3. The weight gain data in Fig. 4 are based on the total weight of the sorbent sample after each sorption test and they include the weight of physically sorbed cesium. However, the effect of increasing temperature on capturing rate suggests that high-temperature cesium capture by activated kaolin occurs mainly by an endothermic chemical reaction. An increase in the sorbent bed temperature results in an increase in the cesium-capturing rate. There was, however, no change in the maximum cesium uptake by changing the sorbent bed temperature.

3.2 Influence of Vapor Diffusion

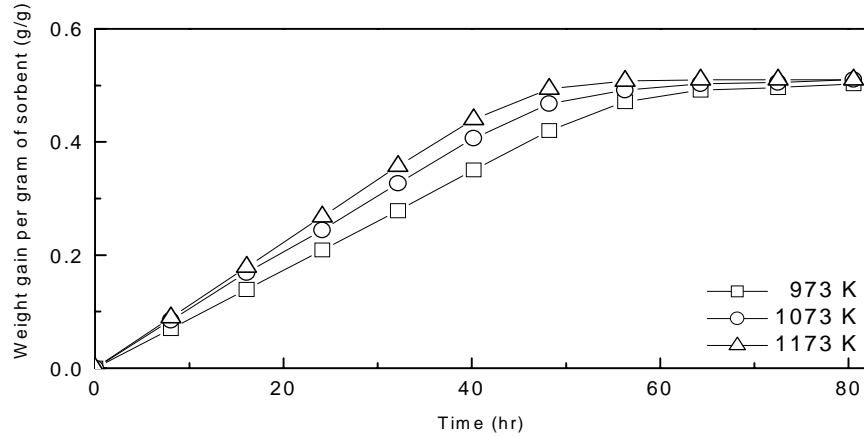


Fig. 3. Cesium sorption in a packed bed of kaolin at 973, 1173 and 1273 K with a constant CsCl-carrying gas passing condition (volumetric flow rate = 20 LPM, CsCl concentration = 74 ppmv).

The decreasing effect of CsCl diffusion on the overall sorption reaction rate was evaluated by determining the effectiveness factor, η , for used activated porous kaolin. The effectiveness factor can be determined from packed bed sorption data on the rate of the sorbent reaction per unit bed volume. The experimental sorption data, which are shown in Fig. 4, provides the molar reaction rate of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ into $\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ as

$$M_R = -\frac{1}{V_R (1 - \varepsilon)} \frac{dn}{dt} \quad (1)$$

where $-(dn/dt)$ is the molar reaction rate of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ in the bed volume, V_R , and ε is the void volume fraction in the bed [12]. The void volume fraction, ε , was roughly estimated as 0.6, regarding that all activated kaolin particles were spherical with a mean diameter of 350 μm . The volume of the sorbent bed used for this study, V_R , was 15.2 cm^3 . Averaged molar reaction rates were calculated by Eq. (1) and the results are plotted in Fig. 4. The molar reaction rate at each sorption temperature did not greatly decrease and remained nearly constant until the conversion reached about 80%.

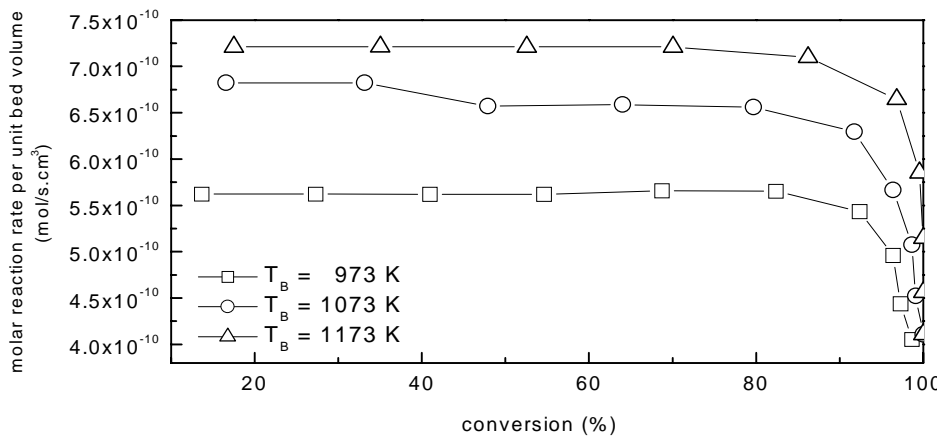


Fig. 4. Molar reaction rate of metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) into cesium aluminum silicate ($\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) in unit bed volume, as a function a conversion.

From the determined molar reaction rate per unit bed volume, M_R , the ratio of the chemical reaction rate to the molecular diffusion rate, Φ , could be quantified as [12]

$$\Phi = \psi^2 \eta = \frac{r_o^2}{D_p C_s} M_R \quad (2)$$

where ψ is the Thiele modulus ($\psi = r_o(S_v k_s C_s^{m-1})^{0.5}$), r_o is the average radius of the spherical sorbent particles in the bed, D_p is the effective diffusion coefficient of CsCl vapor in the porous sorbent and C_s is the CsCl vapor concentration at the sorbent surface. From the published correlation between ψ and η for spherical particles, $\eta = 3\psi^{-1}(\tanh^{-1}\psi - \psi^{-1})$, the effectiveness factor, η , was estimated using above Eq. (2). The applied D_p values in calculating $\psi^2 \eta$ were obtained from the definition $D_p = D\theta\tau^{-1}$, where D is the ordinary diffusion coefficient and θ is the void volume fraction of the spherical particles. The values of D , θ and τ were obtained from the available data books and previously applied data from other investigators' [13-14]. The calculated Φ values for all test conditions were in the range of 0.01 to 0.02. In this range of Φ values ($\Phi \ll 1$), the effectiveness factors are known as essentially unity for various geometries and reaction orders [12]. From the analysis of the long time packed bed sorption data, it is clear that the sorption of cesium vapor by activated porous kaolinite under the present experimental conditions is not influenced by the resistance of pore diffusion. This suggests that the resistance of cesium vapor diffusion into the porous kaolin is not significant in the design of the high-temperature bed for practical application. Little increase of cesium sorption efficiency can be expected by reducing the sorbent particle size, but this has the practical disadvantage of increasing the pressure drop across the packed bed of sorbent particles.

3.3 Influence of Volatile Heavy Metals

Fig. 5 shows metal uptakes from the results of simultaneous sorption tests as a function of sorption time at 1173 K. No additional metal uptakes were found after about 60 hr. Of the three metals, cesium exhibited the largest equilibrium uptake. In addition to capturing the metal, ideal sorbents would retain metal species in the sorbent matrices when they are disposed of. The results of the extraction of metal-sorbed sorbent by the toxicity characteristic leachability procedure (TCLP) are shown in Table 1 (U.S. EPA, 1992). Fractional leachability in Table 1 represents the ratio of water-soluble metal to total captured metal. A half of captured cesium was water-soluble. The results of powdered X-ray diffraction (XRD) showed the presence of water-soluble CsCl, which is physically-sorbed cesium species in the presence of chlorine. Although relatively small quantities of lead and cadmium were captured, most captured cadmium and lead was water insoluble. This suggested that most captured cadmium and lead species were in the form of water insoluble metal-mineral complexes, such as $\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and $\text{PbO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, which are the products of reaction between metal vapors and activated kaolinite (metakaolinite).

4. Conclusions

The high-temperature reaction between cesium vapor and activated kaolinite generated water-insoluble cesium aluminum silicate ($\text{Cs}_2\text{Al}_2\text{Si}_2\text{O}_8$). An increase in kaolin bed temperature results in an increase in cesium capturing rate, but it has no effect on maximum cesium uptake. The resistance of CsCl vapor diffusion into the pores of activated kaolin particles was negligible and the chemical reaction at the kaolin surface controlled the overall sorption reaction rates. In the presence of lead and cadmium chlorides, cesium was more preferentially

adsorbed onto activated kaolinite, but a half of captured cesium appeared to be physically-sorbed cesium compounds, CsCl.

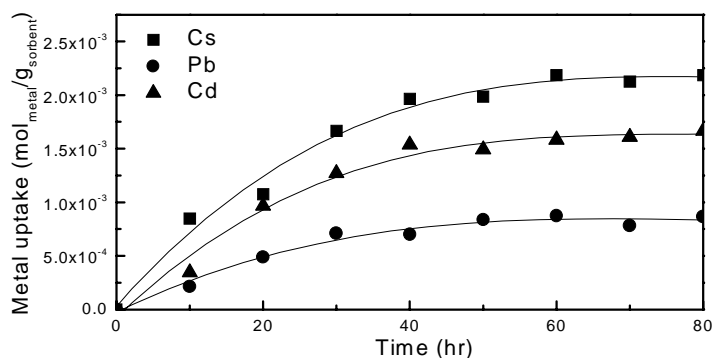


Fig. 5. Metal uptakes as a function of time at 1173 K

Table 1. Result of TCLP extraction test of fully saturated sorbent

Captured metal species	Cd	Pb	Cs
Fractional leachability	0.54%	<0.1%	48.6%

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