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Stable solidification of silica-based ammonium molybdophosphate by allophane: Application to treatment of radioactive cesium in secondary solid wastes generated from fukushima

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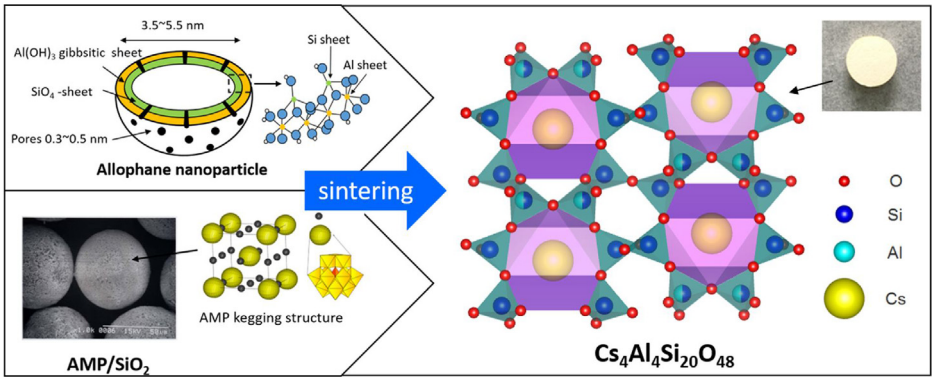
HIGHLIGHTS

- Pressing/sintering method was used to solidify secondary solid wastes.
- The kegging structure of AMP had no effect for formation of stable ceramic solid form.
- Crystal phase of $Cs_4Al_4Si_{20}O_{48}$ was formed and decreased by 300 °C compared with zeolite.
- The ceramic solid form exhibited excellent leaching resistance properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Silica-based ammonium molybdophosphate (AMP/SiO_2) is an absorbent material that can effectively remove Cs from radioactive-contaminated wastewater (RCW) generated by Fukushima nuclide accident. Pressing/sintering method was used for final disposal of secondary waste (spent absorbent) to achieve the volume reduction of $AMP–Cs/SiO_2$ (AMP/SiO_2 saturation adsorption of Cs) and stable solidification of Cs by adding natural allophane. The structure of AMP–Cs completely collapsed at approximately 700 °C, and most Mo and P species in AMP sublimed. The optimal sintering temperature was estimated as 900 °C. The stable crystalline phase of $Cs_4Al_4Si_{20}O_{48}$ was recrystallized by the reaction of Cs_2O, Al_2O_3, and SiO_2, and the immobilization ratio of Cs was approximately 100%. The leachability of Cs from the sintered product in distilled water was approximately 0.41%. The high immobilization and low leachability of Cs were attributed to the excellent solidification properties of the sintered products of $AMP–Cs/SiO_2$–allophane.

1. Introduction

Large amounts of radioactive-contaminated wastewater (RCW) were generated from the nuclear accident of Fukushima NPP-1 caused by the Great East Japan Earthquake. RCW was produced from the contact of cooling water with nuclear fuel and mainly contains the following radionuclides: water-soluble Cs (Cs-134,

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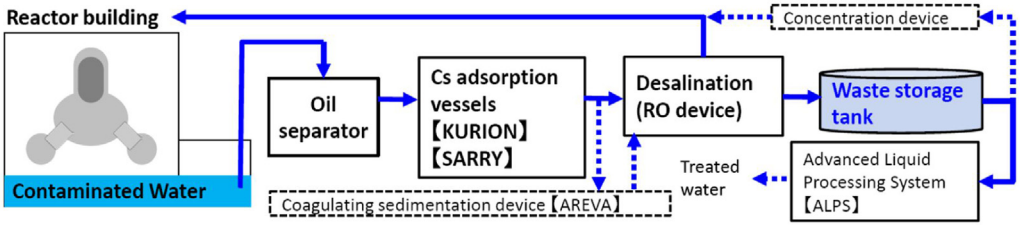

Fig. 1. Circulating injection cooling system in Fukushima NPP-1 [3].

Cs-137), Sr (Sr-90), and I (I-131, I-129). Currently, cold shutdown is facilitated by the circulating injection cooling system (Fig. 1), which consists of oil separator, Cs adsorption vessel, osmosis membrane for desalination, evaporative concentrator, and advanced liquid-processing system (ALPS) [1–3]. However, the process also produces large amounts of secondary solid wastes, such as zeolites, insoluble ferrocyanide sludge, and spent adsorbents (SARRY:178 vessel, KURION:758 vessel, ALPS:2179 vessel, respectively, on November 17, 2016) [3]. ^{137}Cs exhibits high radioactivity and heat generation and possesses half-life of 30 years. In general, mineral adsorbents, including zeolites, present several drawbacks, such as low uptake capacity, slow adsorption kinetics, and significantly decreased adsorption capacity for Cs owing to the competition of Na and K, which are abundant in seawater or ground water. Moreover, insoluble ferrocyanide sludge contains highly radioactive ^{137}Cs and exhibits low thermal stability, which leads to the release of hydrogen cyanide under inert and reducing atmosphere [4,5]. Hence, an effective method for treatment and disposal of Cs must be developed particularly for Japan.

Scholars have investigated the removal of Cs from RCW, such as crown ether hybrid and membrane [6–8], hexacyanoferrate granules [9,10], and zeolite–polymer composite fibers [11] after the Fukushima NPP-1 nuclear accident. Ammonium molybdophosphate (AMP), a kind of heteropolyacid, is composed of Keggin-type polyanions [$(PM_{12}O_{40})^{3-}$] and exchangeable NH_4^+ ions; AMP is a promising adsorbent for removal of Cs because of its high selectivity toward the Cs ion [12–15]. In our previous study, silica-based ammonium molybdophosphate (AMP/SiO_2), with large capacity, fast kinetics, and low column loss, was successfully applied to remove Cs from radioactive wastewater [16,17]. However, these studies are limited to the adsorption process; thus far, strategies for dealing with spent absorbent for final safe disposal of radioactive cesium have been rarely reported.

Treatment of radioactive wastes aims to convert the waste into forms that exhibit excellent physical and chemical stability for handling, transport, and disposal. Radioactive wastes can be treated through various methods, such as glass solidification, cement solidification, ceramic solidification, and rock solidification cementation [18–20]. However, these methods present several limitations, such as easy devitrification, low thermodynamic stability, and high leaching rate [21–23]. Sintering solidification is the optimal method for immobilization of radioactive Cs considering immobility, leachability resistance, volume reduction, and economical aspects [24–26]. In 2012, Japan Atomic Energy Agency (JAEA), Union Showa K.K. and Kurita Water Industries Ltd. performed a joint research on sintering secondary solid wastes from Fukushima NPP-1 cooling system by using zeolites [5].

Allophane, a kind of a nano-sized hydrated aluminosilicate with short-range order and Al/Si ratio of 1–2, is present in soils derived from volcanic ash and weathered pumice [27]. The unit particle of allophane possesses a shape of spherical hollow, outer diameter of 3.5–5.5 nm, and spherule wall with 0.6–1.0 nm thickness; the wall is composed of an outer $Al(OH)_3$ gibbsitic sheet and an inside SiO_4 sheet (Fig. 2). The wall structure of allophane contains many

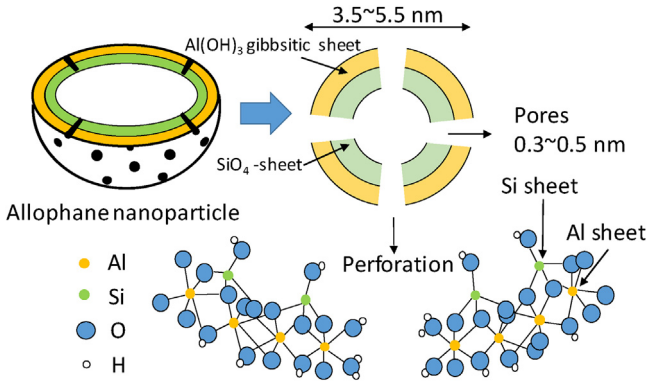

Fig. 2. Schematic representation of allophane structure.

defects arising to approximately 0.3 nm wide perforations. Allophane exhibits high retention capacity for various ions because of its high surface area and surface activity [28]. Moreover, allophane features self-sintering and gas-trapping abilities attributed to its special structure.

In this study, allophane was selected as solidification matrix to achieve volume reduction, enhance the immobilization of Cs, and minimize the volatilization and release of Cs into the environment. AMP/SiO_2-absorbed Cs (AMP-Cs/SiO_2) and allophane were mixed, pulverized, and solidified by high-temperature sintering. Specifically, this study deals with (1) preparation of sintered products, (2) estimation of Cs immobilization ratio, (3) clarification of the solidification mechanism, and (4) determination of the leachability of Cs.

2. Experimental

2.1. Materials

Allophane, with amorphous structure, was purchased from Hattori Company, Ltd. Japan. Allophane exhibits an average particle diameter of approximately 5.9 μm (Fig. 3), and its chemical formula is 1–2 $SiO_2 \cdot Al_2O_3 \cdot 5$–$6\ H_2O$. AMP/$SiO_2$ adsorbent was prepared by successive impregnation of molybdophosphoric acid and ammonium chloride into the macropores of SiO_2 to form ammonium molybdophosphate precipitation [16,17]. AMP/SiO_2 was then placed in 0.2 M $CsNO_3$ solution for 5 h to achieve the adsorption equilibrium and obtain AMP-Cs/SiO_2. The main components of allophane and AMP-Cs/SiO_2-allophane (mass ratio of AMP-Cs/SiO_2: allophane = 1:0.5) were analyzed by X-ray fluorescence (XRF-1800, Shimadzu, Japan) (Table 1).

2.2. Solidification and determination of Cs immobilization ratio

After treatment with $CsNO_3$, AMP-Cs/SiO_2 was sintered up to 1200 °C for 1 h to evaluate the immobility of AMP/SiO_2 toward Cs. Cs content (wt%) was measured by XRF analysis. The immobilization ratio (%) of Cs was determined by differences in Cs content