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A novel hydrothermal method to convert incineration ash into pollucite for the immobilization of a simulant radioactive cesium

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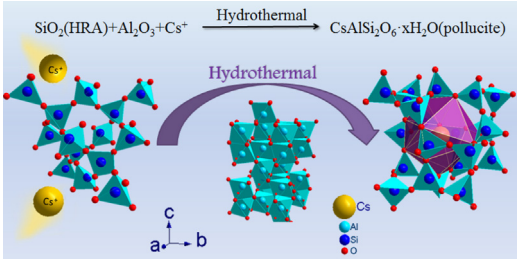
HIGHLIGHTS

- Incineration ash could be converted hydrothermally to pollucite to immobilize Cs.
- Pollucite could be synthesized readily with a wide range of Cs/Si ratios.
- With $Ca(OH)_2$ added, a tough pollucite could be used to solidify Cs-polluted RHA.
- Leaching results showed that the amount of Cs leached from specimen was very low.

GRAPHICAL ABSTRACT



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ABSTRACT

The Fukushima nuclear accident in Japan on March 11, 2011 produced huge amounts of Cs-polluted incineration ashes; conventional solidification methods seem unsuitable for the treatment of large amounts of Cs-polluted ashes. A novel hydrothermal method was developed to directly convert Cs-polluted incineration ash (rice husk ash) into pollucite to immobilize Cs in its crystal structure in situ. Results revealed that pollucite could be synthesized readily over a wide range of added Cs (Cs/Si = 0.2–0.6); the addition of more Cs (Cs/Si ≥ 0.5) caused the formation of a small amount of cesium aluminosilicate ($CsAlSiO_4$), which exhibits poor immobilization behavior for Cs. Pollucite could be formed even for a short curing time (1 h) or at a low curing temperature (150 °C). However, a high curing temperature or a long curing time favored the formation of a pure pollucite. With the added calcium hydroxide, a tough specimen with a flexural strength of approximately 22 MPa could be obtained, which suggested that this technology may be applied directly to the solidification of Cs-polluted incineration ashes. Hydrogarnet and tobermorite formations enhanced the strength of the solidified specimens, and meanwhile the formed pollucite was present in a matrix steadily. Leaching test demonstrated that the amount of Cs that leached from the synthesized specimens was very low (0.49×10^{-5}–2.31×10^{-5}) and even lower than that from the reference hollandite-rich synroc (2.0×10^{-2}), although a higher content of Cs was found in the synthesized pollucite specimens (6.0–31.7%) than in the reference (3.7%). Therefore, the hydrothermal conversion of Cs-polluted incineration ash into pollucite can be applied to immobilize Cs directly.

1. Introduction

Nuclear energy provides incomparable advantages over traditional energy; for instance, nuclear energy not only produces lower greenhouse gas emissions, but also is more powerful, efficient,

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reliable, and cost effective than traditional energy. However, nuclear power plants constantly produce radioactive nuclear wastes, which must be treated. The Fukushima nuclear accident in Japan on March 11, 2011 led to a leakage of large amounts of radioactive Cs, which polluted the surrounding soil, crops [1,2], trees [3,4], and structural timbers. Wood, woody and herbaceous substances, and other annually grown materials have been treated via incineration method to reduce volume; as a consequence, huge amounts of radioactive incineration ashes have been produced.

Radioactive nuclear wastes have been treated by several methods, such as cement solidification, asphalt and plastic solidification for low and medium radioactive wastes, and glass and artificial rock solidification for high radioactive wastes [5–8]. However, these methods may be unsuitable for the treatment of huge amounts of Cs-polluted incineration ashes because the same amount of solidification basis materials (cement, asphalt, plastic, or glass) are required; furthermore, numerous radioactive solidification blocks are also generated.

Artificial rock method can be applied to immobilize crystalline radioactive wastes, and this method is considered optimal for radioactive waste immobilization. Suitable artificial rocks have been developed because these rocks provide advantages for radioactive waste immobilization [9]. For instance, pollucite ($CsAlSi_2O_6$) has been considered as a promising material to immobilize radioactive Cs [10–14] because the channel system of pollucite is composed of six oxygen-containing rings with a diameter of 2.8 Å [15–17]; the diameter of Cs^+ in pollucite is 3.34 Å; once pollucite is formed, Cs^+ ions trapped inside are not released from the pollucite structure without breaking the whole framework [18]; moreover, the channel system can accommodate more than 40 wt% Cs into the structure and thus can produce highly dense wastes [18,19]. Pollucite is synthesized via a sintering method at approximately 1200 °C in air [20–22] now; as a result, radioactive materials evaporate and equipment corrodes easily.

Hydrothermal technology can artificially create a high-temperature and high-pressure liquid environment. This technology can shorten the duration of the digenetic process of sedimentary rocks from millions of years to a laboratory level or a few hours by simulating underground digenetic process. Therefore, hydrothermal technology may be applied to synthesize pollucite hydrothermally.

The elemental compositions of polluted incineration ashes are often used to characterize their properties [23] because of the complexity of mineral compositions. The elemental compositions of the polluted incineration ashes in Fukushima can be divided into two kinds [24]: (1) ashes from herbaceous and other annually grown materials, such as straws, husk, grasses, and leaves, and (2) ashes from wood and woody materials. The elemental composition of incineration ashes from herbaceous and woody materials consists mainly of silicon, calcium, and potassium. Herbaceous ashes usually contain greater amounts of silicon but less amounts of calcium and potassium than woody ashes; by comparison, the latter is composed of greater amounts of calcium but less amounts of silicon and potassium. In this study, incineration rice husk ash (RHA), which belongs to a herbaceous ash, was used as a raw material representing incineration ashes from herbaceous and other annually grown materials to synthesize pollucite in situ. The synthesized pollucite was then applied to immobilize Cs in Cs-polluted herbaceous incineration ashes.

Coal fly ash has also been treated hydrothermally to immobilize Cs, Sr, or other heavy metals. For instance, Cs was immobilized with alkaline activated coal fly ash [25]; Cs, Cd, Pb, and Cr were immobilized by hydrothermally synthetic zeolites from coal fly ash [26]; Zn, Cu, Mn, and Pb were adsorbed with hydrothermally modified coal fly ash [27]; Cs and Sr were immobilized through first the hydrothermal zeolitization of coal fly ash and then the conversion of the resulting zeolites into glass ceramics at 900–1000 °C [28]. Pollucite should be also synthesized hydrothermally with coal fly ashes, and the zeolite rather than pollucite formation in above researches might be due to no or few Cs added (the formed pollucite is too few to detect).

Table 1
Chemical composition of RHA (mass%).

SiO_2	83.60
CaO	1.27
K_2O	3.88
Fe_2O_3	0.37
MgO	0.41
Al_2O_3	0.82
Na_2O	0.08
Ig-loss	9.57

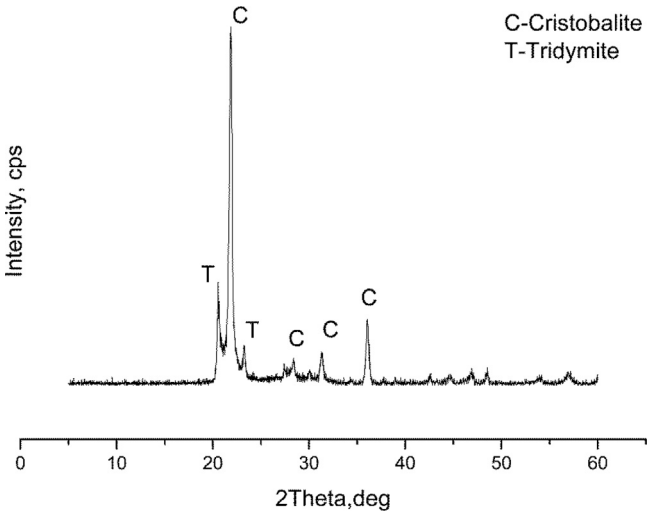

Fig. 1. XRD pattern of RHA.

The hydrothermal conversion of RHA into pollucite to immobilize polluted Cs in situ has been rarely reported yet. Our study aimed (1) to hydrothermally convert incineration ash (RHA) into pollucite at ≤200 °C under saturated vapor pressure to immobilize the polluted Cs in situ; (2) to investigate the effects of the Cs (Cs/Si) and Ca (Ca/Si) contents of starting materials, curing temperature, and curing time on the formation of pollucite and on the strength of the hydrothermally solidified body; and (3) to examine the leaching behavior of Cs dissolved from some of the synthesized pollucite specimens. The work provide a novel method to convert Cs-polluted incineration ashes into pollucite to immobilize Cs into its crystal structure in situ; thus, the generation of huge amounts of solidified materials through traditional methods can be avoided. Our results can also provide practical information on the low-temperature synthesis of pollucite to immobilize Cs in situ with a simple process and at a low cost. The radioactive waste of Cs can also be immobilized with incineration ashes.

2. Experimental

2.1. Materials

The incineration RHA obtained from a factory in Anhui Province (China) was used as a raw material in this study. The chemical composition of this material was determined through X-ray fluorescence spectroscopy (Table 1); the mineral composition of this material was identified through X-ray diffraction (Fig. 1) and Fourier transform infrared (FTIR) spectrometry (Fig. 2).