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Letter to the Editor

Fabrication of rare earth calcium phosphate glass waste forms for the immobilization of rare earth phosphates generated from pyrochemical process

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ABSTRACT

The pyrochemical process for the recycling of used nuclear fuels generates LiCl and LiCl–KCl waste salt during a series of processes. In particular, for the reduction of LiCl–KCl waste volume, radioactive rare earth nuclides in the LiCl–KCl waste salt are separated by a phosphorylation precipitation reaction, generating rare earth phosphate waste in a powder form. In this study, for the immobilization of rare earth phosphate wastes, rare earth calcium phosphate (RCP) glass waste forms have been fabricated using a $CaO–P_2O_5$ glass system under a moderate vitrification temperature of below 1200 °C. Vitrification properties of $NdPO_4$, which is a representative rare earth phosphate material have been investigated through XRD, SEM, EDX, DSC, IR, and density measurements. The RCP glass waste form fabricated from the $4CaO–6P_2O_5$ system showed an immobilization capacity of about 32 wt.% $NdPO_4$ waste loading. Also, chemical durabilities of RCP glass waste forms are investigated by PCT-A test.

1. Introduction

The separation and immobilization of radioactive rare earth nuclides representing one of the most abundant groups of fission products in used nuclear fuels have been intensively studied to achieve a reduction of radioactive waste volume and fabrication of durable waste form in the pyrochemical process currently developing at KAERI (Korea Atomic Energy Research Institute) [1–3]. The pyrochemical process uses LiCl molten salt and LiCl–KCl molten salt as an electrolyte to recover uranium and transuranic (TRU) elements from used nuclear fuels as a fuel of next-generation nuclear reactors such as a sodium-cooled fast reactor (SFR). Therefore, the wastes in the pyrochemical process arise as a chloride salt form, in particular, LiCl–KCl salt waste containing rare earth nuclides is generated after electrorefining and electrowinning processes for the recovery of U and U/TRU metals, respectively.

To minimize LiCl–KCl waste salt during the pyrochemical process, it is beneficial to separate radioactive rare earth nuclides from the salt and reuse the purified salt in the electrorefining and electrowinning processes. At KAERI, a phosphorylation precipitation reaction promoted by $Li_3PO_4–K_3PO_4$ precipitant is being considered as one of the options to separate rare earth nuclides from molten state of LiCl–KCl waste salt [4–6]. The phosphorylation reaction proceeds through the following reaction.

$$RECl_3 + Li(\text{or } K)_3PO_4 \rightarrow REPO_4\downarrow + 3Li(\text{or } K)Cl \ (RE: \text{rare earth nuclides}).$$

Through an optimization of the operation conditions, such as the operation temperature and stirring condition, it was reported that the conversion efficiency of $NdCl_3$ to $NdPO_4$ reached over 99% with very high reaction kinetics [5]. Then, the purified LiCl–KCl eutectic salts are obtained in a powder form by a vacuum distillation process, which uses the temperature gradient between the vaporization chamber and condensation chamber [7–9]. It was revealed that the vacuum distillation is a highly efficient process to separate LiCl–KCl eutectic salt and rare earth phosphates showing a salt recovery ratio of over 99%. Due to the high radioactivity of rare earth nuclides, the residual rare earth phosphates in the vaporization chamber should be immobilized in a proper solidification matrix to make a durable waste form.

RE-rich glass waste forms have been intensively studied to immobilize actinide-rich waste because rare earth nuclides such as Gd have a large neutron cross-section. For example, lanthanide borosilicate (LaBS) glass has been developed to conduct Pu disposition with a high waste loading of rare earth oxides [10–12]. LaBS glasses showing considerably high chemical durability probably originated from the high glass transition temperature due to their high content of rare earth nuclides. However, the relatively high melting temperature of LaBS glass (T_m ~ 1450 °C) could increase the volatility of radioactive nuclides during the fabrication process of the glass waste form. Therefore, it is desirable to lower the melting temperature of the RE-rich glass waste form even with a high content of rare earth nuclides. Most of the RE-rich glass waste forms are fabricated from rare earth oxides as feeding

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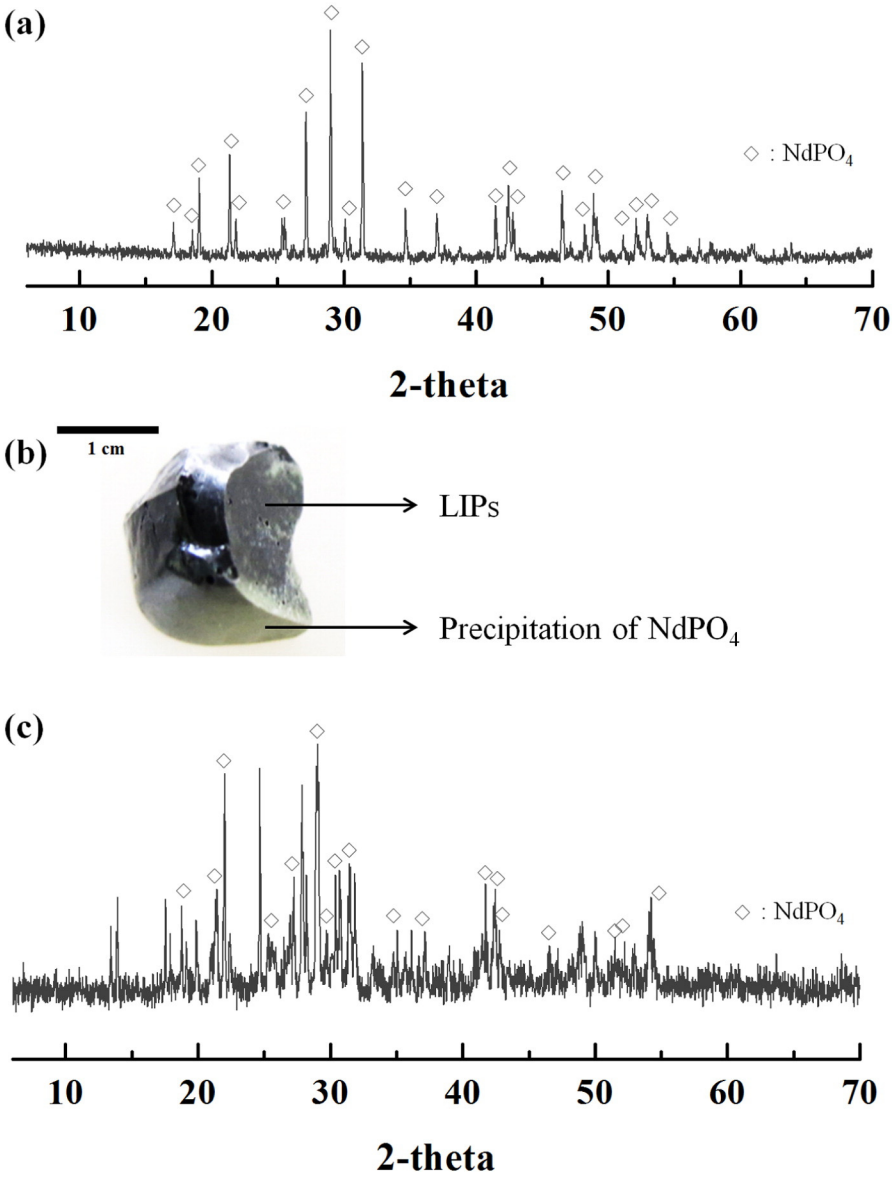

Fig. 1. (a) XRD pattern of $NdPO_4$ synthesized by dry method, (b) glass frit of lead–iron phosphate glass having 30 wt.% $NdPO_4$ waste (black and green regions indicate LIP glass and precipitated $NdPO_4$, respectively), (c) XRD pattern of lead–iron phosphate glass with $NdPO_4$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

materials [13], whereas the immobilization of rare earth phosphates has rarely been studied. The phosphorylation precipitation reaction of the waste salt treatment process in pyrochemical process generates rare earth wastes as a rare earth phosphate form, and thus it is crucial to develop a glass matrix for the immobilization of rare earth phosphates.

The present study reports the fabrication of rare earth calcium phosphate (RCP) glass waste forms to immobilize the rare earth phosphate generated from the waste salt treatment during the pyrochemical process. An RCP glass waste form having 32 wt.% rare earth phosphate waste loading was obtained under a moderate vitrification temperature below 1200 °C. The physical properties of RCP glass waste forms are investigated under varying waste loadings of rare earth phosphates.

2. Experimental

Neodymium phosphate ($NdPO_4$) was prepared by mixing Nd_2O_3 and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) with a 1:2 mole ratio and heating under 500 °C for 2 h and 1000 °C for 1 h. A lead–iron phosphate glass waste form having 30 wt.% waste loading of $NdPO_4$ was fabricated using a $PbO–Fe_2O_3–P_2O_5–NdPO_4$ system with a ratio of 38.89 wt.% PbO, 7.78 wt.% Fe_2O_3, 23.33 wt.% P_2O_5, and 30 wt.% $NdPO_4$. The mixture of $PbO–Fe_2O_3–P_2O_5–NdPO_4$ was melted at 1000 °C and a lead–iron phosphate glass waste form was obtained by quenching on a graphite plate.

Rare earth calcium phosphate (RCP) glass waste forms have been fabricated using a $CaO–P_2O_5–NdPO_4$ system where the dihydrogen phosphate ($NH_4H_2PO_4$) was used as a source of P_2O_5 and $NdPO_4$ was synthesized from Nd_2O_3 as mentioned above. The mixture of CaO, $NH_4H_2PO_4$, and $NdPO_4$ was pre-heated for the decomposition of

Table 1
Formulations of glass matrix and $NdPO_4$ waste.

Elements	RCP-0	RCP-10	RCP-20	RCP-30	RCP-40	RCP-50
CaO	20.85	18.76	16.68	14.59	12.51	10.42
P_2O_5	79.15	71.24	63.32	55.41	47.49	39.58
$NdPO_4$	0.00	10.00	20.00	30.00	40.00	50.00
Total	100.00	100.00	100.00	100.00	100.00	100.00