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Development of iron phosphate ceramic waste form to immobilize radioactive waste solution

Jongkwon Choi [a], Wooyong Um [a,b,*], Sungwook Choung [a]

[a] Division of Advanced Nuclear Engineering, Pohang University of Science and Technology (POSTECH), San 31, Hyoja-Dong, Pohang, South Korea
[b] Pacific Northwest National Laboratory, Richland, WA 99354, United States

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ABSTRACT

The objective of this research was to develop an iron phosphate ceramic (IPC) waste form using converter slag obtained as a by-product of the steel industry as a source of iron instead of conventional iron oxide. Both synthetic off-gas scrubber solution containing technetium-99 (or Re as a surrogate) and LiCl–KCl eutectic salt, a final waste solution from pyrochemical processing of spent nuclear fuel, were used as radioactive waste streams. The IPC waste form was characterized for compressive strength, reduction capacity, chemical durability, and contaminant leachability. Compressive strengths of the IPC waste form prepared with different types of waste solutions were 16 MPa and 19 MPa for LiCl–KCl eutectic salt and the off-gas scrubber simulant, respectively, which meet the minimum compressive strength of 3.45 MPa (500 psi) for waste forms to be accepted into the radioactive waste repository. The reduction capacity of converter slag, a main dry ingredient used to prepare the IPC waste form, was 4136 meq/kg by the Ce(IV) method, which is much higher than those of the conventional Fe oxides used for the IPC waste form and the blast furnace slag materials. Average leachability indexes of Tc, Li, and K for the IPC waste form were higher than 6.0, and the IPC waste form demonstrated stable durability even after 63-day leaching. In addition, the Toxicity Characteristic Leach Procedure measurements of converter slag and the IPC waste form with LiCl–KCl eutectic salt met the universal treatment standard of the leachability limit for metals regulated by the Resource Conservation and Recovery Act. This study confirms the possibility of development of the IPC waste form using converter slag, showing its immobilization capability for radionuclides in both LiCl–KCl eutectic salt and off-gas scrubber solutions with significant cost savings.

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1. Introduction

The nuclear energy industry has accumulated a large amount of high-level radioactive wastes, including plutonium and actinides as well as by-product elements from the nuclear fission process, which causes problems in the environment. The high-level wastes, which were generated during nuclear weapon production, spent fuel recycling, and nuclear power plant operation, should be immobilized using various waste forms. Although various methods to immobilize diverse types of the radioactive wastes have been studied globally, waste form studies for high-level radioactive waste immobilization over the past 40 years have been focused primarily on glass and ceramics [1].

Vitrification using a borosilicate has been viewed as a promising immobilization method based on the high physicochemical durability of the final glass product [2]. However, the vitrification method is not considered ideal for immobilizing the volatile radionuclides, because the vitrification process operates at high temperature (~1150 °C), which can lead to volatilization of some radionuclides such as technetium-99, iodine-129, and cesium-137. Volatile radionuclides should be captured by an off-gas scrubber system and treated separately even during the vitrification process. In particular, ^{99}Tc is very volatile in the metal oxide state due to its low boiling point (310 °C for Tc_2O_7) [3]. Most of the volatilized ^{99}Tc is collected by a filter in the off-gas system and separated by a scrubber solution. Additionally, ^{99}Tc remains on inside surfaces of the off-gas system lines, so an off-gas scrubber solution prepared using highly alkaline NaOH solution is widely used to clean the off-gas lines.

The radioactive ^{99}Tc as a man-made fission product is major concern for the environment because of its long half-life (2.11×10^5 years) and higher mobility as an oxidized species (TcO_4^-) than a reduced species, ^{99}Tc(IV) [3,4]. As an oxidized species, ^{99}Tc(VII) can flow in groundwater without any retardation from sorption onto mineral surfaces [5–7]. The high mobility of oxidized ^{99}Tc species makes it necessary to develop a low-temperature waste

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* Corresponding author at: Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop P7-54, Richland, WA 99354, United States. Tel.: +1 (509) 372 6227.
E-mail address: wooyong.um@pnnl.gov (W. Um).

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form that can retain reduction capacity to reduce ^{99}Tc(VII) to ^{99}Tc(IV) and has high chemical durability for long-term immobilization of ^{99}Tc in the repository.

In addition, the pyrochemical process as a spent nuclear fuel reprocessing technique still generates some radioactive wastes, one of which is an electrolyte material that includes a LiCl molten salt and LiCl–KCl eutectic salt [8]. Although the electrolytes are collected for reuse, partial LiCl–KCl eutectic salt waste needs to be disposed of in a solid waste form because it includes high-level radioactive waste [9,10]. To immobilize the radioactive wastes generated by the pyrochemical process, the Research Institute of Atomic reactors in Russia developed a way to solidify and sinter molten salt in a glass form by precipitating fission products in molten salt waste with Na_3PO_4 as a phosphate source, and then adding sintering glass powder [5]. Additionally, the Korea Atomic Energy Research Institute is currently working on the solidification of the wastes with $x\mathrm{SiO_2}$–$y\mathrm{Al_2O_3}$–$z\mathrm{P_2O_5}$ in the temperature range 600–800 °C [11,12]. Despite these various approaches to waste form development, a convincing method has not reached the commercialization stage yet, and more follow-up research is required because this LiCl–KCl eutectic salt waste has a highly volatile radionuclide and low compatibility with borosilicate glass material [11].

Chemically bonded phosphate ceramic (CBPC) is one of the methods to immobilize radionuclides in solid form under low-temperature process conditions using crystal phases similar to natural phosphate minerals, which have low solubility [13–17]. In addition, the CBPC is used to make solid waste forms by reacting with various metal cations and a phosphate anion at room temperature [18]. Iron phosphate ceramic (IPC) is a typical waste form made with the CBPC method using iron oxides such as FeO, Fe_2O_3, or Fe_3O_4 as a metal cation source. Iron oxide sites can be used to sequester ^{99}Tc after it has been reduced from ^{99}Tc(VII) to ^{99}Tc(IV) in a reducing environment [19,20]. The advantage of the IPC waste form is its ability to immobilize ^{99}Tc for the long term under more reductive conditions than others if ferrous iron (Fe^{2+}) oxide is used.

The goal of this research project was to develop an economical and durable IPC waste form to immobilize ^{99}Tc as a representative of volatile radionuclide. For this, converter slag, which is a waste material from the steel industry that includes high ferrous iron, was used as a source of iron oxide instead of conventional iron oxide materials to make the IPC waste form. Converter slag can be obtained much more easily and cheaply than conventional iron oxides, because the largest percentage of steel production wastes and by-products consists of steel slag. For example, ~17 million tons/year of steel slags have been generated in South Korea, approximately 80% of them by Pohang Iron and Steel Company. Another specific objective of this research was to evaluate the immobilization capability and physicochemical characteristics of the developed IPC waste form for LiCl–KCl eutectic salt and the off-gas scrubber simulant wastes containing ^{99}Tc (or Re as a stable surrogate).

2. Materials and methods

2.1. Production of converter slag

The main materials (molten pig iron, scrap) and auxiliary material (limestone) are added to a steel converter along with high pressure oxygen to oxidize carbon, silicon, phosphorus, and steel in the material. Oxides generated in this process react with calcium oxide and form converter slag, and the converter slag is separated from the steel using differences in their weights. Converter slag is heavier than natural stone, because part of the steel is oxidized during the steel-making process and becomes slag. The main crystalline components of converter slag are C_2S (dicalcium silicate, Ca_2SiO_4), C_3S (tricalcium silicate, Ca_3SiO_5), wüstite [(Fe, Mg, Ca, Mn)O], C_2F (dicalcium ferrite, $Ca_2Fe_2O_5$), and lime [(Ca, Mg, Mn, Fe)O]. The remaining calcium oxide, CaO, that failed to react with the newly formed oxides is called free CaO. The free CaO in the converter slag reacts with H_2O and becomes $Ca(OH)_2(s)$ with an approximate doubling of its volume [21]. In other words, if converter slag, still containing the free CaO, is used as aggregate, the free CaO reacts with oxygen in the air and expands the converter slag, which damages the life expectancy of the construction. However, if converter slag is used as a dry ingredient material of IPC formation, CaO reacts with phosphoric acid instead of oxygen, and all the reaction products are used in the generation of phosphate salt. Thus, it would not cause any of the aforementioned issues. Converter slag includes total iron of approximately 20–30 wt.%; more details on converter slag composition are given in Table 1.

2.2. Preparation of waste simulants

Two types of waste solutions were prepared and used in this study. The first waste solution is LiCl–KCl eutectic salt, which is a final waste solution from the pyrochemical process that separates the uranium and transuranic elements from spent nuclear fuel for recycling [22]. The LiCl–KCl eutectic salt simulant was made of 99% pure potassium chloride and lithium chloride reagents (from Sigma–Aldrich) in a composition that is the eutectic point for LiCl–KCl salt. Fig. 1 shows the phase diagram of mole concentrations of LiCl and KCl for the formation of the LiCl–KCl eutectic salt waste solution [23]. The mole concentration ratio of LiCl:KCl at the eutectic point is 0.592:0.408 (approximately 1.45:1) and the weight ratio is 45:55 wt.%. The LiCl–KCl eutectic salt was dissolved in water purified by a Milli-Q system (Merck Millipore, Massachusetts), and three different compositions (i.e., LiCl:KCl = 1.45:1, 2.9:2, and 4.3:3) were prepared for use in the IPC waste form development. The LiCl–KCl eutectic salt is completely dissolved at 1 or 2 mol of KCl, but not at 3 mol of KCl. Because the LiCl–KCl salt reached its maximum solubility in deionized (DI) water between compositions of 2.9:2 and 4.3:3, the compositions of 1.45:1 and 2.9:2 were used to prepare the LiCl:KCl eutectic salt waste solution in this study.

The second waste solution was the off-gas scrubber simulant containing ^{99}Tc or Re as a surrogate for ^{99}Tc. The simulant was prepared with 4 N NaOH solution containing ^{99}Tc or Re. The off-gas scrubber simulant was prepared at 50 ppm concentration of ^{99}Tc or Re.

2.3. Compositions for the IPC waste form development

In previous research on IPC waste form development, most IPC was made using either hematite (Fe_2O_3) or magnetite (Fe_3O_4) [17]. In contrast with conventional single iron oxide material, the converter slag used in this study contains magnetite as well as diverse elements including Ca, Al, Si, Mn, Cr, Mg, Na, K, and P as shown in Table 1. Waste forms using the converter slag contain a large amount of Ca and additional elements that do not exist in the

Table 1
Composition of converter slag by X-ray fluorescence analysis.

Element	wt.%	Element	wt.%
CaO	46.72	Al_2O_3	2.28
FeO	17.03	MnO	0.744
Fe_2O_3	11.84	TiO_2	0.257
MgO	10.13	Na_2O	0.222
SiO_2	8.39	Cr_2O_3	0.093
P_2O_5	2.35	K_2O	0.016