



Vitrification processes of simulated cesium sorbing zeolite waste

Ryou Kimura*, Yaohiro Inagaki, Kazuya Idemitsu, Tatsumi Arima

Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Fukuoka, Japan, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

ARTICLE INFO

Keywords:
Waste treatment
Zeolite waste
Vitrification
Cesium

ABSTRACT

A large amount of high-activity-level water (HALW) contaminated with mainly radioactive cesium has been generated at Fukushima Dai-ichi Nuclear Power Plant (NPP), and a decontamination system for the HALW has been operated. For decontamination of the HALW, modified chabazite-type zeolite has been used as a sorbent, and the amount of the cesium bearing zeolite waste is still increasing. One of conditioning options for the zeolite waste is vitrification into borosilicate glass waste form, which is considered to be a promising option for the back-end of nuclear fuel cycle. For the purpose of the optimum treatment and disposal, the effects of the vitrification conditions on the total performance are required to be evaluated quantitatively. In this study, vitrification tests of simulated zeolite waste, which is the same type of zeolite used in the decontamination system at Fukushima Dai-ichi NPP and is sorbing non-radioactive cesium, were examined to evaluate the homogeneity of glass products and the volume reduction ratio (glass specific volume to zeolite specific volume) with respect to the temperature of melting process. Furthermore, the volatilization loss of cesium was evaluated as a function of the additive loading, processing temperature and processing time. The results showed that the glass products are in a completely amorphous state and their volume reduction ratios were around 0.4 at any vitrification condition above 1100 °C. In addition, a certain amount of the volatilization loss occurred under the conditions of high additive loading and high temperature.

1. Introduction

Zeolites are one of the important inorganic cation exchangers and effectively used for selective removal of radionuclides in nuclear energy field. Their structures of aluminosilicate framework are durable in contacting with waste water and their ion selectivity is effective even in the solution containing other competing ions (Pansini, 1996; Colella, 1996).

After the accident in Fukushima Dai-ichi NPP, a large amount of high-activity-level water (HALW) accumulated in the reactor, the turbine building and the trench in the facility has been treated using a circulating cooling system with a decontamination system, which have been operated for decontamination of radioactive cesium (134, 135, 137 Cs) in the waste water (Mimura et al., 2011). In this system, modified chabazite-type zeolite has been used as an adsorbent, and the zeolite waste resulting has been generated and accumulated. The amount of the waste generated so far has reached 632 vessels (on Oct 21, 2014) (Tokyo Electric Power Comp), which are temporarily restored in Fukushima site, consequently, the treatment and final disposal of the zeolite waste is problem to solve.

One of the options for the zeolite waste treatment for final disposal is vitrification into borosilicate glass waste form. From the viewpoint of

the back-end of nuclear fuel cycle, the vitrification is a promising method for solidification of high-level radioactive waste (HLW) accepted by most countries and the performance for final geological disposal has been investigated for several tens of years (Inagaki et al., 2004). This option also enables a reduction of the waste volume and immobilization of the radioactive cesium over geological timescales, thus it is expected to be one of the most suitable solutions for zeolite waste treatment and disposal.

For the goal of final disposal of the zeolite waste, the total performance of the glass waste form has to be assessed. It consists of both of the product performance and processing factors, e.g., chemical durability during storage and disposal, waste loading, complexity-reliability of vitrification process, and so on, which are closely related to the vitrification conditions. For instance, a large amount of glass forming additives such as Na₂O and B₂O₃ provides lower processing temperatures of zeolite melting, however, it may also cause a decrease in chemical durability of the glass waste form. In addition, the volatilization loss of cesium is a significant issue for the vitrification of zeolite waste (Bryan et al., 1987; Mimura and Kanno, 1978).

In the present study, aimed at contributing to further development of zeolite waste vitrification, the simulated zeolite wastes prepared by sorbing non-radioactive cesium were examined to be vitrified into a

* Corresponding author.

E-mail address: kimura@nucl.kyushu-u.ac.jp (R. Kimura).

<https://doi.org/10.1016/j.pnucene.2018.01.001>

Received 3 February 2015; Received in revised form 20 April 2016; Accepted 2 January 2018
0149-1970/ © 2018 Published by Elsevier Ltd.

Table 1
Conditions for preparation of simulated zeolite waste.

Simulated zeolite waste	CSZ-1	CSZ-2
Zeolite type	Modified chabazite	Modified chabazite
Initial CsCl concentration (M)	1.7×10^{-4}	2.3×10^{-3}
Zeolite/Liquid ratio (g ml ⁻¹)	0.03	0.03
Temperature (°C)	25	25
Immersion period (hour)	72	72
Amount of adsorbed Cs (wt%)	0.076	1.0

Table 2
Matrix of vitrification conditions in Cs volatilization test.

Additive loading ratio (–) (Na ₂ B ₄ O ₇)/(CSZ-2 + Na ₂ B ₄ O ₇)	Temperature (°C)			
	1050	1100	1150	1200
0.20	3h	3h, P	3h	3h
0.30	–	2h, 3h, 4h, 5h, P	–	–
0.35	–	3h	–	–
0.40	–	2h, 3h, 4h, 5h, P	–	–
0.45	3h	3h	3h	–

2h - 5h are the processing time for zeolite melting. The test using fine powdered specimen was described as P.

Table 3
Nominal composition of glass products (wt%).

Additive loading ratio (–)	Na ₂ O	Cs ₂ O	B ₂ O ₃	Al ₂ O ₃	SiO ₂
0.20 ^a	17.3	0.07	14.6	20.3	47.8
0.20	18.1	0.97	13.8	20.0	47.1
0.30	19.7	0.85	20.8	17.5	41.2
0.35	20.5	0.79	24.2	16.2	38.3
0.40	21.3	0.73	27.7	15.0	35.3
0.45	22.1	0.67	31.1	13.7	32.4

^a H₃BO₃ and Na₂CO₃ were added as additive.

borosilicate glass waste form under various conditions. The amorphous character of the glass waste form was confirmed and its volume reduction ratio was evaluated with respect to melting temperature. Furthermore, the volatilization loss of cesium was evaluated as a function of the additive loading ratio, melting temperature, and processing time.

2. Experimental

2.1. Preparation of simulated zeolite waste

Modified chabazite (20–50 mesh), which is the same type of zeolite used in the decontamination system at Fukushima Dai-ichi NPP, was used as a specimen in this study. The ideal chemical formulation is Na₂(AlO₂)₂(SiO₂)₄·3H₂O. The specimen was immersed in CsCl aqueous solution for 72 h at room temperature to reach the apparent sorption equilibrium. The adsorbed amount of cesium was determined from the decrease in cesium concentration in the solution which was measured by using ICP-MS (Agilent Technologies, Agilent 7500c). The details of immersion conditions and the amount of adsorbed cesium are shown in Table 1. The simulated zeolite waste named CSZ-1 had a cesium content of 0.076 wt%, which is similar to that of the waste generated in the actual system at Fukushima Dai-ichi NPP, and was used for vitrification tests described in the following section. The simulated zeolite waste named CSZ-2, whose cesium content was 1.0 wt%, was prepared for using in cesium volatilization tests because the content of cesium in CSZ-1 is too small to evaluated the volatilization loss of cesium quantitatively. CSZ-2 was also obtained by the immersion method under the condition shown in Table 1.

2.2. Vitrification tests

The simulated zeolite waste CSZ-1 was placed into an alumina crucible with additives of H₃BO₃ (powder, purity of 99.8%, Kanto Chemical Co. Inc.) and Na₂CO₃ (powder, purity of 99.8%, Kanto Chemical Co. Inc.), and melted for 3 h at temperatures ranging from 1100 °C to 1300 °C. The additive loading ratio which was defined as a weight ratio of (H₃BO₃ + Na₂CO₃ as oxide)/(CSZ-1 + H₃BO₃ + Na₂CO₃ as oxide) was set at 0.20. The final glass product contains 14.6 wt% B₂O₃, 17.3 wt% Na₂O, and 68.1 wt% of other oxides originally from the zeolite. The photographs of the glass products were taken by digital camera, and the amorphous character of the glass products was confirmed by powder XRD analysis (Rigaku, Multi-Flex). Powders were prepared by crushing with zirconia mortar to obtain the grain size under 50 μm.

Furthermore, for efficient zeolite melting, the simulated zeolite waste CSZ-2 was crushed into fine powder and mixed with Na₂B₄O₇ (powder, purity of 99.0%, Kanto Chemical Co. Inc.) in zirconia mortar for about 15 min. The additive loading ratio, defined as (Na₂B₄O₇)/(CSZ-2 + Na₂B₄O₇) was 0.20. The fine powdered mixture was melted at 1100 °C for 3 h, and the amorphous character of the glass product was also confirmed by powder XRD analysis.

In addition, the volume reduction ratio, defined as a volume ratio of glass products to original bulky zeolite, was evaluated. Density measurements were made using Archimedes method (SHIMADZU, AUW220D), with ethyl alcohol being used as the displacement fluid. The specimens were prepared by breaking the glass products into several pieces. The volume reduction ratio was derived from the Eq. (1):

$$\frac{v_{\text{glass}}}{v_{\text{zeolite}}} = \frac{1/d_{\text{glass}}}{1/d_{\text{zeolite}}} \quad (1)$$

where v_{glass} and v_{zeolite} is the specific volume, the inverse of the apparent density (d_{glass} and d_{zeolite}) of the glass product and zeolite respectively.

2.3. Cesium volatilization tests

For the evaluation of volatilization loss of cesium during vitrification, the simulated zeolite waste CSZ-2 was melted with Na₂B₄O₇ for 2 to 5 h at the temperatures ranging from 1050 °C to 1200 °C with various additive loading ratio of (Na₂B₄O₇)/(CSZ-2 + Na₂B₄O₇) from 0.20 to 0.45 (summarized in Table 2). The nominal compositions of the glass products are shown in Table 3. For the calculation of nominal composition of the glass, it is assumed that all the components participate in forming borosilicate glass with no volatilization loss or crystallization. The values of SiO₂, Al₂O₃, and Cs₂O are estimated from loading zeolite, B₂O₃ is estimated from loading additive, and Na₂O is estimated from both loading zeolite and additive.

In order to evaluate the volatilization loss of cesium, it was required to measure the cesium content of the glass product quantitatively. In this study, following two methods were applied to the measurement of cesium content of glass product; one was acid digestion method, another was the direct measurement by using X-ray fluorescence (XRF method). A critical analytical result can be obtained by acid digestion, although it takes much more time for sample decomposition. On the other hand, rapid measurement with easy preparation for sample can be provided by the direct measurement by using XRF. The accuracy of XRF method, however, depends on the standard samples used for elemental calibration: the standard samples whose character and compositions are similar to the glass products are preferable for precise measurement.

In this study, therefore, both the acid digestion method and the XRF method were applied to a certain glass product, and an adjustment coefficient, which was the ratio of analytical results obtained by the acid digestion method to that obtained by the XRF method, was determined. Assuming that the adjustment coefficient was constant for any sample, the volatilization loss was determined from the results by

Download English Version:

<https://daneshyari.com/en/article/8084176>

Download Persian Version:

<https://daneshyari.com/article/8084176>

[Daneshyari.com](https://daneshyari.com)