

Immobilisation of caesium by zeolites and characterisation of ceramic solid forms

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Abstract

The selective separation and immobilisation of a heat-generating nuclide, ^{137}Cs , contained in high-level liquid waste (HLLW) is an important subject for the advancement of the nuclear fuel cycle. The selective separation and immobilisation of Cs have been studied by using various kinds of zeolite in Tohoku University and JAEA. As a promising method, the immobilisation of Cs in the stable ceramic solid forms of $\text{CsAlSi}_5\text{O}_{12}$ was accomplished by the calcination of the Cs-form of mordenites [2]. In this study, the effective parameters such as calcining temperature and time, density, components in mordenites, pressing conditions for cold and hot pressing, on the immobilisation of Cs in ceramic products are evaluated by using X-ray diffractometry (XRD), density balance (Archimedes' method), scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and the promising immobilisation conditions are discussed.

- Immobilisation of Cs by calcination of mordenites

Mordenites are well known as having high selectivity to Cs^+ ions, and are readily converted to a stable caesium aluminium silicate ($\text{CsAlSi}_5\text{O}_{12}$) by heat treatment at temperatures exceeding 1 200°C. In this study, three kinds of mordenite [synthetic mordenite-A (SM-A), synthetic mordenite-B (SM-B) and synthetic mordenite-C (SM-C)], were used, and their chemical components were determined by wet elemental analysis using HF. The recrystallisation of $\text{CsAlSi}_5\text{O}_{12}$ depended on the kinds of mordenite; only SM-C with binder containing Ti and Fe (TiO_2 : 0.26±0.07 wt.%, Fe_2O_3 : 0.38 wt.%) was recrystallised to $\text{CsAlSi}_5\text{O}_{12}$, while other binderless mordenites were converted to an amorphous phase and no recrystallisation was observed.

- Characterisation of calcined products immobilising Cs

The Cs-form mordenite was pelletised at 500 kg/cm² into a disk (10 mm ϕ) by cold isostatic pressing (CIP), whereupon the calcining conditions for the disk were varied; calcining temperatures of 900 to 1 200°C, and calcining times of 5 min to 3 h. In either case, the ceramic products immobilising Cs^+ ions were obtained and uniformly dispersed in the solid form. The density of the solid forms increased with calcining temperature; in the case of SM-A, the density of the products calcined at 1 200°C was 2.48 g/cm³ and 2.5 times larger than that of the original SM-A ($d = 1.05 \text{ g/cm}^3$). The density of the products tended to increase steeply with calcining time within 30 min at 1 200°C. As for hot-pressing (50, 300 and 500 kg/cm², 1 300°C), solidified products with no cracks were obtained only in the case of SM-C pressed at 50 kg/cm².

The stable ceramic solid forms ($\text{CsAlSi}_5\text{O}_{12}$) immobilising ^{137}Cs have considerable potential for the development of radiation source and heat source.

Introduction

Special attention has been given to the separation and recovery of radioactive nuclide from high-level liquid wastes (HLLW). The selective separation of a heat-generating nuclide contained in HLLW is very important subject for the advancement of the nuclear fuel cycle [1-3]. Large amounts of Cs (3-4 kg/MTU, 45 GWd/t, 5 years of cooling time) exist in HLLW [4]. Large part of Cs in HLLW is a heat-generating nuclide of ^{137}Cs and ^{137}Cs has high decay heat and radioactivity. If ^{137}Cs nuclides in HLLW can be separated and immobilised in the stable solid forms, it can be expected that they are utilised for the resources such as heat source and radiation source. For the selective uptake of Cs, many ion-exchangers have been developed; insoluble ferrocyanides (NiFC), heteropolyacids (AMP, AWP) and zeolite (mordenite) are well known to have high ion-exchange property for Cs^+ [5-6]. The selective separation and immobilisation of Cs have been studied in Tohoku University and JAEA by using various kinds of zeolite [7-9]. Mordenite is an aluminosilicate having tunnel-structure, high stability on irradiation and high selective ion-exchange property for Cs^+ . Mordenite adsorbing Cs^+ can be readily converted to a stable caesium aluminium silicate ($\text{CsAlSi}_5\text{O}_{12}$) by calcinations.

The present paper deals with the preparation of ceramic products immobilising Cs by using three kinds of powdered synthetic mordenites (SM) with different particle sizes, surface morphology, recrystallised phase, density, wet elemental analysis of CsSM (Cs form of SM) and phase transformation by the addition of zeolite A.

Experimental

Materials

Three kinds of powdered mordenites (synthetic mordenite-A (SM-A), synthetic mordenite-B (SM-B) and synthetic mordenite-C (SM-C)) are listed in Table 1. The maximum uptake capacity of Cs^+ was determined by batch method. SM-A, SM-B and SM-C were purchased from Wako Pure Chemical Ind., Kurita Water Ind. and Norton, respectively. Additive of zeolite A was purchased from Wako Pure Chemical Ind.

Table 1: Particle size and maximum uptake capacity of synthetic mordenites

Synthetic mordenite		Particle size [μm]	Maximum uptake capacity of Cs^+ [mmol/g]
SM-A	Without binder	10	1.00
SM-B	Without binder	15	1.24
SM-C	With binder	100	0.96

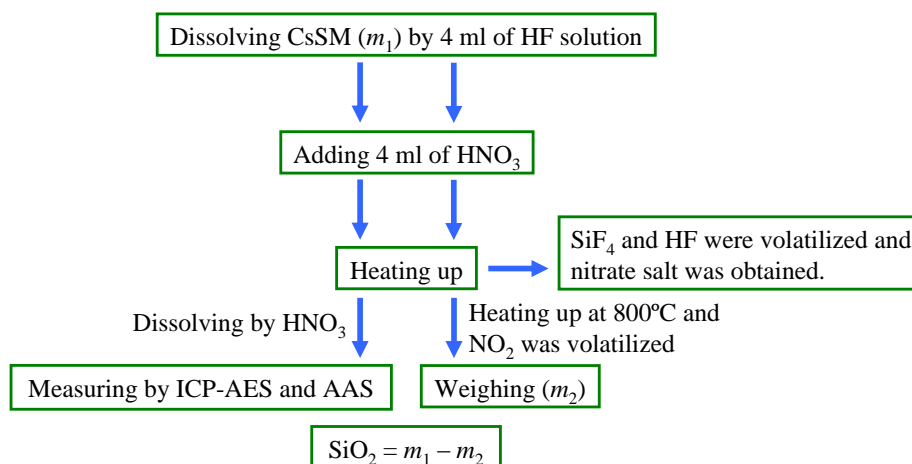
Preparation of solid products and characterisation

CsSMs were prepared by contacting with a 0.5 M CsCl solution. After 24-h shaking, the supernatant was removed and replaced by a fresh solution. The synthetic mordenites saturated with Cs^+ were separated by filtration, washed with water and then dried at 50°C for 24 h in an electric oven. The CsSMs were weighed by 300 mg and pelletised at 500 kg/cm² into a disk (10 mm ϕ) by cold isostatic pressing (CIP), whereupon the calcining conditions for the disk were varied; calcining temperature of 900 to 1 200°C, and calcining times of 5 min to 3 h. In either case, the ceramic products immobilising Cs were obtained. The characterisation of ceramic products was evaluated by using X-ray diffractometry (XRD, Rigaku MiniFlex-BMS), density balance (Archimedes' method), scanning electron microscopy (SEM, Hitachi S-4100L) and electron probe microanalysis (EPMA, JEOL, JXA-8200WD/ED).

Wet elemental analysis of CsSMs

Figure 1 shows a procedure for wet elemental analysis using HF solution. CsSM weighed by 200 mg (m_1) was prepared in Pt crucible and dissolved by a HF solution. The dissolved liquid was then added into a HNO_3 solution. After heating up the solution, SiF_4 and HF were volatilised and nitrate salt was obtained. The nitrate salt was dissolved by HNO_3 solution, and another was calcined at 800°C for 1 h. The concentrations of metal ions in the dissolved solution were measured by ICP-AES (SII, SPS 1200AR) and AAS (PERKIN ELMER, AAnalyst 300). The calcined salt was weighed (m_2) and the content of SiO_2 was determined by subtracting m_2 from m_1 .

Figure 1: Procedure for wet elemental analysis using HF



Phase transformation

The mixtures of CsSM (CsSM-A and CsSM-B) and zeolite A (Na-form of synthetic zeolite) were pelletised at 500 kg/cm^2 by CIP and calcined at $1\,200^\circ\text{C}$ for 1 h. Recrystallised phases in the calcined products were identified by XRD [10].

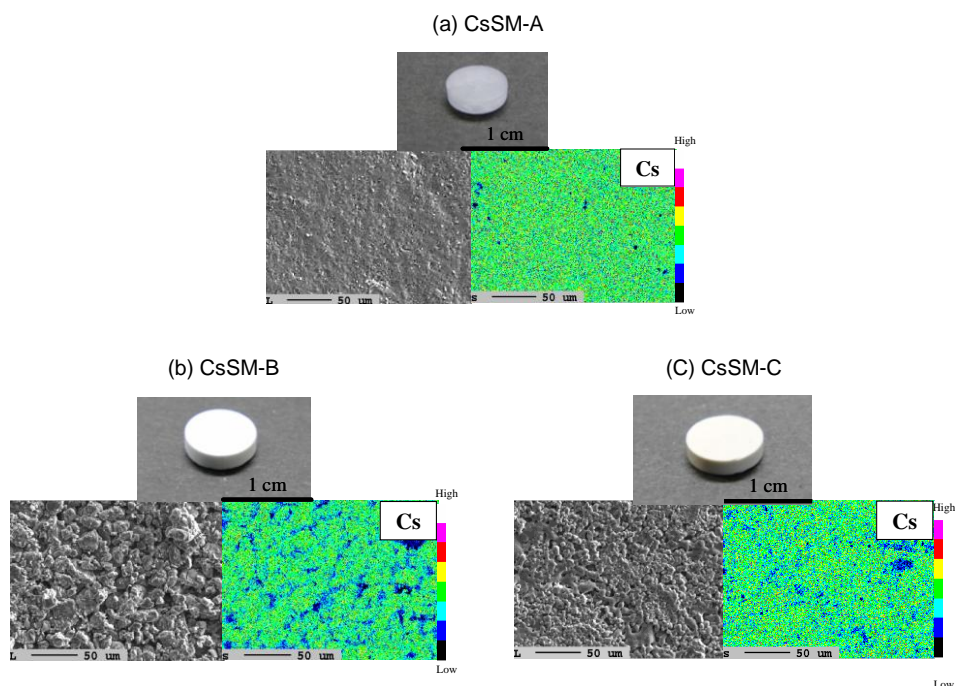
Preparation of ceramic products by hot pressing

Four kinds of zeolite specimens (CsSM-B, CsSM-C, mixture of CsSM-A/zeolite A, and mixture of CsSM-B/zeolite A) were weighed by 5 g and pelletised into a disk ($20 \text{ mm } \phi$) by hot pressing (HP) under the conditions: pressing at 50, 300 and 500 kg/cm^2 , calcining at $1\,200^\circ\text{C}$ and $1\,300^\circ\text{C}$ for 1 h. The ceramic products by HP were evaluated by using XRD and density balance, and the results were compared to the products obtained by CIP.

Results and discussion

Surface morphology

The whole image, magnified SEM image and colour mapping (Cs) for each ceramic product prepared by CIP at $1\,200^\circ\text{C}$ for 1 h are shown in Figures 2(a), 2(b) and 2(c). The ceramic products with 7.2-9.0 mm in diameter and 2.4-2.8 mm in thickness were obtained. From the magnified SEM images, the surface of CsSM-A is seen to be smooth and slightly melted, while the surface of CsSM-B and CsSM-C are rather porous. From the colour mapping, Cs^+ ions were uniformly dispersed, indicating the immobilisation of Cs^+ ions in the ceramic products.

Figure 2: Whole images, magnified SEM images and colour mappings for ceramic products**Recrystallised phase and density of ceramic products**

As for CIP (900 to 1 200°C, 5 min to 3 h), phase transformations of Cs form of mordenites are summarised in Table 2. Mordenite structure is stable up to 1 000°C and no phase transformation was observed. As for CsSM-A and CsSM-B, they were converted to amorphous phase above 1 100°C. In contrast, the structure of CsSM-C was destroyed at 1 100°C and recrystallised to caesium aluminium silicates ($\text{CsAlSi}_5\text{O}_{12}$) at 1 200°C. At 1 200°C, CsSM-A and CsSM-B were amorphous, while the CsSM-C readily recrystallised to $\text{CsAlSi}_5\text{O}_{12}$ by the calcination for 15 min.

Table 2: Phase transformations of Cs form of mordenites at high temperatureMor.: Mordenite, Am.: Amorphous, R_1 : $\text{CsAlSi}_5\text{O}_{12}$

	Calcining time of 3 h	Calcining temperature of 1200°C
CsSM-A		
CsSM-B		
CsSM-C		

Figure 3 shows the effect of calcining temperature on the density of the products by CIP for 3 h. The density of the products increased with calcining temperature. In the case of CsSM-A, the density of the products calcined at 1200°C was 2.48 g/cm³ and 2.5 times larger than that of the original SM-A ($d = 1.05$ g/cm³). The density of the products of CsSM-B and CsSM-C calcined at 1200°C were 2.47 and 2.50 g/cm³. Figure 4 shows the effect of calcining time on the density of the products by CIP calcined at 1200°C. The density of the products increased with calcining time within 30 min, while it was almost constant after 1 h.

Figure 3: Effect of calcining temperature on density

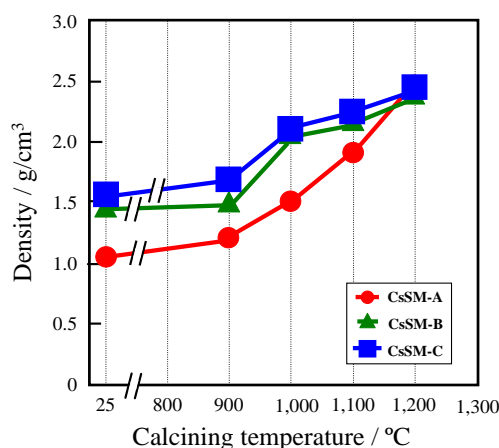
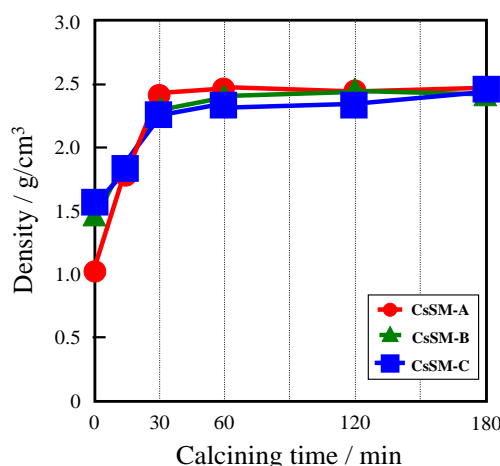


Figure 4: Effect of calcining time on density



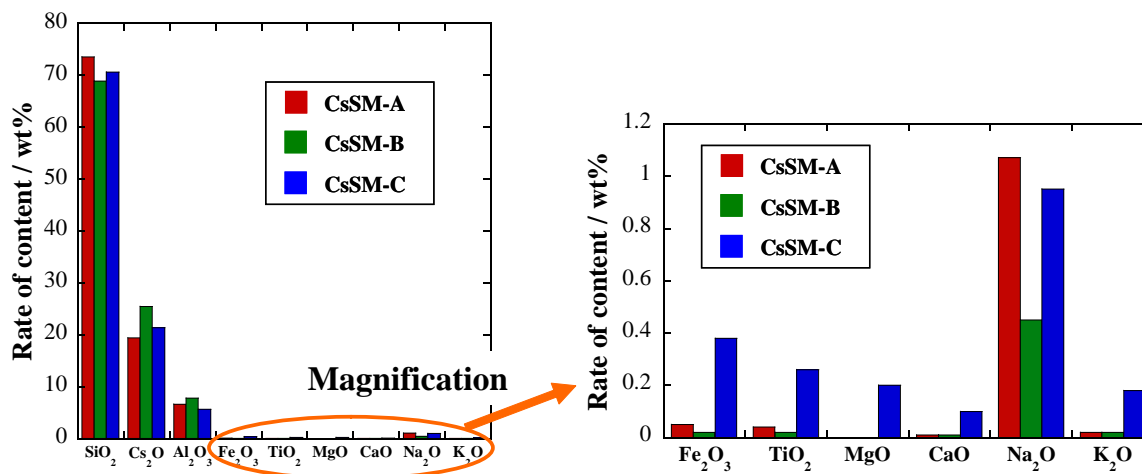
Wet elemental analysis of CsSM

As shown in Table 2, Cs form of mordenites converted to amorphous or recrystallised phase of CsAlSi₃O₁₂. In order to check the difference in phase transformation, the chemical components of CsSM were determined by wet elemental analysis as already shown in Figure 1. Figure 5 shows the estimated contents for CsSM. As clearly shown in the figure, Cs form of mordenites contained SiO₂, Al₂O₃ and Cs₂O as major components; there was no difference in the contents of major components. The contents of SiO₂ and Al₂O₃ for CsSM were as follows:

- SiO₂ content: CsSM-A: 73.5±0.35 wt.%, B: 68.8±0.18 wt.%, C: 70.6±1.34 wt.%
- Al₂O₃ content: CsSM-A: 6.60±0.05 wt.%, B: 7.79±0.05 wt.%, C: 5.60±1.73 wt.%.

The Si/Al ratios of these mordenites (SM-A, B and C) were estimated to be 9.4, 7.5 and 10.7 which were larger than that of stoichiometric Si/Al ratio (Si/Al = 5) of mordenite, indicating the existence of excess Si. The excessive amount of Si may be responsible for the obstruction of recrystallisation. In addition, relatively large amounts of Ti and Fe (TiO_2 : 0.26 ± 0.07 wt.%, Fe_2O_3 : 0.38 wt.%) were contained in CsSM-C compared to other CsSM.

Figure 5: Estimated contents of components in Cs form of mordenites

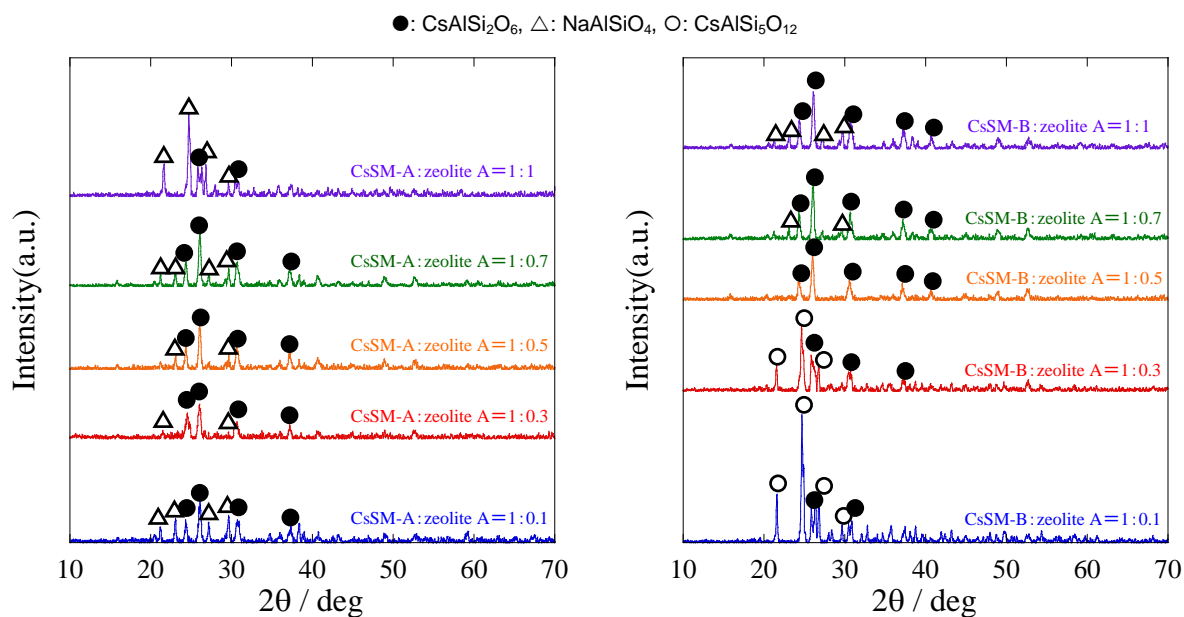
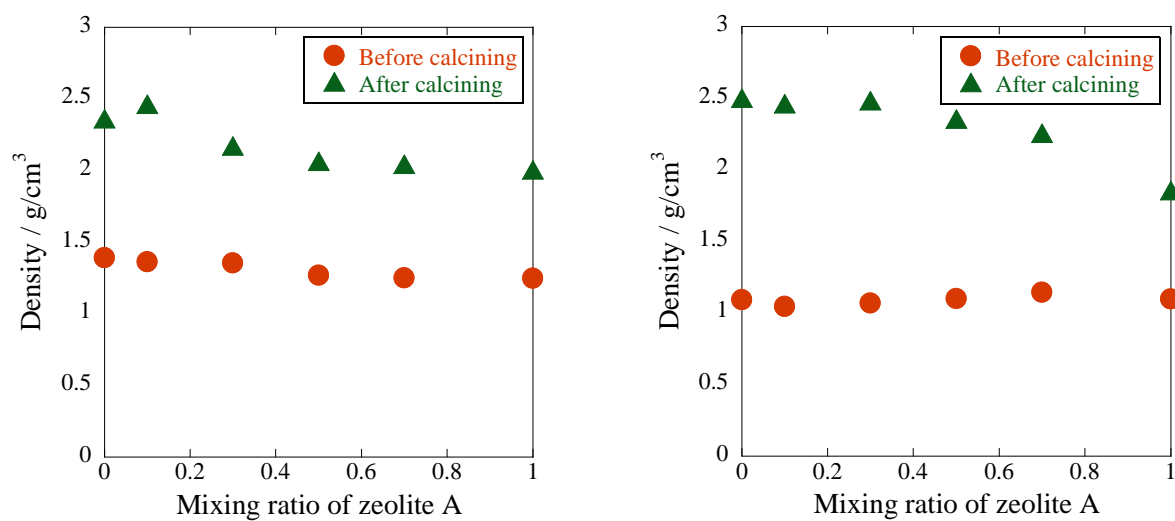


Phase transformation by the addition of zeolite A

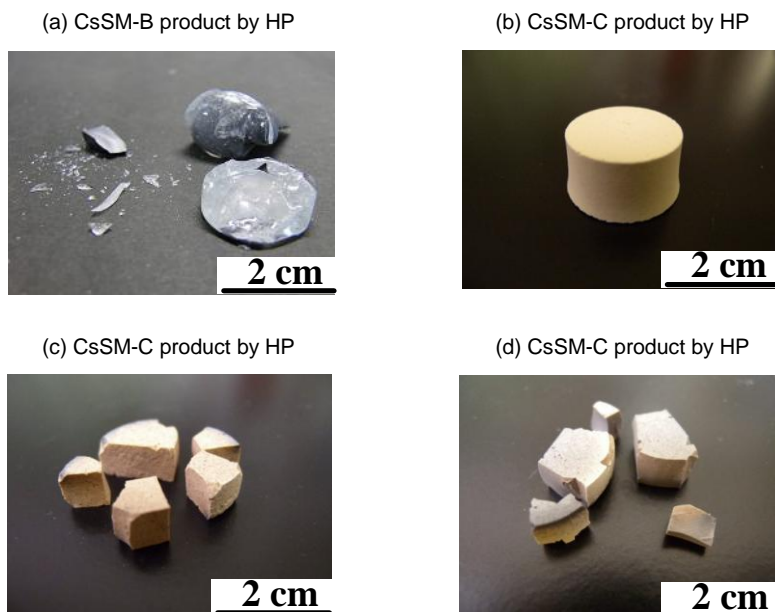
The mixtures of CsSM and zeolite A were calcined at 1 200°C for 1 h. Figures 6 and 7 show the effects of mixing ratio of CsSM-A and CsSM-B to zeolite A on the recrystallisation and the density change of the products by CIP. As already shown in Table 2, CsSM-A and B calcined at 1 200°C were not recrystallised and converted to amorphous phase. In contrast, the mixtures of CsSM and zeolite A with higher content of Al_2O_3 were recrystallised to $\text{CsAlSi}_2\text{O}_6$ (pollucite), NaAlSiO_4 (nepheline) and $\text{CsAlSi}_5\text{O}_{12}$. The $\text{CsAlSi}_2\text{O}_6$ phase was obtained by calcining the mixtures of CsSM and zeolite A, and NaAlSiO_4 phase was obtained by calcining zeolite A. As for the mixture of CsSM-A and zeolite A, the increase of added amounts of zeolite A resulted in the recrystallisation of $\text{CsAlSi}_2\text{O}_6$ and NaAlSiO_4 . In the case of the mixture of CsSM-B and zeolite A, the mixture (CsSM-B:zeolite A = 1:0.1 and 1:0.3) was recrystallised to $\text{CsAlSi}_5\text{O}_{12}$ and $\text{CsAlSi}_2\text{O}_6$. At higher ratio of zeolite A (1:0.5 ~ 1:1), the mixtures were recrystallised $\text{CsAlSi}_2\text{O}_6$ and NaAlSiO_4 . The density of the products obtained by the calcination of the mixtures of CsSM and zeolite A tended to decrease with increasing the mixing ratio of zeolite A.

Characterisation of ceramic products by hot pressing

The ceramic products were obtained by hot pressing (HP) in the SiC mold. The whole images of the CsSM-B and C products by HP (50, 300 and 500 kg/cm^2 , 1 300°C, 1 h) are shown in Figures 8(a), 8(b), 8(c) and 8(d), and the recrystallised phase and estimated density are listed in Table 3. The CsSM-B product for HP was as transparent as glass and sintered with mould [Figure 8(a)]. The recrystallised phase was amorphous and its density was 2.65 g/cm^3 which was 1.1 times larger than that of CsSM-B product obtained by CIP at 1 200°C ($d = 2.42 \text{ g/cm}^3$). As for CsSM-C products by HP at 50 kg/cm^2 [Figure 8(b)], the sintering with SiC mould was not observed and solidified products with no cracks were obtained. On the other hand, the products obtained at higher pressing above 300 kg/cm^2 were sintered with the mould [Figures 8(c) and 8(d)]. In either case, the recrystallised phase was identified as $\text{CsAlSi}_5\text{O}_{12}$.

Figure 6: Effects of mixing ratio of CsSM-A (left) and CsSM-B (right) to zeolite A on the recrystallisation**Figure 7: Effects of added amount of zeolite A to CsSM-A (left) and CsSM-B (right) on density change****Table 3: Recrystallised phases and estimated density**

	Conditions	Recrystallised phase	Density (g/cm^3)
CsSM-B	1 300°C, 1 h, 500 kg/cm^2	Amorphous	2.65
CsSM-C	1 300°C, 1 h, 50 kg/cm^2	$\text{CsAlSi}_5\text{O}_{12}$	2.05
CsSM-C	1 300°C, 1 h, 300 kg/cm^2	$\text{CsAlSi}_5\text{O}_{12}$	2.55
CsSM-C	1 300°C, 1 h, 500 kg/cm^2	$\text{CsAlSi}_5\text{O}_{12}$	2.62

Figure 8: Whole images of the CsSM-B and CsSM-C products by HP

In order to avoid the sintering problem, SiC mould was further coated with BN. The mixtures of CsSM and zeolite A were converted to the ceramic products by HP (500 kg/cm^2 , $1\,200$ and $1\,300^\circ\text{C}$, 1 h). The whole images of the products by HP are shown in Figures 9(a), 9(b) and 9(c), and the recrystallised phase and estimated density are summarised in Table 4. In either products, the sintering with the pressing rod was not observed, while the products tended to be broken due to the sintering with the side of the SiC mould. The BN coating was effective for the preventing of sintering. The density of the products (CsSM-B:zeolite A = 1:0.7) was estimated to be 2.63 g/cm^3 which was 1.3 times larger than that of the CIP product calcined at $1\,200^\circ\text{C}$ ($d = 2.04 \text{ g/cm}^3$).

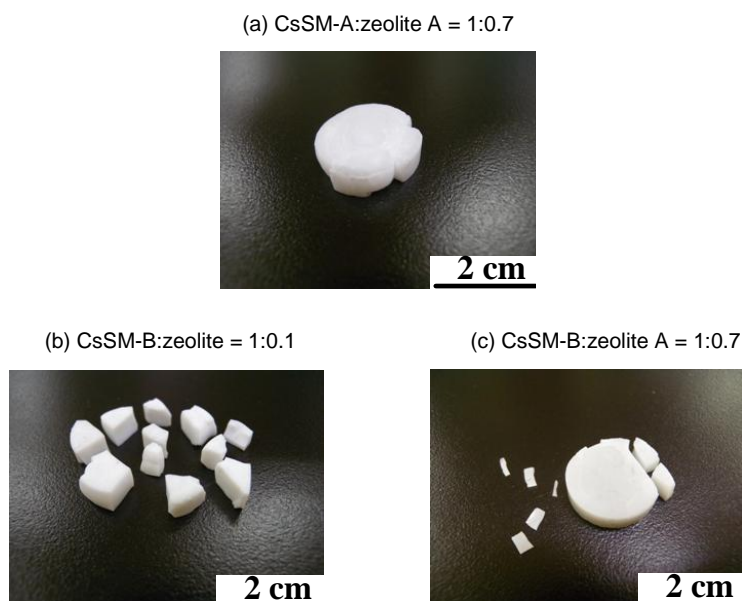
Figure 9: Whole images of the products by HP

Table 4: Recrystallised phase and estimated density

Mixing ratio	Conditions	Recrystallised phase	Density (g/cm ³)
CsSM-A:zeolite A = 1:0.7	1 200°C, 1 h, 500 kg/cm ²	CsAlSi ₂ O ₆ , NaAlSiO ₄	2.54
CsSM-B:zeolite A = 1:0.1	1 300°C, 1 h, 500 kg/cm ²	CsAlSi ₅ O ₁₂ , CsAlSi ₂ O ₆	2.67
CsSM-B:zeolite A = 1:0.7	1 300°C, 1 h, 500 kg/cm ²	CsAlSi ₂ O ₆ , NaAlSiO ₄	2.63

Conclusions

The ceramic products immobilising Cs⁺ ions were obtained by the heat treatment using CIP and HP at higher temperature above 1 200°C. The phase transformation and characterisation of the ceramic products were examined and the following results were obtained:

- 1) The CsSM-A and B products were amorphous above 1 200°C, while the CsSM-C product was identified as recrystallised phase of CsAlSi₅O₁₂. The density of the products tended to increase with calcining temperature and time.
- 2) The content of the chemical components in CsSM were determined by wet elemental analysis. The Si/Al ratios of mordenites (SM-A, B and C) were estimated to be 9.4, 7.5 and 10.7 which were larger than that of stoichiometric Si/Al ratio (Si/Al = 5) of mordenite, indicating the existence of excess Si. The excessive amount of Si may be responsible for the obstruction of recrystallisation.
- 3) The mixtures of CsSM and zeolite A were recrystallised to CsAlSi₂O₆ (pollucite), NaAlSiO₄ (nepheline) and CsAlSi₅O₁₂. As for the mixture of CsSM-A and zeolite A, the increase of added amounts of zeolite A resulted in the recrystallisation of CsAlSi₂O₆ and NaAlSiO₄. The mixture of CsSM-B and zeolite A (CsSM-B:zeolite A = 1:0.1 and 1:0.3) was recrystallised to CsAlSi₅O₁₂ and CsAlSi₂O₆.
- 4) As for CsSM-C products by HP at 50 kg/cm², the sintering with SiC mould was not observed and solidified products with no cracks were obtained. The BN coating was effective for the preventing of sintering. The density of the products (CsSM-B:zeolite A = 1:0.7) was estimated to be 2.63 g/cm³ which was 1.3 times larger than that of the CIP product calcined at 1 200°C ($d = 2.04 \text{ g/cm}^3$).

Acknowledgements

The authors wish to thank Mr. T. Kamaya (Tohoku University, IMRAM) for SEM and EPMA analysis and discussion.

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