

Development of Stable Solidification Method for Insoluble Ferrocyanides-13170

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ABSTRACT

The development of stable solidification method of insoluble ferrocyanides sludge is an important subject for the safety decontamination in Fukushima NPP-1. By using the excellent immobilizing properties of zeolites such as gas trapping ability and self-sintering properties, the stable solidification of insoluble ferrocyanides was accomplished. The immobilization ratio of Cs for $K_2[CoFe(CN)_6] \cdot nH_2O$ saturated with Cs^+ ions ($Cs_2[CoFe(CN)_6] \cdot nH_2O$) was estimated to be less than 0.1% above 1,000°C; the adsorbed Cs^+ ions are completely volatilized. In contrast, the novel stable solid form was produced by the press-sintering of the mixture of $Cs_2[CoFe(CN)_6] \cdot nH_2O$ and zeolites at higher temperature of 1,000°C and 1,100°C; Cs volatilization and cyanide release were completely depressed. The immobilization ratio of Cs, under the mixing conditions of $Cs_2[CoFe(CN)_6] \cdot nH_2O:CP=1:1$ and calcining temperature: 1,000°C, was estimated to be nearly 100%. As for the kinds of zeolites, natural mordenite (NM), clinoptilolite (CP) and Chabazite tended to have higher immobilization ratio compared to zeolite A. This may be due to the difference in the phase transformation between natural zeolites and synthetic zeolite A. In the case of the composites ($K_{2-x}Ni_{x/2}[NiFe(CN)_6] \cdot nH_2O$ loaded natural mordenite), relatively high immobilization ratio of Cs was also obtained. This method using zeolite matrices can be applied to the stable solidification of the solid wastes of insoluble ferrocyanides sludge.

INTRODUCTION

In Fukushima NPP-1, high-activity-level water accumulated in the reactor, turbine building and the trench in the facility is treated by the circulating injection cooling system (**Fig. 1**). At present, this system is effectively operated and the cold shutdown is completed. However, large amounts of solid wastes such as zeolites (346 vessel) and insoluble ferrocyanide sludge (581 m³) are generated (on March 14, 2012) [1], and hence the development of effective treatment and disposal methods are very urgent and important subjects in Japan. Especially, insoluble ferrocyanide sludge contains high radioactivity of Cs-137 and has low thermal stability, which tends to release hydrogen cyanide under inert and reducing atmosphere [2]. Thus, the development of stable solidification method contributes to the advancement of the decontamination system and environmental remediation. In this study, the stable solidification of insoluble ferrocyanides saturated with Cs^+ ions was accomplished by using the immobilization ability of zeolites, i.e., Cs trapping and self-sintering abilities. The present study deals with (1) effects of calcining temperature, mixing ratio and the kinds of zeolite on the immobilization of Cs, (2) characterization of solid forms, (3) stable solidification of composite (zeolites loaded

with insoluble ferrocyanides), and (4) analysis of Cs concentrated spots.

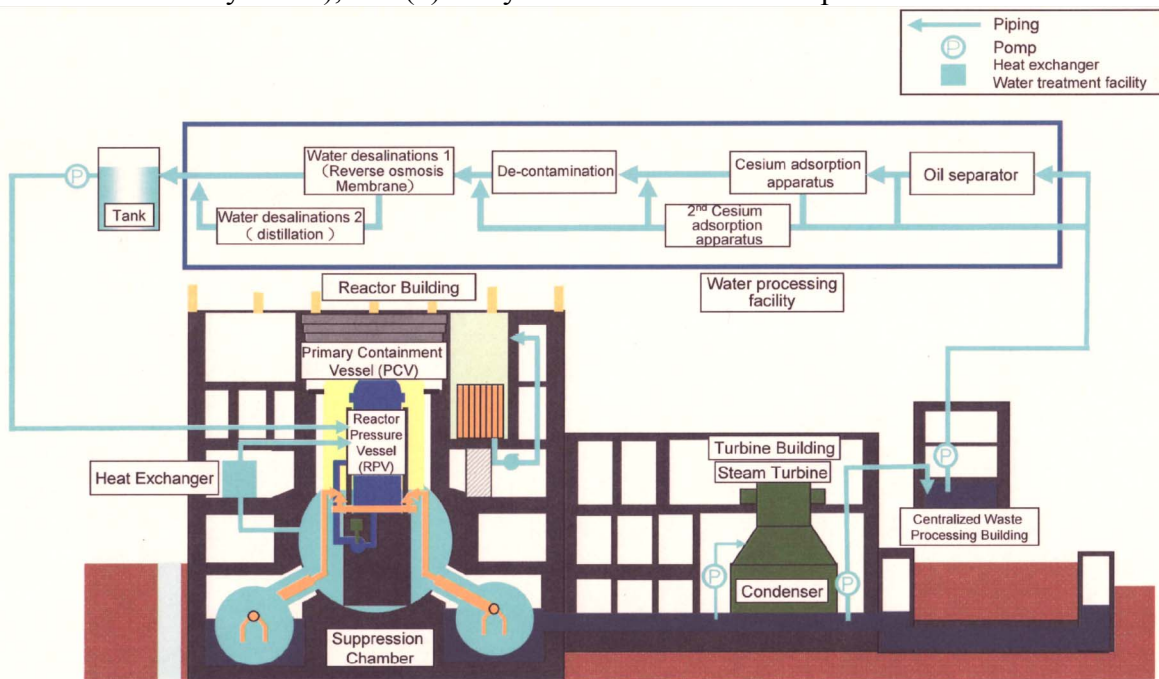


Fig. 1. Decontamination system for high-activity-level water[3].

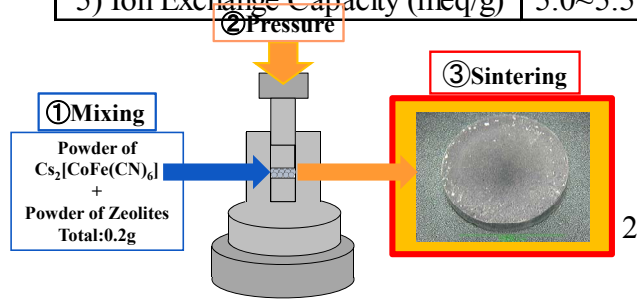
EXPERIMENTAL

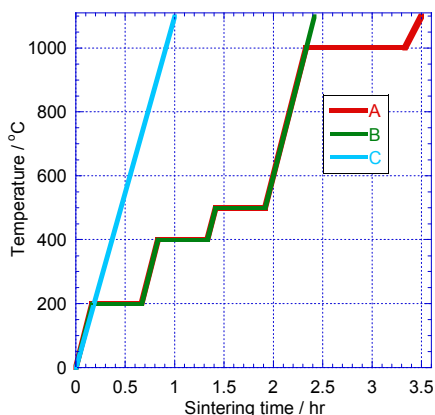
Materials and Preparation Procedure

The press-sintering samples of Cs saturated insoluble ferrocyanides and zeolites were prepared as follows. Cesium saturated insoluble ferrocyanides ($\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$) were prepared by the treatment with 0.5 M CsNO_3 . Insoluble ferrocyanides ($\text{K}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$) were obtained from Fluka. Cesium saturated samples were then pulverized and mixed with zeolites (NM=SA-5, CP, chabazite=IE-96, zeolite A=A-51J). The characteristics of zeolites used are shown in **TABLE I**. The mixture was molded as a disk by cold-pressing (**Fig. 2**), and then the molded disks were calcined at different temperatures up to 1,200°C by the different calcination schedules: stepwise and direct calcination (**Fig. 3**).

TABLE I. Characteristics of zeolites

	1	2	3	4
Sample Name	4A	CP	SA-5	IE-96
1) Structure	A	Clinoptilolite	Mordenite	Chabazite
2) Si / Al	1	5	5	2~2.5
3) Exchangeable Cation Group	Na	Na, K, Ca	Na, K	Na, Ca
4) Kinetic Diameter (Å)	4Å	3.5Å	3.9Å	5Å
5) Ion Exchange Capacity (meq/g)	5.0~5.5 (Na)	1.5 (Cs)	1.1 (Cs)	2.0~2.5 (Na)





Parameter	
Pressure:	200 kg/cm ²
Calcination temperature:	1,000°C~1,200°C
Calcination time:	1 h~3.5 h

Fig. 3. Sintering schedule.

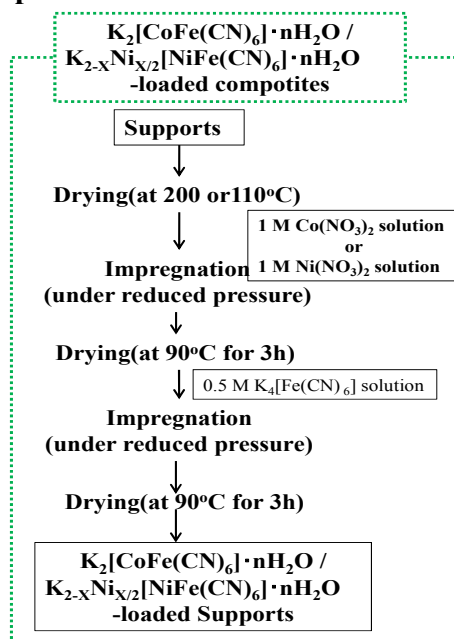
Fig. 2. Preparation Procedure for press-sintering.

Characterization and Determination of Cs Immobilization Ratio

Surface morphologies of the calcined specimens were examined by scanning electron microscopy (SEM, HITACHI, Miniscope TM-1000) and digital microscope (DM, HiROX, KH-1300). The chemical composition was determined by energy dispersive spectroscopy (EDS, SwiftED-TM, HITACHI, TM-1000) and fourier transform infrared spectroscopy (FT-IR, HORIBA, FT-200). The Cs immobilization ratio (%) was determined from the difference of the Cs content before and after calcination.

Preparation of Insoluble Ferrocyanides Loaded Composites and Characterization

The novel insoluble ferrocyanides ($K_{2-x}Ni_{x/2}[NiFe(CN)_6] \cdot nH_2O$) loaded zeolites were prepared as follows (Fig. 4). The $K_{2-x}Ni_{x/2}[NiFe(CN)_6] \cdot nH_2O$ loaded composites were prepared by the repeated impregnation of $Ni(NO_3)_2$ and $K_4[Fe(CN)_6]$ solutions into the zeolite macropores under the experimental conditions of zeolite: 3 g, 1 M $Ni(NO_3)_2$ solution: 20 cm³, 0.5 M $K_4[Fe(CN)_6]$ solution: 20 cm³, impregnation time: 3 h and reaction temperature: 25°C. The composites were then treated with 0.1 M $CsNO_3$ solution to obtain the Cs saturated composites samples for the immobilization test. Similarly to the press-sintering of the mixture, the Cs saturated composites were calcined at different temperatures up to 1,200°C. The calcined composites were submitted to SEM and DM observation and IR analysis. The Cs content in the calcined composites was determined by EDS analysis and the Cs immobilization ratio (%) was obtained.


 Fig. 4. Preparation procedure of $K_2[CoFe(CN)_6] \cdot nH_2O / K_{2-x}Ni_{x/2}[NiFe(CN)_6] \cdot nH_2O$ -loaded zeolites[4].

RESULTS AND DISCUSSION

Surface Morphology and Cs Immobilization Ratio of $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$

Surface morphology of $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ specimens calcined at different temperatures is shown in **Fig. 5**. In the case of 500°C calcination, the disc surface of $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ is seen to be thermally decomposed, indicating the decomposed gases are released. The Cs immobilization ratio was similarly lowered above 500°C. This is probably due to the volatilization of Cs_2O gas. The immobilization ratio above 1,000°C was estimated to be less than 0.1 % (**Fig. 6**); the adsorbed Cs^+ ions were completely volatilized, indicating the poor immobilization ability of $\text{K}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ for Cs. Thus the development of stable solidification method for insoluble ferrocyanides is urgent subject considering the low thermal stability and cyanide release under the reductive atmosphere.

Cs Immobilization Ratio for the Mixture of $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ and Zeolite

By using the immobilization ability of zeolites, *i.e.*, Cs trapping and self-sintering abilities, the discs of the mixture of $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ and zeolite were sintered at higher temperatures up to 1,200°C. In contrast to the insoluble ferrocyanides, in either case, relatively high Cs immobilization ratios were obtained by high temperature calcination of the mixtures, indicating that the volatilization of Cs was effectively depressed. The optimal condition for the stable solidification was examined by varying calcination schedule, calcining temperature (up to 1,200°C), mixing ratio ($\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$: zeolite= 1:1, 1:2 and 1:3) and the kinds of zeolites (natural mordenite (NM), clinoptilolite (CP), chabazite and zeolite A). The Cs immobilization ratios under the different calcination conditions were summarized in **TABLE II**.

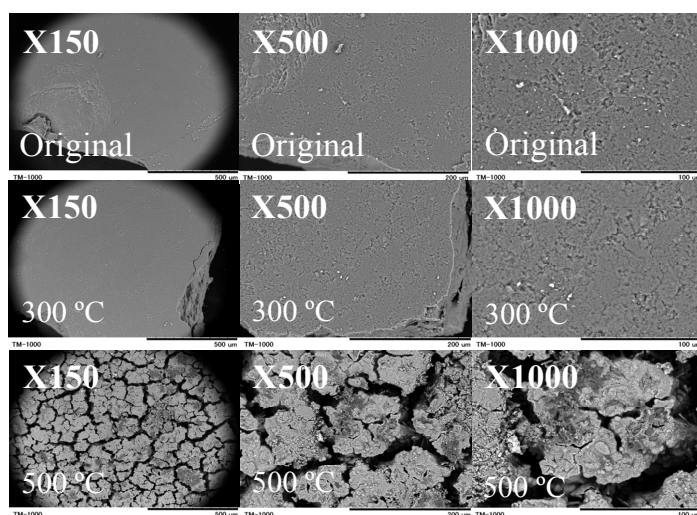


Fig. 5. SEM images of $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$.

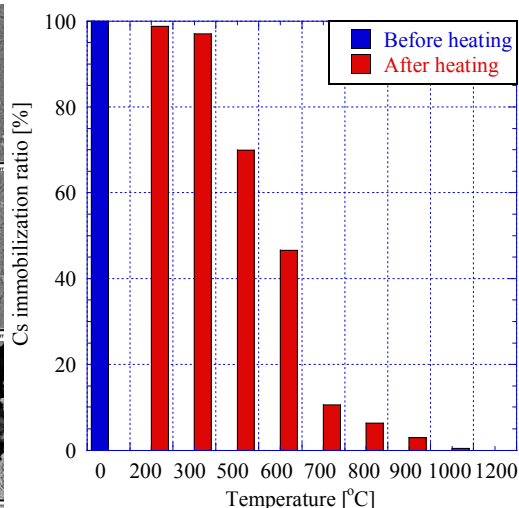


Fig. 6. Cs immobilization ratio vs. calcination temperatures of $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$.

TABLE II. EDS data of the mixture of $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ and zeolites by different calcination conditions.

Sample name	Mixing ratio	Heat treatment (maximum temp.)	Calcination mode (temp. method)	EDS (before heating) Cs%	EDS		Percentage (%)		Remarks
					data1	data2	data1	data2	
CsCoFC - CP ¹⁾	1 : 1	1,000	A	4.5	4	4.2	89	93	
CsCoFC - CP	1 : 1	1,200	A	4.5	2.1	2.4	47	53	melted
CsCoFC - CP	1 : 1	1,000	B	5.2	5.1	5.2	98	100	highest percentage in CsCoFC : CP mixing
CsCoFC - CP	1 : 2	1,000	B	3.2	2.3	2.5	72	78	
CsCoFC - CP	1 : 2	1,100	B	3.2	1.9	2.6	59	81	melted
CsCoFC - CP	1 : 3	1,000	B	2.1	1.9	2.1	90	100	
CsCoFC - CP	1 : 3	1,100	B	2.1	1.8	2.6	86	124	melted
CsCoFC - SA-5 ²⁾	2 : 1	1,100	B	6.8	3.2	3.5	47	51	melted
CsCoFC - SA-5	1 : 1	1,000	B	5.0	4.5	4.6	90	92	highest percentage in CsCoFC : SA-5 mixing
CsCoFC - SA-5	1 : 2	1,000	B	3.4	2.8	3.3	82	97	
CsCoFC - SA-5	1 : 2	1,100	B	3.4	2.1	2.7	62	79	melted
CsCoFC - SA-5	1 : 3	1,000	B	2.4	1.9	2.2	79	92	
CsCoFC - CP	1 : 1	1,000	A	5.2	5.2	5.3	100	102	
CsCoFC - CP	1 : 1	1,000	C	5.2	5.3	5.5	102	106	% in method A = B = C
CsCoFC - SA-5	1 : 1	1,000	A	5.0	4.5	4.6	90	92	
CsCoFC - SA-5	1 : 1	1,000	C	5.0	5.1	5.2	102	104	% in method C > B = A
CsCoFC - A-51J ³⁾	1 : 1	1,000	C	6.8	5.5	5.4	81	79	highest percentage in CsCoFC : A-51J mixing
CsCoFC - A-51J	1 : 1	1,100	C	6.8	5.4	5.3	79	78	
CsCoFC - IE-96 ⁴⁾	1 : 1	1,000	C	7.5	7.6	7.5	101	100	highest percentage in CsCoFC : IE-96 mixing
CsCoFC - IE-96	1 : 1	1,100	C	7.5	6.7	6.5	89	87	
CsCoFC - SA-5	1 : 1	1,000	B	5.0	3.9	4.2	78	84	powder(not pellet),low Cs%
CsCoFC - CP	1 : 1	1,000	C	5.1	4.4	4.7	86	92	powder(not pellet),low Cs%
CsCoFC - CP	1 : 1	1,000	A	5.1	5.0	5.0	98	98	powder(not pellet),low Cs%
CsCoFC - SA-5	1 : 1	1,000	A	5.0	3.6	4.5	72	90	powder(not pellet),low Cs%
CsCoFC		1,100	B	11.8	0	0	0	0	
		200	C	11.8	11.6	11.7	98	99	
		300	C	11.8	11.2	11.7	95	99	
		500	C	11.8	6.7	9.8	57	83	
		600	C	11.8	5.3	5.7	45	48	
		700	C	11.8	1.2	1.3	10	11	
		800	C	11.8	0.7	0.8	6	7	
		900	C	11.8	0.3	0.4	3	3	
		1,000	C	11.8	0	0.1	0	1	
		1,200	C	11.8	0	0	0	0	

1)CP,Clinoptilolite,Made by Zeekite Corporation

2)SA-5,Natural Mordenite,Made by SHIN TOHOKU Chemical Industry Corporation

3)A-51J,A Zeolite,Made by UNION SHOWA K.K.

4)IE-96,Chabazite, Made by UNION SHOWA K.K.

As for the calcination schedule, high immobilization ratio of nearly 100% was obtained by direct calcination (no stepwise calcination, C) under the calcination conditions of zeolite: CP and SA-5, mixing ratio 1:1, calcination temperature:1,000°C (TABLE II, Fig. 7). The calcination at 1,000°C is suitable for the stable solidification, while at higher temperatures the immobilization ratio tends to decrease with calcination temperature (Fig. 8). The mixing ratios of 1:1, 1:2 and 1:3 are also suitable for the stable solidification. As for the kinds of zeolites, NM, CP and chabazite tend to have higher immobilization ratio compared to zeolite A (Fig. 9). This may be due to the difference in the phase transformation between natural zeolites and synthetic zeolite A; natural zeolites converts to amorphous above 1,000°C, while synthetic zeolite A converts to aluminosilicate mineral such as Nepheline above 1,000°C. In addition, the immobilization ratio for the mixture without pressing was also estimated to be 90% (Fig. 10).

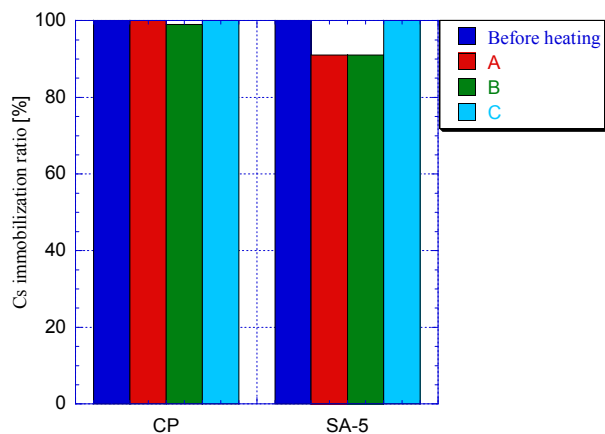


Fig. 7. Cs immobilization ratio vs calcination schedules.

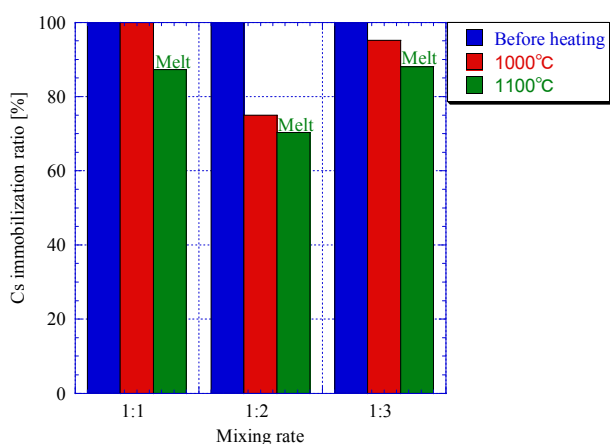


Fig. 8. Cs immobilization ratio at different mixing ratios and temperatures.

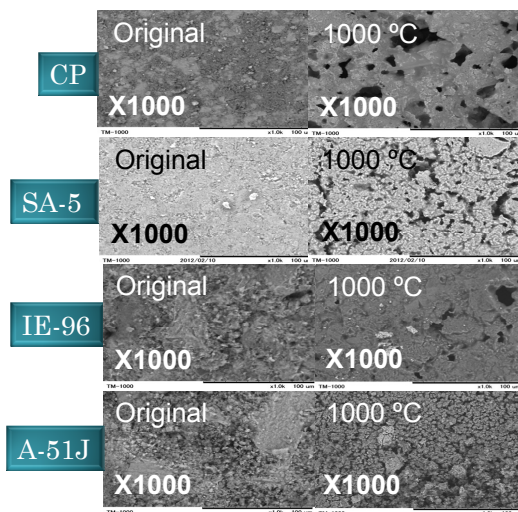
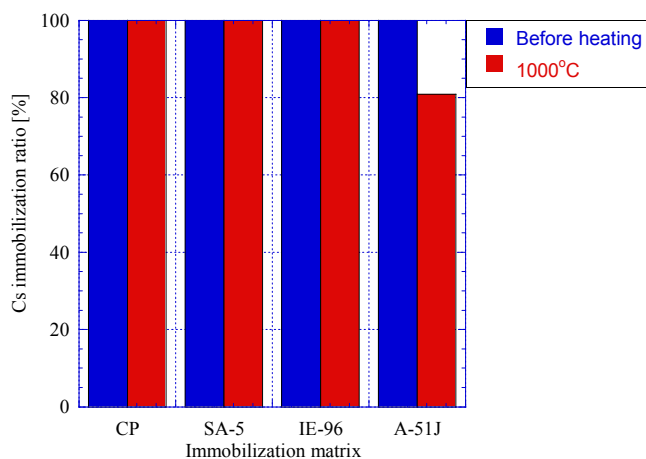


Fig. 9. Cs immobilization ratio (left) and SEM images (right) for different immobilization matrices.

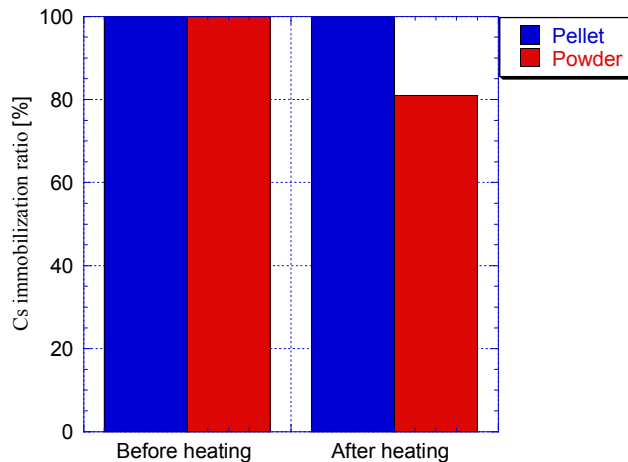
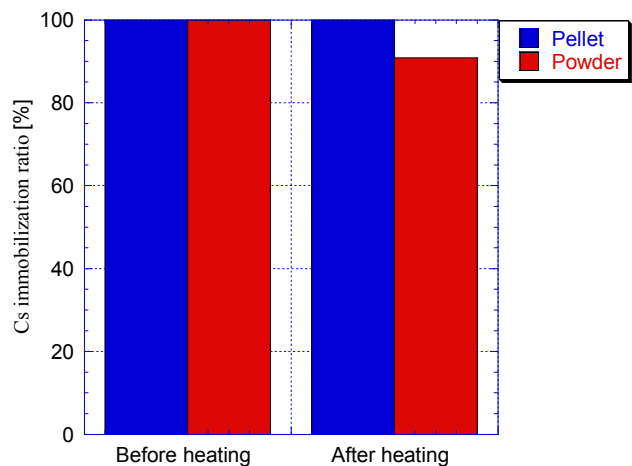


Fig. 10. Cs immobilization ratio for pellet and powder. Left: $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}/\text{CP}$, Right: $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}/\text{SA-5}$.

As for the composites, natural mordenite, clinoptilolite and chabazite loaded with $K_{2-x}Ni_{x/2}[NiFe(CN)_6] \cdot nH_2O$ were used for the evaluation of stable solidification. For example, the immobilization ratio for the composite saturating Cs^+ ions ($Cs_{2-x}Ni_{x/2}[NiFe(CN)_6] \cdot nH_2O$ –NM) was estimated to be above 99% at 1,000°C (Fig. 11, TABLE III). On the other hand, in the case of composites of A zeolite loaded with $K_{2-x}Ni_{x/2}[NiFe(CN)_6] \cdot nH_2O$, the immobilization ratio tended to decrease markedly above 1,100°C, and specific Cs concentrated spots were observed on the surface of the calcined composites (Fig. 12, TABLE IV). The stable solidification of insoluble ferrocyanides was thus accomplished by using the excellent Cs immobilization abilities of zeolites (Cs trapping and self-sintering abilities). Further, the immobilization mechanism and optimal conditions should be clarified in detail. This method can be applied to the stable solidification of the solid wastes such as insoluble ferrocyanide sludge.

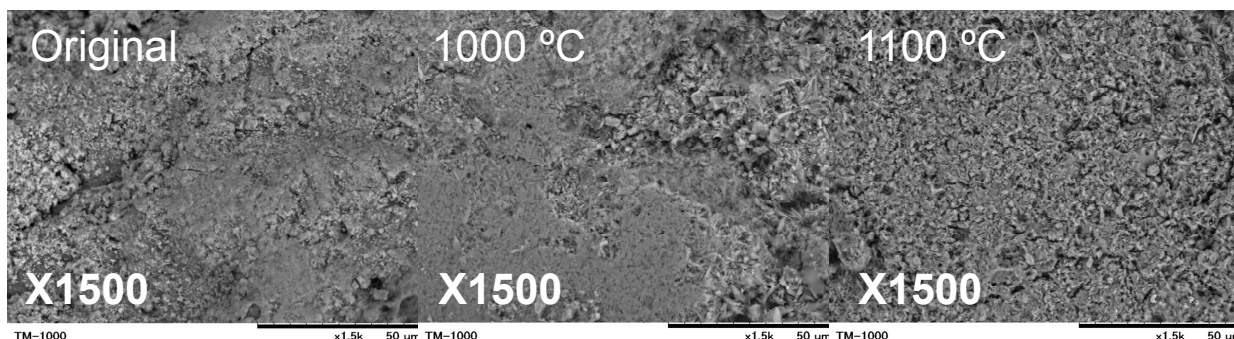


Fig. 11. SEM images of $Cs_{2-x}Ni_{x/2}[NiFe(CN)_6] \cdot nH_2O$.

TABLE III. EDS data of $Cs_{2-x}Ni_{x/2}[NiFe(CN)_6] \cdot nH_2O$.

EDS (before heating)	EDS (after heating)		Percentage(%)	
	Cs%			
orig	1,000°C	1,100°C	1,000°C	1,100°C
29.4	29.3	28.5	99.8	97.1

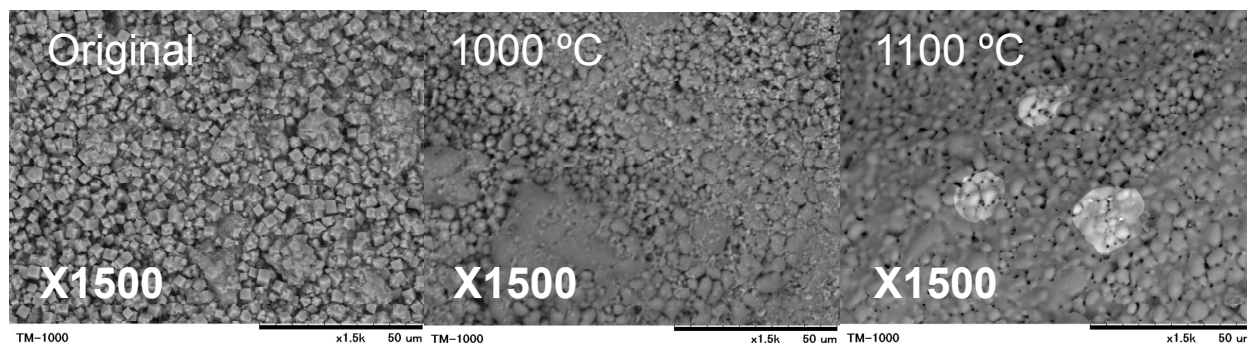


Fig. 12. SEM images of $Cs_{2-x}Ni_{x/2}[NiFe(CN)_6] \cdot nH_2O$ -zeolite A.

TABLE IV. EDS data of $\text{Cs}_{2-x}\text{Ni}_{x/2}[\text{NiFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ -zeolite A

EDS (before heating)	EDS (after heating)		Percentage(%)	
	Cs%			
orig	1,000°C	1,100°C	1,000°C	1,100°C
25.1	25.4	14.5	101	57.7

CONCLUSIONS

By using the excellent immobilizing properties of zeolites such as gas trapping ability and self-sintering properties, the stable solidification of insoluble ferrocyanides was accomplished. The immobilization ratio of Cs for $\text{K}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ saturated with Cs^+ ions ($\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$) was estimated to be less than 0.1% above 1,000°C; the adsorbed Cs^+ ions are completely volatilized. In contrast, the novel stable solid form was produced by the press-sintering of the mixture of $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ and zeolites at higher temperature of 1,000°C and 1,100°C; Cs volatilization and cyanide release were completely depressed. The immobilization ratio of Cs, under the mixing conditions of $\text{Cs}_2[\text{CoFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}:\text{CP} = 1:1$ and calcining temperature: 1,000°C, was estimated to be nearly 100%. As for the kinds of zeolites, natural mordenite (NM), clinoptilolite (CP) and Chabazite tended to have higher immobilization ratio compared to zeolite A. This may be due to the difference in the phase transformation between natural zeolites and synthetic zeolite A. In the case of the composites ($\text{K}_{2-x}\text{Ni}_{x/2}[\text{NiFe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ loaded natural mordenite), relatively high immobilization ratio of Cs was also obtained. Further, the immobilization mechanism and optimal conditions should be clarified in detail. This method can be applied to the stable solidification of the solid wastes such as insoluble ferrocyanide sludge in Fukushima NPP-1.

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