Processing of Radioactive Waste Solution with Zeolites (I) : Thermal-Transformations of Na, Cs and Sr Forms of Zeolites

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Thermal-Transformations of Na, Cs and Sr Forms of Zeolites

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Synopsis

Thermal-transformations of several kinds of zeolites have been studied by means of differential thermal analysis (DTA), thermo-gravimetric analysis (TGA) and X-ray powder diffraction. Some synthetic zeolites (A, X, Y, mordenite), natural mordenite and clinoptilolite were used.

Sodium forms of A and X zeolites recrystallized above 1000°C to nepheline ($NaAlSiO_4$), whereas the structure of zeolite Y, synthetic and natural mordenites, and clinoptilolite collapsed above around 900°C and did not recrystallize below 1200°C.

Cesium-form zeolites changed to pollucite ($CsAlSi_2O_6$) above 1000°C for A and X, and above 1100°C for Y. The mordenites and clinoptilolite were destroyed on heating above 1000°C to form amorphous phases.

In the case of Sr forms, A and X zeolites recrystallized to strontium aluminosilicate ($SrAl_2Si_2O_8$) above 1100°C and Y zeolite above 1200°C; on the other hand, mordenite and clinoptilolite became amorphous above 1200°C.

Microscopic examination and density measurement support these results.

I. Introduction

Much interest has been focused on the solidification of high-level liquid wastes generated through the nuclear fuel reprocessing. Solidification process improves the safety handling and the storage of radioactive wastes. Some different methods have been proposed in order to

obtain the solidified products suitable for further treatment and disposal.

Recently, the methods of solidification with glass or ceramics have been become of interest, because these products have some excellent properties in leachability, thermal conductivity and radiation resistance. However, the solidification process involves many problems, e.g. the volatilization of cesium and ruthenium, the durability of crucible and the cost of treatment. The leachability is one of the most important factors in the safety evaluation, and the developement of solidified products with lower leachability is desired.

It is well known that a zeolite is an aluminosilicate having three dimentional cage-structure, high stability on radioactive irradiation and selective ion-exchange property for cesium ion. Several works have been reported on the separation and recovery of cesium ion using some zeolites or clays, and on the thermal-transformations of sodium forms of zeolites.[1],[2] The sorption of wastes into clinoptilolite and its storage were studied by Honstead et.al.[3]

In this paper, the thermal-transformations of zeolites were studied by means of thermal analyses, X-ray powder diffraction, microscopic observation and the measurement of density. The fixation of cesium and strontium with zeolites was investigated.

II. Experimental

1. Zeolites

The compositions of six kinds of zeolites used here are given in Table 1. Synthetic zeolites A-4 and F-9 were obtained from Wako Pure Chemical Industry and Tekkosya. These Zeolites were identified to be Linde (Union Carbide Corp., UCC) A and X by means of X-ray powder diffraction. Synthetic zeolite Y and mordenite (Zeolon, abbreviated as SM) were obtained by Norton. Natural mordenite (abbreviated as NM) from the surburbs of Sendai and clinoptilolite (abbreviated as CP) from Futatsui were used. Sodium forms of these zeolites were abbreviated as NaA, NaX, NaY, NaSM, NaNM and NaCP. Zeolites saturated with cesium and strontium were represented as CsA and SrA, respectively. All zeolites were stored in a desiccator over a saturated NH_4Cl solution (humidity; 79.3% at 25°C) to keep the water content constant.

2. Apparatus and procedures

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out by High-Temperature Type Differential Thermo-Balance (Rigaku Denki). The conditions of DTA and TGA were as follows; sensitivity of amp.:±100 μV, temp. sensitivity:20mV, heating rate:10°C/min,

Table 1 Composition of synthetic and natural zeolites.

Zeolite	structure	typical unit cell content	Si/Al
A	Linde A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]27H_2O$	1
X	near faujasite	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]264H_2O$	1.25
Y	faujasite	$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]250H_2O$	2.5
SM	synthetic mordenite	$Na_{8.7}[(AlO_2)_{8.7}(SiO_2)_{39.3}]24H_2O$	5
NM	natural mordenite	$Na_8[(AlO_2)_8(SiO_2)_{40}]24H_2O$	5
CP	clino-ptilolite	$Na_6[(AlO_2)_6(SiO_2)_{30}]24H_2O$	5

temp. range:25~1200°C, atmosphare:air. The zeolites calcined for 3hr at 800, 900, 1000, 1100 and 1200°C in an electric furnace were used as the specimens for the measurement of X-ray powder diffraction, and the conditions were as followes; target:Fe, filter:Mn, voltage:30KVP, current:6mA, scale factor:800×1. The densities of calcined zeolites were measured using Berman Density Balance (Roller-Smith Coop.)

III. Results and discussions

The low-temperature endotherm of DTA curve for zeolite represents in general the loss of adsorbed water and zeolitic water, while the high-temperature exotherm indicates the transformation of the zeolite structure to amorphous or crystalline phase.[4] The zeolite used here showed no evidence of structural change and gave the successive dehydration below about 500°C. The termal-transformation of each zeolite is discussed in detail.

1. A type zeolite

DTA curves and X-ray diffraction patterns are represented in Figs. 1 and 2 (a)~(c). The exothermic peaks of NaA at 860 and 955°C correspond to the destruction of zeolite structure followed by the recrystallization to carnegieite (low form, NaAlSiO₄) and to nepheline

(NaAlSiO₄), respectively. Though Breck et.al. reported that NaA chang-
ed to β-cristobalite at 800°C[5] , this phase was not detected; whereas
the recrystallization was observed to nepheline through carnegieite.

In NaA zeolite, eight of the twelve sodium ions are located near
the six-membered rings and the other four ions are presumably dissolved
in the zeolitic water.[6] The measurment of the ion exchange capacity
for cesium suggested that only four of the twelve ions are exchanged
with cesium ions, and unit cell content can be expressed as
$(Na_8, Cs_4)Al_{12}Si_{12}O_{48} \cdot 27H_2O$.[7]

The exothermic peaks of CsA were observed at 870, 1040 and 1146°C.
The first pesk corresponds to the destruction of zeolite structure fol-
lowed by the recrystallization to carnegieite, and the others to
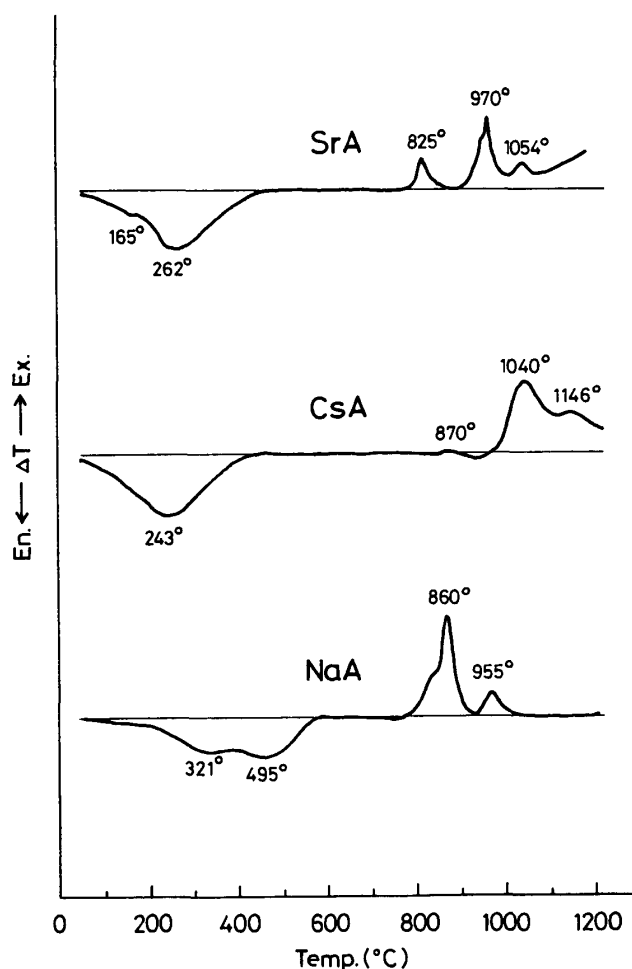nepheline and to pollucite $(CsAlSi_2O_6)$, respectively.
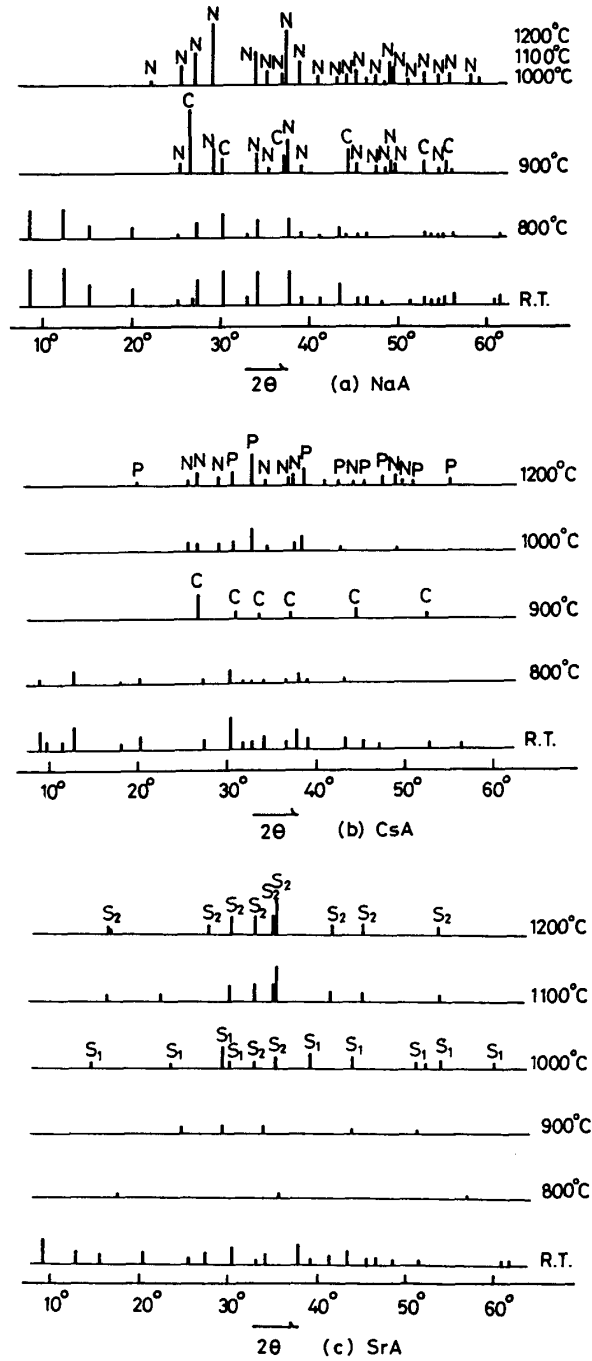

Fig. 1 DTA curves of Na, Cs and Sr formed of zeolite A

Fig. 2 X-ray diffraction patterns (Calcining time; 3hr., C:Carnegieite,
N:Nepheline, P:Pollucite, S_1:$SrAl_2Si_2O_8$(Hexagonal),
S_2:$SrAl_2Si_2O_8$(Triclinic))

Photograph 1 shows the optical micrograph through cross-nicol of the thin plate of CsA calcined for 3hr at 1100°C. Black and glittering parts correspond to pollucite (cubic) and to nepheline (hexagonal),
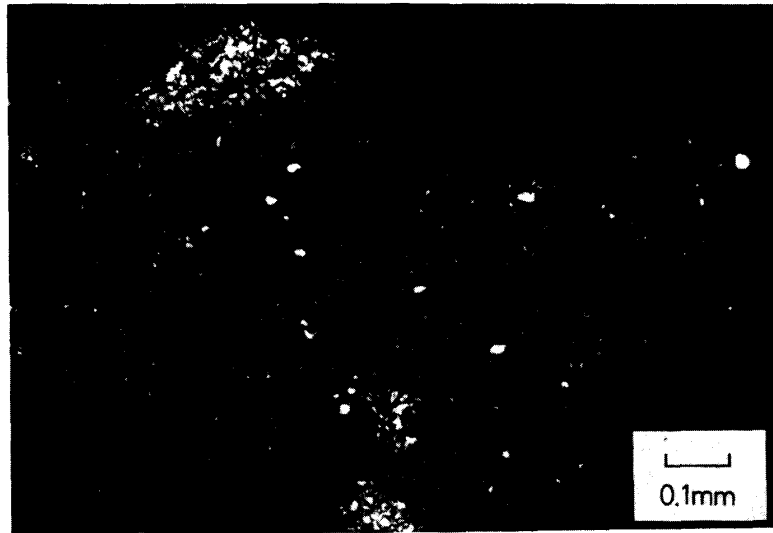

Photo. 1 Microscopic photography of calcined CsA
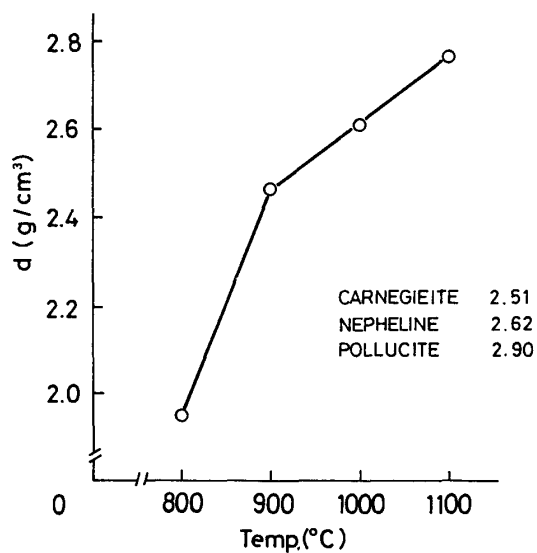(Calcining condition; 1100°C, 3hr.)

Fig. 3 Temperature dependence on the density of CsA (Calcining time: 3hr.)

respectively; these phases existed together and the partial concentration of nepheline was observed.

Figure 3 shows the temperature dependence on the density of CsA. The density increased steeply with calcining temperature of 800 to 900°C and then the slope became lower with further increase in temperature. These phenomena are corresponded to the transformation of zeolite.

The effect of calcining time on the degree of recrystallization is shown in Fig. 4. There is little difference in X-ray diffraction patterns of CsA calcined at 1100°C for 5 min. to 3hr. Figure 5 shows the effect of calcining time on the density of CsA calcined at 1100°C.
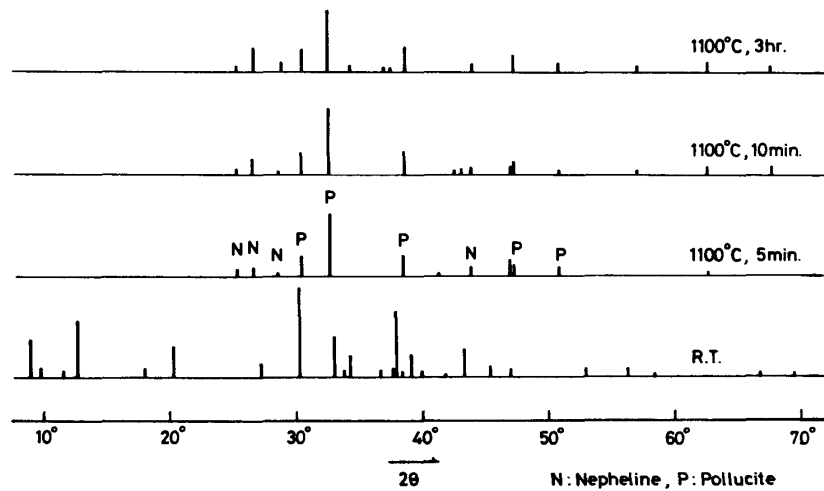

Fig. 4 Effect of calcining time on the degree of crystallization of CsA
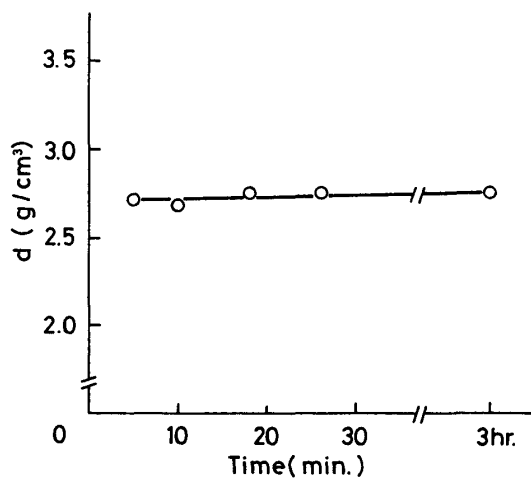(Calcining temp.; 1100°C)

Fig. 5 Effect of calcining time on the density of CsA (Calcining temp.; 1100°C)

The complete recrystallization is achieved by the calcination for a few minutes, thus the rate of crystallization seems to be fast. The density of CsA calcined at 1100°C for 3hr was 2.76 which is average value between 2.90 for pollucite and 2.62 for nepheline. This fact supports that these phases coexisted in calcined CsA zeolite. As for SrA zeolite, the recrystallization at high temperature took place also, as shown in Figs. 1 and 2(c).

2. X type zeolite

Phase transformations of different forms of zeolites at high temperature are given in Table 2. The exothermic peaks of NaX at 846 and 1055°C correspond to the recrystallization to carnegieite and to nepheline, respectively. The temperature range of crystallization to carnegieite seems very narrow, and the X-ray diffraction pattern of carnegieite was not obtained. In the case of CsX, no nepheline phase was detected and only pollucite recrystallized. Thermal behaviour of

Table 2 Phase transformation of different forms of zeolites at high temperature.

Cation / Zeolite	Na	Cs	Sr
A	900° >1000° Carn. + Neph. → Neph.	900° >1000° Carn. → (Neph. + Pol.)	800° 900 ~ 1000° >1100° Am. → Hex. → Tric.
X	850° >1000° Am. → Neph.	800 ~ 900° >1000° Am. → Pol.	800 ~ 900° 1000° >1100° Am. → Hex. → Tric.
Y	>800° Am.	1000° >1100° Am. → Pol.	900° 1000° 1100° 1200° Am. → ? → Am. → Tric.
SM	>900° Am.	1100° 1200° Am. → ?	900 ~ 1000° 1100° 1200° Am. → ? → Am.
NM	>1000° Am.	>1000° Am.	>1000° Am.
CP	>1000° Am.	>1000° Am.	>1000° Am.

Am. : Amorphous,   Carn. : Carnegieite ($NaAlSiO_4$)
Neph.: Nepheline ($NaAlSiO_4$), Pol. : Pollucite ($CsAlSi_2O_6$)
Hex.: Hexagonal ($SrAl_2Si_2O_8$), Tric.: Triclinic ($SrAl_2Si_2O_8$)

SrX is similar to that of SrA.

3. Y type zeolite

NaY was completely destroyed at 800°C and remained amorphous up to 1200°C. CsY recrystallized to pollucite above 1100°C, and this led many sharp peaks in the X-ray diffraction pattern. SrY changed to strontium aluminosilicate ($SrAl_2Si_2O_8$) at 1200°C. Some different results of X and Y may be due to the change in Si/Al ratios.

4. Synthetic mordenite

Mordenite is the most stable zeolite, hence there is no evidence of any change in the structure at temperatures as high as 800°C. Mordenite gave exothermic peaks of DTA at different temperatures for a variaty of cations; the peak of CsSM at about 1100°C indicates the destruction of mordenite structure.

5. Natural mordenite and clinoptilolite

The experiments were made with natural zeolite in order to campare with the data of synthetic mordenite. The structures of NaNM, CsNM and SrNM were stable below 800°C, and the exothermic peaks of DTA of these zeolites were observed at 1040, 1100 and 1040°C. The exothermic peak of CsNM shifted to a higher temperature region than that of NaNM. Thermal change of clinoptilolite is similar to that of mordenite. The mordenite structure is probably stabilized by exchanging the cation with the large ionic radius, and the similar result was reported for Cs form of chabazite.[8] Thus, the difference in Si/Al ratios perhaps affects the thermal behavior of zeolites.

IV. Conclusions

Thermal transformations of Na, Cs and Sr forms of zeolites were studied by the thermal analyses and the following results were obtained.

(1) NaA and NaX recrystallized to nepheline above 1000°C, but NaY, NaSM, NaNM and NaCP collapsed at about 900°C and remained amorphous to 1200°C.

(2) CsA recrystallized to nepheline and pollucite abouve 1000°C. CsX and CsY changed to only pollucite above 1000°C and 1100°C, respectively. CsSM, CsNM and CsCP did not recrystallize and became amorphous.

(3) SrA and SrX changed to $SrAl_2Si_2O_8$(Hex.) at 1000°C and to $SrAl_2Si_2O_8$(Tric.) above 1100°C. SrY recrystallized to $SrAl_2Si_2O_8$(Tric.) above 1200°C. SrSM, SrNM and SrCP did not reerystallize and remained amorphous.

(4) The difference in Si/Al ratios affects the thermal behavior of

zeolites, and the zeolites with low Si/Al ratios especially have a tendency to recrystallize easily.

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