Leachability and Thermal Properties of Ceramic Solid Forms Immobilizing Cesium and/or Strontium

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ABSTRACT

Solid forms immobilizing nuclides were prepared from Cs-mordenite and Sr-A zeolite by calcination at 1,200 °C for 1 h. Cesium and strontium were fixed in the crystal phases of pollucite (CsAlSi2O6) and Sr-feldspar (SrAl2Si2O8), respectively. The leachability of Cs and Sr was rather high in 0.1 M HNO3 leachant, while the leached percentage was lowered in 0.1 M NaOH, 0.1 M NaCl and deionized water. The recrystallized phases formed on the surface after leaching in 0.1 M NaOH resulted in the lowering of the leachability of Cs and Sr. The thermal conductivities (κ) of solid forms of Cs-MOR, Sr-A, (Cs,Sr)-A and Al-matrix (calcined Cs-mordenite dispersed in Al metal matrix) were determined to be 0.83-1.00, 0.55-0.64, 0.83-1.01 and 47 W/(m·K), respectively. The central temperature of solid forms with the same diameter was in the order of Sr-A > Cs-MOR > Al-matrix.

1 INTRODUCTION

Zeolites, a kind of aluminosilicate with three-dimensional cage structure, are well known to have a high selectivity to heat-generating nuclides, 137Cs and 90Sr, contained in high-level liquid wastes (HLLWs) [1], and they are readily converted to stable ceramic solid forms by heat treatment at high temperature [2-3]. The preparation method for large size solid forms containing Cs and/or Sr has been reported in the previous paper [4]. The evaluation of leachability and thermal property of these solid forms is of great importance, from the viewpoint of the utilization of radioactive nuclides; solid forms immobilizing 137Cs and 90Sr are potentially useful by-products for radiation and heat sources [5].

In order to evaluate the chemical durability, the leachability of Cs and Sr was investigated under different leaching conditions varying the kind of leachants, leaching period and temperature. The resultant surface alteration of the solid forms was then examined in connection with the leachability of Cs and Sr. The thermal constants of the solid forms were measured and the maximum heat loading and maximum permissible diameter were further estimated from the thermal conductivity.
2 EXPERIMENTAL

2.1 Preparation of Solid Forms

Synthetic mordenite (MOR) and zeolite A (A) were pulverized and sieved to give a particle size of 20-50, 50-100 and >100 mesh. They were contacted with 1 M CsNO₃ and/or 1 M Sr(NO₃)₂ solutions. Cesium and Sr forms of MOR and A were dried at 250 °C and then molded into a cylindrical shape by cold isostatic pressing (CIP) at 78 MPa. The molded samples were then converted into ceramic solid forms with monolithic shapes of 130 mm in diameter and 130 mm in height by calcination at 1200 °C for 1 h. The solid forms were cut to desired shapes for leachability and thermal tests. These specimens are abbreviated as Cs-MOR(20-50M), Sr-A(50-100M) and (Cs, Sr)-A(-100M), etc. Figure 1 shows the photograph of Cs-MOR(-100) solid forms cut to cubes and rectangular parallelepipeds.

![Figure 1: Solid forms cut to cubes and rectangular parallelepipeds](image)

2.2 Leach Test

The cubes of solid form (10 mm edge) were used for leach tests. The leachability of Cs and Sr was determined by varying the kind of leachants (0.1 M HNO₃, 0.1 M NaOH, 0.1 M NaCl and deionized water (DW)), leaching period (1 day – 3 months) and temperature (90 – 160 °C). After leach tests, the surface of the solid forms was analyzed with scanning electron microscope (SEM, Hitachi S4100L) and electron probe microanalysis (EPMA, Hitachi X-650S); the surface morphology was examined and the concentration profiles of Cs, Sr, Al and Si in the solid were determined by line analysis.

2.3 Measurement of Thermal Constants

Thermal conductivity (κ) of a disk specimen with 10 mm in diameter and 2.3-2.7 mm thickness was calculated from the equation of \(\kappa = \alpha \cdot C_p \cdot \rho\), where thermal diffusivity (\(\alpha\)) and heat capacity (\(C_p\)) were measured by a laser flash method (Sinku Riko, TC-7000). The sapphire attached glassy carbon with silicon grease was used as the standard material for the measurement of the heat capacity. The density (\(\rho\)) of the specimen was determined by Archimedes’ method.
3 RESULTS AND DISCUSSION

3.1 Leachability of Cs and Sr

The leachability is an important factor for the evaluation of long-term chemical durability of solid forms. The leachability of Cs and Sr was estimated under different leaching conditions. The leachability of Cs for Cs-MOR(-100M) solid forms was in the order of 0.1 M HNO₃ >> 0.1 M NaOH > 0.1 M NaCl > DW (Fig. 2(a)). In deionized water, the leached percentage was estimated to be less than 0.1% at 90 °C. The leachability of Cs in 0.1 M NaOH was almost constant, suggesting a recrystallization on the surface. On the other hand, the leached percentage of Cs in 0.1 M HNO₃ markedly increased with leaching period and was determined to be 11.0 % after 3 months-leaching at 160°C. The leachability of Sr for Sr-A (-100M) solid forms was rather high in 0.1 M HNO₃, while the leached percentage in the other leachants were less than 1.4 x 10⁻¹ % (Fig. 2(b)). The leachability of Sr in 0.1 M NaOH decreased with leaching period and temperature, showing a different tendency from other leachants.

(a) Cs/Cs-MOR
(b) Sr/Sr-A
(c) Cs/(Cs,Sr)-A
(d) Sr/(Cs,Sr)-A

Figure 2: Leachability of Cs and Sr in the different leachants
The leachability of Cs and Sr for (Cs,Sr)-A(-100M) solid forms shows a similar tendency to those for Cs-MOR and Sr-A (Figs. 2(c) and (d)). The leaching of Cs and Sr was also depressed in 0.1 M NaOH leachant.

The surface morphologies of Cs-MOR and Sr-A solid forms after leaching in different leachants at 160°C for 3 months are shown in Figs. 3 (a)-(d) and Figs. 4 (a)-(d), respectively. The surface tended to be very porous after leaching in 0.1 M HNO₃ and DW, while a number of fine precipitates were formed after leaching in 0.1 M NaCl and 0.1 M NaOH; in the case of

![Figure 3: Surface alteration of Cs-MOR solid form in different leachants at 160°C](image)

![Figure 4: Surface alteration of Sr-A solid form in different leachants at 160°C](image)
0.1 M NaOH leachant, a number of fine particles of silica (~ 10 µm in diameter) and pollucite (~ 1 µm in diameter) were recrystallized on the surface (Fig. 3(d)), resulting in the lowering of Cs leachability. The surface of Sr-A solid form after leaching in 0.1 M NaOH was also covered with fine precipitated particles of sodium aluminosilicates (Al : Si : Sr : Na= 1 : 1 : 0.1 : 1.3, molar ratio) (Fig. 4(d)).

Thus, the surface tended to be porous in 0.1 M HNO₃ and DW leachants, while the Na⁺ ions in the leachants (0.1 M NaCl and 0.1 M NaOH) acted as a component of the recrystallized precipitates formed on the surface; the precipitated particles were formed by the hydrothermal reaction between dissolved species (Al and Si) and sodium ions in the leachant [6].

### 3.2 Thermal Properties

The evaluation of thermal properties is essential for the utilization of solid forms as heat or radiation sources. The thermal conductivities (κ) of solid forms of Cs-MOR, Sr-A and (Cs,Sr)-A were determined to be 0.83-1.00, 0.55-0.64 and 0.83-1.01 W/(m·K), respectively. The maximum permissible diameters (Dₘₐₓ) of solid forms can be roughly estimated by assuming the uniform heat dissipation on the surface of a cylindrical product. For example, the Dₘₐₓ values of Cs- MOR (~100M) were estimated to be 0.18 m in the air, 0.29 m in the air (5 m/s) and 0.38 m in the water-cooling and those of Sr-A(100M) were estimated to be 0.12 m in the air, 0.19 m in the air (5 m/s) and 0.23 m in the water-cooling. In either case, the Dₘₐₓ value was largest in the water-cooling [5].

In order to increase the thermal conductivity of the solid form, the Al-matrix products were further prepared by dispersing the sintered Cs-mordenite granules in the molten Al metal (Fig. 5); this product was produced by the injection of molten Al under reduced pressure in...
the column packed with particles of calcined Cs-mordenite. The calcined Cs-mordenite is seen to be uniformly dispersed in the Al metal (Fig. 6). The $\kappa$ value of Al-matrix product was determined to be 47 W/(m·K) and the $D_{\text{max}}$ value was estimated to be 2.14 m in the water-cooling due to its relatively high thermal conductivity.

The central temperatures are estimated by varying the diameter of the solid forms as shown in Figs. 7 and 8. The central temperature ($T_c$) at the same diameter was in the order of Sr-A(-100M) > Cs-MOR(-100M) > Al-matrix; for example, the $T_c$ values in the air for the

![Figure 7: Effect of diameter of solid form on central temperature in the air](image1)

![Figure 8: Effect of diameter of solid form on central temperature in the water](image2)
solid forms of Sr-A(-100M), Cs-MOR(-100M) and Al-matrix (0.1 m in diameter) were estimated to be 776, 443 and 325°C, respectively. Here the softening temperatures of solid forms of Sr-A(-100M), Cs-MOR(-100M) and Al-matrix were determined to be 1040, 957 and 660 °C by thermal analysis (DTA and TG), respectively.

4 CONCLUSIONS

Large solid forms immobilising nuclides were prepared from Cs-mordenite and Sr-A zeolite by calcination at 1,200 °C for 1 h. Cesium and strontium were dispersed in the crystal phases of pollucite (CsAlSi2O6) and Sr-feldspar (SrAl2Si2O8), respectively. The calcined Cs-mordenite particles were further dispersed in the molten Al metal and the Al-matrix product were obtained.

The leachabilities of Cs and Sr for solid forms were rather high in 0.1 M HNO3 leachant, while the leached percentage was lowered in 0.1 M NaOH, 0.1 M NaCl and deionized water. The recrystallized phases formed on the surface after leaching in 0.1 M NaOH resulted in the lowering of the leachability of Cs and Sr.

The thermal conductivities ($\kappa$) of solid forms of Cs-MOR, Sr-A, (Cs,Sr)-A and Al-matrix (calcined Cs-mordenite dispersed in Al metal) were determined to be 0.83-1.00, 0.55-0.64, 0.83-1.01 and 47 W/(m·K), respectively. The maximum permissible diameter was estimated by assuming the uniform heat dissipation on the surface of a cylindrical product. The central temperature at the same diameter of the solid form was in the order of Sr-A > Cs-MOR > Al-matrix.

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REFERENCES


