Hydrothermal Treatment of Radioactive Waste:
Solidification of High-Level Radioactive Waste by Hydrothermal Hot-Pressing

Kazumichi Yanagisawa, Mamoru Nishioka, Nakamichi Yamasaki

Research Laboratory of Hydrothermal Chemistry,
Faculty of Science, Kochi University,
Akebono-cho 2-5-1, Kochi-shi 780

Abstract

Simulated high-level radioactive waste was immobilized into a silica matrix by hydrothermal hot-pressing. The optimum conditions to produce a waste form with high mechanical strength and low leachability were determined as follows; starting composition: 21.8wt% waste, 10wt% $Al(OH)_3$, 47.7wt% low-quartz and 20.5wt% amorphous aluminosilicate with the addition of 10N NaOH solution (2.5 cm^3 /20g of starting powder), reaction temperature: 350 ℃, reaction pressure: 66 MPa, reaction time: 6 hours.

The waste form produced under the optimum conditions was mainly composed of low-quartz of the matrix and the waste components (Fe_2O_3, CeO_2, ZrO_2). It was porous, apparent density 2.3 g/cm^3, porosity over 20%, and BET specific surface area 10 m^2/g. It had high mechanical strength, compressive strength 200MPa. The leach rate of the waste form, determined by static leach tests at 90℃ in distilled water for 28 days, was much lower than a concrete waste form and was comparable with glass and ceramic waste forms. The waste form was stable under hydrothermal conditions in comparison with a glass waste form. It had high thermal and thermal shock resistance. Its thermal conductivity was about 0.01 J/cm·sec·K, a value similar to that of a glass waste form.

1. Introduction

In natural circumstances, mineral particles in sediment are transformed into sedimentary rock by a chemical process that reduces the original porosity by compaction and cementation[1]. In laboratories, aggregation of particles by means of dissolution and deposition is usually observed when a large amount of silica powder is hydrothermally treated by a small amount of alkaline solution. In order to enhance the densification to produce hard compacts like sedimentary rock, the solution must be removed from grain boundaries. A hydrothermal hot-pressing technique is intended for artificial transformation of powders into densified bodies under hydrothermal conditions[2]. In this method, an inorganic powder including water or alkaline mineralizer solution is mechamically compressed under hydrothermal conditions from outside an autoclave to expell the medium from grain boundaries, and linkage of grains by the action of hydrothermal solution results in conversion of the powder to a solidified body with high mechanical strength.

The hydrothermal hot-pressing method has two characteristics; continuous compression of starting powder under hydrothermal conditions and space for water retreat. Compression accelerates compaction of the starting powder and prevents development of cracks due to heterogeneous shrinkage. Compaction depends on the rate at which water can be expelled from the starting powder. The space water for retreat, into which water included in the starting powder is released, is essential to the hydrothermal hot-pressing technique. Without the space, water exists in pore space of the starting powder and hinders compaction of the powder.

Under hydrothermal conditions, increase in solubility of many inorganic compounds results in linkage of their particles by means of dissolution and deposition, and the compounds react with each other to produce new compounds with low solubility, which may contribute to cementation of the particles.

Solidified bodies of silica powders such as low-quartz and borosilicate glass[3-6], mixtures of silica powders with metal hydroxides or oxides[7,8], calcium carbonate[9], zirconia[10], and hydroxyapatite[11] have been produced by the hydrothermal hot-pressing technique. Alkaline solutions accelerated the densification of silica powders. Borosilicate glass powders included glass network modifying oxides were densified even by the addition of pure water at low temperatures below 300℃[5]. Shrinkage of the powder started by viscous flow mechanism after soluble components in the glass, such as alkaline metal, were dissolved into water under hydrothermal conditions[6]. Futhermore, this method has applied to immobilization of high-level[12-15] and low-level radioactive

wastes[16,17]. This paper deals with the immobilization of high-level radioactive wastes by hydrothermal hot-pressing.

The most generally accepted concept for disposal of high-level radioactive wastes is to incorporate it into a solid waste form that is placed into a deep geologic repository[18]. The waste form is a first barrier in multiple barrier system.

Many kinds of the waste forms have been proposed to immobilize high-level radioactive wastes. Immobilization into borosilicate glass is considered to be the most realizable process. The process is appealing because of its relative simplicity and utilization of conventional glass-making technology. In a quantitative evaluation of candidate waste forms, the high process rating for borosilicate glass and its intermediate product performance score resulted in the overall top-ranking position[19]. It is, however, obvious that glass is thermodynamically unstable relative to a chemically equivalent assemblage of crystalline phases[20]. Under some circumstances, it may devitrify to form the stable crystalline assemblage.

The immobilization of the wastes into crystalline phases has been researched for supercalcine[21-23], synroc[20,24,25], high-alumina tailored ceramics[26-28], and so on. The production process of these ceramic waste forms is rather complicated, though the waste forms produced by the processes have excellent properties in comparison with the glass waste forms.

These processes mentioned above require high temperatures above 1000 ℃, which may cause evaporation of volatile radioactive isotopes and corrosion of the process equipment.

Solidification with cement is cost-effective for immobilization of the wastes, because of its ease of processing[29,30]. Concretes formed under elevated temperatures and pressures (FUETAP concretes), however, have higher leach rates than those of other waste forms[19,29].

The hydrothermal hot-pressing technique would be useful to solidification of radioactive wastes, because powders of silica mixed with metal oxides and hydroxides were easily converted to solidified bodies by this technique[7,8]. The technique has the following advantages as a process for solidification of high-level radioactive wastes;

   (1) Simplicity of an apparatus and ease of operation.

   (2) Low temperature reaction around 300 ℃.

   (3) Reaction in closed system (solidification in an autoclave), which prevents evaporation of volatile materials.

   (4) Low leachability of the solidified bodies, which is supported by the fact

that soluble components in the wastes can be reacted under hydrothermal conditions with each other or a silica matrix to form crystalline phases with low solubility.

(5) Stability of the solidified bodies under repository conditions, because of the products formed under hydrothermal conditions.

In this paper, a simulated high-level radioactive waste was solidified using a silica matrix composed of low-quartz and amorphous aluminosilicate by hydrothermal hot-pressing. The effects of hydrothermal hot-pressing conditions on compressive strength and leachability of the waste forms were investigated to dertermine the optimum conditions to produce a waste form with high mechanical strength and low leachability. The properties of the waste form produced under the optimum conditions were clarified.

2. Experimental

2 — 1 Starting Materials

The silica matrix was a mixture of 70wt% low-quartz powder passed through a 200 mesh (silicastone from Fukushima Prefecture, Japan) and 30wt% amorphous aluminosilicate (siliceous sinter, porous and friable rock deposited by the water of hot springs, from Kagoshima Prefecture, Japan). Their chemical analyses are shown in Table 1. In some cases, $Al(OH)_3$ (Wako Pure Chem. INd., LTD) was added to the mixture. The composition of a simulated high-level radioactive waste from reprocessing of nuclear fuels is shown in Table 2. It was estimated by Japan Atomic Energy Research Institute (JAERI), and Tc, Pm, Ru, Rh, Pd and actinides were simulated by Mn, Nd, Fe, Co, Ni and Ce, respectively[31]. In the waste, Na was not added because NaOH solution was used as a mineralizer to accelerate the solidification by hydrothermal hot-pressing. The waste was prepared by mixing appropriate chemicals in a ball mill.

2 — 2 Apparatus for Hydrothermal Hot-Pressing

An autoclave for hydrothermal hot-pressing used in this study is shown in Fig.1. The cell is made of Hastelloy-C and is composed of an inner and an outer case. The inner case, 1.4cm in inner diameter, is divided into three parts in order to remove a solidified body from the cell without its destruction. The outer case is used to keep the inner case in cylindrical shape. The autoclave is made of carburizing steel with a liner of Hastelloy-C. It has the space for water retreat (about $25cm^3$) unoccupied by the cell. The starting powder in the cell is uniaxially compressed during hydrothermal treatment, via the push rod of the autoclave with gland packing to prevent leakage.

Table 1. Chemical Analyses of Starting Materials (wt%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Other oxides	Ignition loss
Silicastone [*1]	99.5	0.2	0.02	0.02	0.01	0.25	0
Siliceous sinter [*2]	71.7	12.9	2.3	2.4	0.4	5.7	4.6

*1 ; from Fukushima Prefecture, Japan.

*2 ; from Kagoshima Prefecture, Japan.

Table 2. Composition of Simulated High-Level
Radioactive Waste (wt%)

Fe_2O_3	39.05	SrO [*3]	1.69
MoO_3	8.66	Sm_2O_3	1.64
Nd_2O_3	8.24	MnO_2	1.29
ZrO_2	8.21	TeO_2 [*4]	1.12
CeO_2	6.77	CoO	1.00
NiO	4.92	Y_2O_3	1.00
Cs_2O [*1]	4.88	Rb_2O [*1]	0.61
BaO [*3]	3.12	Gd_2O_3	0.19
La_2O_3	2.54	CdO [*1]	0.16
Pr_6O_{11}	2.47	Ag_2O [*1]	0.15
Cr_2O_3	2.26	Sb_2O_3 [*2]	0.13

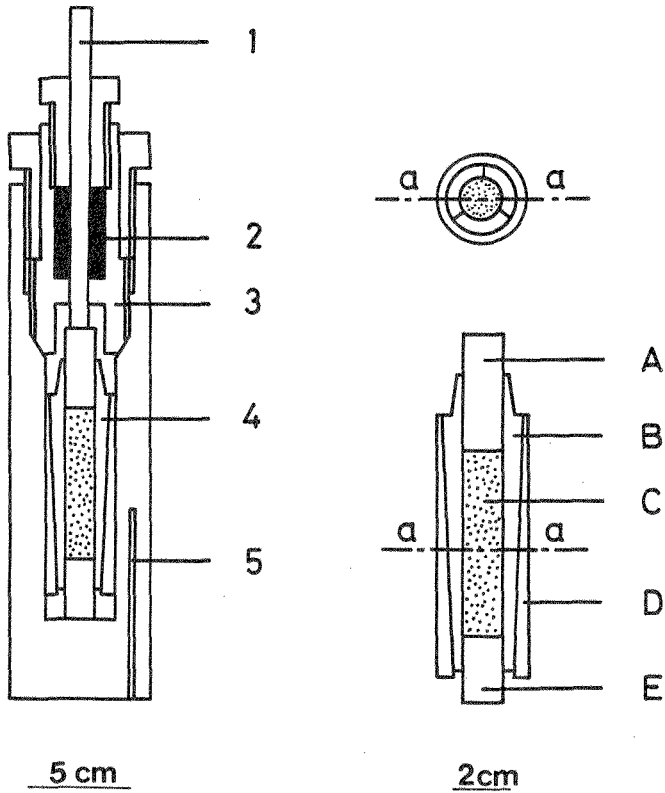Added as *1 nitrate, *2 chloride, *3 carbonate, *4 metal.

Fig.1 Autoclave and cell for hydrothermal hot-pressing.
  Autoclave(left) made of carburizing steel lined with Hastelloy-C:
        1.push rod, 2.gland packing (copper and cotton yarn),
        3. cone, 4.cell, 5.well for thermocouple.
  Cell(right) made of Hastelloy-C:
        A,E. piston, B. inner case, C. sample, D. outer case,
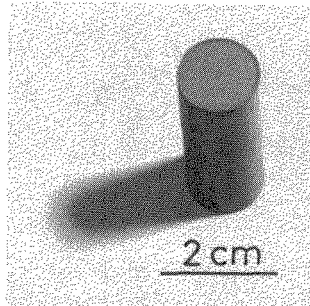   The upper figure is a cross-section of aa.

Fig.2 A typical waste form produced by hydrothermal hot-pressing.

2 — 3 Solidification Method

The waste was mixed well in a porcelain motar with the silica matrix to prepare a starting dry powder. The waste loading was expressed as oxides. The dry powder (20g) was kneaded in the motar with a NaOH solution (2.5cm³) to prepare a starting wet powder. The wet powder was transferred into the hot-pressing cell and the cell was put into the autoclave. The autoclave was heated to a desired temperature from 100 to 350℃ at the rate of 30℃/min by an induction heater, and the temperature was kept constant for 0 to 6 hours. During hydrothermal treatment, the powder in the cell was continuously compressed at 17 to 66 MPa. After the treatment, the autoclave was cooled down to room temperature at the rate of about 20℃/min by an electric fan, and a solidified body was taken out of the cell. A typical waste form produced by hydrothermal hot-pressing is shown in Fig.2.

2 — 4 Leach Tests

Three types of leach tests were performed to evaluate the chemical durability of the waste forms; (1) flow leach test by Soxhlet type apparatus, (2) Static leach test under hydrothermal conditions, (3) modified MCC-1 low temperature static leach test.

(1) Flow leach test: Soxhlet type apparatus was constructed of fused silica glass. Cyrindrical specimens for the test (1.4cm in diameter, about 0.8cm in height) were fabricated by diamond-sawing and dry-abrading. The test was performed at 97℃ for 29 days.

(2) Static leach test under hydrothermal conditions: The autoclave for the test, 27.7cm³ in inner volume, was made of carburizing steel and linned by titanium. Buckwalter and Pederson [32] used many kinds of leaching containers for leach tests of a simulated nuclear waste containment glass and reported that relatively minor effects on glass leaching were found in titanium containers in comparison with those measured in Teflon containers. The leachant was distilled water (15cm³). Cubic specimens (5x5x5 mm^3) were fablicated by diamond-sawing and dry-abrading, giving a specimen surface area / leachant volume ratio 1/10 cm $^{-1}$. The test was performed under hydrothermal conditions up to 350℃ for 1 day. Monolithic glass specimens of JW-A glass waste form (containing the same simulated waste (21.8wt%) that used in this study, prepared by JAERI) were also used for the test.

(3) MCC-1 static leach test: MCC-1 leach test [33,34] is a static low temperature leach test, one of the standard leach tests proposed by the Nuclear Waste Materials Characterization Center established by the U.S.

Department of Energy, to develop standard tests for characterization of the components of the waste package, which include spent fuel, waste forms and so on. The leaching container, 130cm³ in inner volume, was made of Teflon. The leachant was distilled water (40cm³) and each cubic specimen for the test (8.2x8.2x8.2 mm³), fabricated by diamond-sawing and dry-abrading, had surface area of 4cm². The test was performed at 40 and 90 ℃ up to 91 days. The leachant was changed to fresh distilled water when weight loss of a specimen was measured, that is, 3, 7, 14, 28, 56 days in leaching time in this modified MCC-1 leach test.

All leach tests were conducted in duplicate. After the leach tests, each leachant was analyzed by atomic absorption spectrometry. Weight loss was calculated by weight change of a specimen dried at 110 ℃ before and after the leach tests, and normalized by dividing only by geometric surface area of the specimen. Weight loss and elemental mass loss appeared in figures indicated the sum up to a leaching time.

2 − 5 Characterization

The solidified waste forms were cut with a diamond saw to 1.6cm-long sections and dried at 110 ℃ to prepare specimens for strength and density measurement. Uniaxial compression tests were performed at room temperature to measure compressive strength. The compression axis was perpendicular to the base of the cylindrical specimens. The crosshead travel rate of a mechanical machine (Shimazu, RH-100) was 0.02cm/min. The density of the waste form was measured from its weight and apparent volume. The crystalline phases were identified by X-ray powder diffraction (Rigaku 2012). A polished section was examined by a scanning electron microscope (Hitachi S-530). The specific surface area was measured by BET method using N_2 gas as an adsorbent.

The waste forms were heated from 300 to 900℃ for 6 hours, and the weight loss by evapolation was measured. Soxhlet leach tests of the heated specimens were also performed for 1 day. The waste forms heated at 500 ℃ were quenched into water and then their compressive strength was measured. The thermal conductivity of the waste form was calculated from the thermal diffusivity and the specific heat measured at 25 to 900℃ in vacuum (10^{-3}mmHg) by laser flash method (Rigaku PS-7).

3. Results and Discussion

3 — 1 Effect of Hydrothermal Hot-Pressing Conditions on Properties of
       Waste Forms

The weight loss by leach tests at 200℃ for 1 day, the density and the compressive strength of the waste forms (21.8wt% waste loading) produced by the use of the silica matrix containing 70wt% low-quartz and 30wt% amorphous aluminosilicate are shown in Fig.3, vs the hydrothermal hot-pressing condtions; NaOH concentration, reaction temperature, pressure and time.

The increase in the concentration of NaOH solution from 3 to 10N increased the compressive strength and the density(Fig.3A). Above 12N, the strength was reduced and the density was kept constant at $2.7g/cm^3$. The highest compressive strength was achieved by the use of 10N NaOH solution. The weight loss was exponentially increased with the increase in NaOH concentration.

The density was linearly increased along with the increase in the reaction temperature (Fig.3B). The compressive strength was also increased above 150 ℃ and a peak appeared at 100 ℃, at which the amorphous aluminosilicate in the silica matrix began to dissolve in a concentrated NaOH solution to form water glass. The waste form with high compressive strength and low weight loss was produced at 350℃.

The high reaction pressure increased the compressive strength and the density, but reduced the weight loss (Fig.3C). The reaction time up to 30 minutes increased the strength and the density (Fig.3D). The long reaction time (6 hours) reduced the weight loss. It was suggested that the densification of the starting powder was achieved in a short time up to 30 minutes but the hydrothermal reaction of the waste with the silica matrix took time to produce reaction products with low solubility.

Effect of the composition of the starting powder on the leachability, the density and the compressive strength of the waste forms is shown in Fig.4. The starting powder including even 70wt% waste could be solidified to a waste form with high compressive strength over 150MPa (Fig.4A). The waste form with about 20wt% waste loading had high compressive strength and low leachability. Effect of each waste component on solidification of the silica matrix was examined by hydrothermal hot-pressing at 300℃ and 28MPa for 3 hours [7]. When Fe_2O_3 was added to the matrix, a small amount of acmite ($NaFeSi_2O_6$) was formed. Formation of acmite obstructed the linkage of low-quartz grains and reduced the compressive strength of the solidified bodies. On the other hand, addition of ZrO_2 gave no reaction products and accelerated the shrinkage of the starting powder. The compressive strength was also increased to 600MPa by the addition of
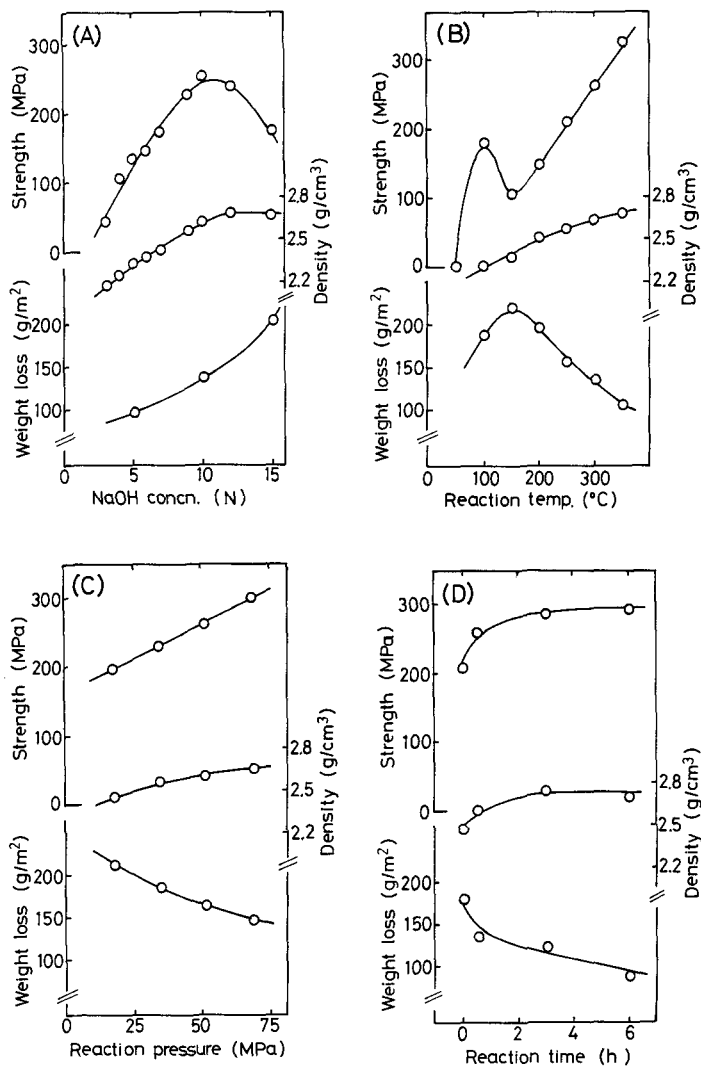
Fig.3 Effect of hydrothermal hot-pressing conditions on properties of waste
forms.
(A) NaOH concentration, (B) Reaction temperature, (C) Reaction pressure,
(D) Reaction time.
Each hydrothermal hot-pressing condition was varied from the standard
condition, i.e., 10N NaOH solution, 300℃, 49MPa, 30 minutes.
Compressive strength, bulk density and weight loss by leach tests at
200℃ for 1 day in distilled water of the produced waste forms, were
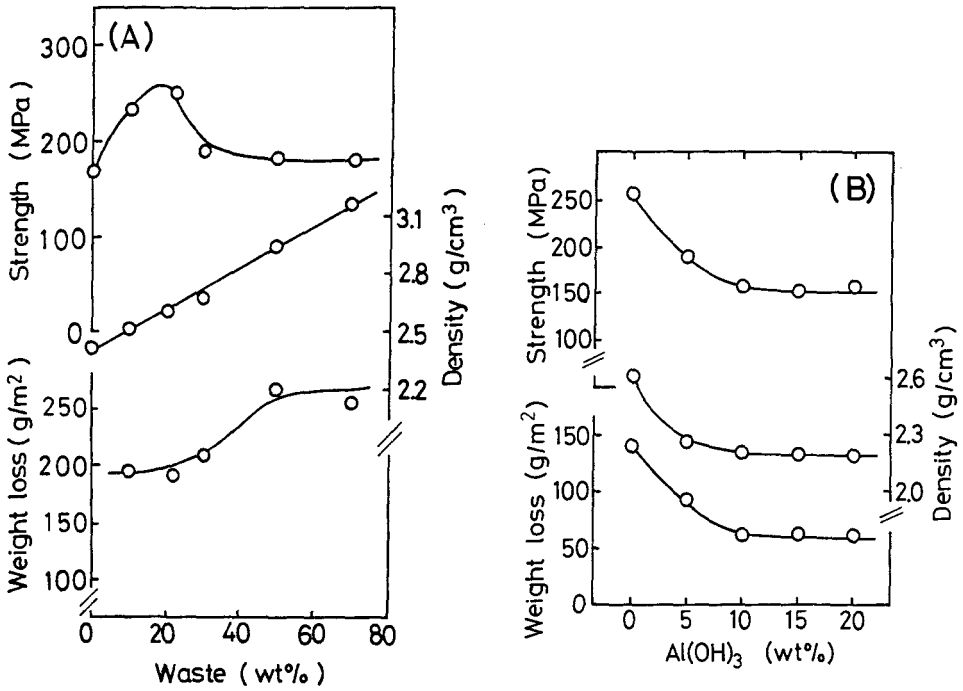measured.

Fig.4 Effect of starting composition on properties of the waste forms.
The waste forms were produced under the standard condition.
(A) Waste loading : Leach tests were performed at 300℃ for 1 day.
(B) Al(OH)₃ addition : Waste loading was 21.8wt%. Leach tests were
performed at 200 ℃ for 1 day.

10wt% ZrO_2. Thus, ZrO_2 in the waste might cause the increase in compressive strength of the waste forms. The density of the waste forms was increased with the increase in waste loading, because the density of the waste was higher than that of the matrix.

The analyses of the leachants showed that the release of Na and Si caused the large weight loss by leach tests. If Na is immobilized into crystalline phases such as aluminosilicates with low solubility, the release of Si from a waste form by leach tests should be also reduced because of the decrease in pH of the leachnts. In order to immobilize Na, $Al(OH)_3$ was added to the starting powder. The addition of $Al(OH)_3$ up to 10wt% reduced the weight loss by the leach test, as well as the compressive strength (Fig.4B); the addition of over 10wt% had no effect on either. The density had the same tendency.

Sodium aluminosilicates such as analcite ($NaAlSi_2O_6 \cdot H_2O$) were easily produced from low-quartz and $Al(OH)_3$ within 10 minutes in 5N NaOH solution under hydrothermal conditions at 300 ℃, though the amorphous aluminosilicate of the matrix component was almost completely dissolved into the solution to form water glass and gave no crystalline phase by the same hydrothermal treatment [35]. Thus, Na might be immobilized in aluminosilicates by the reaction with $Al(OH)_3$ and low-quartz during hydrothermal hot-pressing. It was confirmed by separate experiments [36] that Cs could be immobilized into pollucite structure ($CsAlSi_2O_6$), one of the most stable hosts for Cs immobilization, by the same hydrothermal hot-pressing technique using the silica matrix including $Al(OH)_3$.

It was concluded that a waste form with high compressive strength and resistance to leaching could be produced from the mixture of 10N NaOH solution and the starting powder (21.8wt% waste, 10wt% $Al(OH)_3$, 47.7wt% low-quartz, 20.5wt% amorphous aluminosilicate) by hydrothermal hot-pressing at high temperature (350 ℃) and high pressure (66MPa) for a long time (6 hours).

3 − 2 Evaluation of The Waste Form Produced under The Optimum Conditions

Properties of the waste form produced under the optimum conditions mentioned above were clarified to evaluate the waste form produced by hydrothermal hot-pressing.

3 − 2 − 1 Physical Properties

A polished section of the waste form and its Si Kα X-ray image are shown in Fig.5. The X-ray image showed that large grains were low-quartz of the matrix and the waste components existed between low-quartz grains. The waste
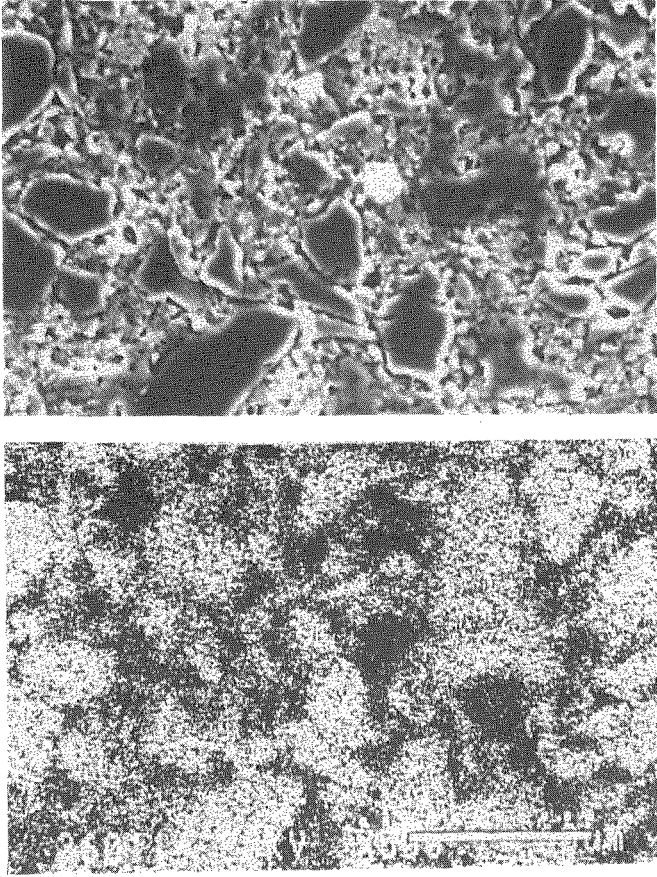
Fig.5 Polished section of the waste form (above) and its Si Kα X-ray image
(below).   (bar:50 μm)

form had many pores and slightly water permeable. Its apparent density was 2.3g/ cm^3 and the density measured by the use of a pycnometer was 2.73 g/cm^3. The waste form might have closed pores, so that its porosity was estimated to be Over 20%. Its specific surface area was found to be 10 m^2/g by BET method.

According to X-ray powder diffraction patterns (Fig.6), the waste form was mainly composed of low-quartz, the main constituent of the silica matrix. Peaks due to α-Fe_2O_3, CeO_2 and ZrO_2 were observed with low intensity. The diffraction patterns showed that MoO_3 and Nd_2O_3 in the waste were disappeared by hydrothermal hot-pressing. A few new peaks with low intensity, probably due to hydrothermal reaction products, were observed, though they were not identified yet. As concerns Sr and Cs, they were immobilized into silicate ($SrSiO_3$) and aluminosilicate ($CsAlSi_2O_6$), when each of them was hydrothermally hot-pressed with the silica matrix.

The compressive strength of the waste form (about 200MPa) was higher than that of concrete waste forms (40-100MPa [29]), and correspoded to that of a glass waste form (269MPa [37]). The thermal conductivity of the waste form produced by hydrothermal hot-pressing was reduced with the increase in temperature up to 500℃ and then incresed above 700℃. The value of the thermal conductivity was in the range from 0.008 to 0.012 J/cm·sec·K, similar to that of a glass waste form (0.009 and 0.0125 J/cm·sec·K at room temperature and 400 ℃, respectively [37]).

After the waste form was heated at various temperatures for 6 hours, the weight loss by evaporation and by Soxhlet leach test for 1 day was merasured (Fig.7). The evaporation loss was increased with the increase in heating temperature and reached 2wt% at 900 ℃, probably due to evaporation of hydrated water and anions in the waste such as NO_3^-, CO_3^{2-}, and Cl^-. The waste form heated at 500℃ had hygroscopity. The weight loss by the leach tests was decreased by heating above 300℃. The release of Mo was especially decreased by heating the waste form above 700℃. The waste form was not melted and had no cracks even by heating at 900℃. The heat treatment at 900 ℃ gave no large changes in X-ray powder diffraction patterns (Fig.6). After quenched from 500℃ , the waste form had no cracks and its compressive strength was about 120MPa. On the other hand, many cracks were observed in the quenched JW-A glass waste form.

3 — 2 — 2 Chemical properties

The weight loss of the waste form due to leaching under hydrothermal conditions is shown in Fig.8, together with that of JW-A glass waste form. The
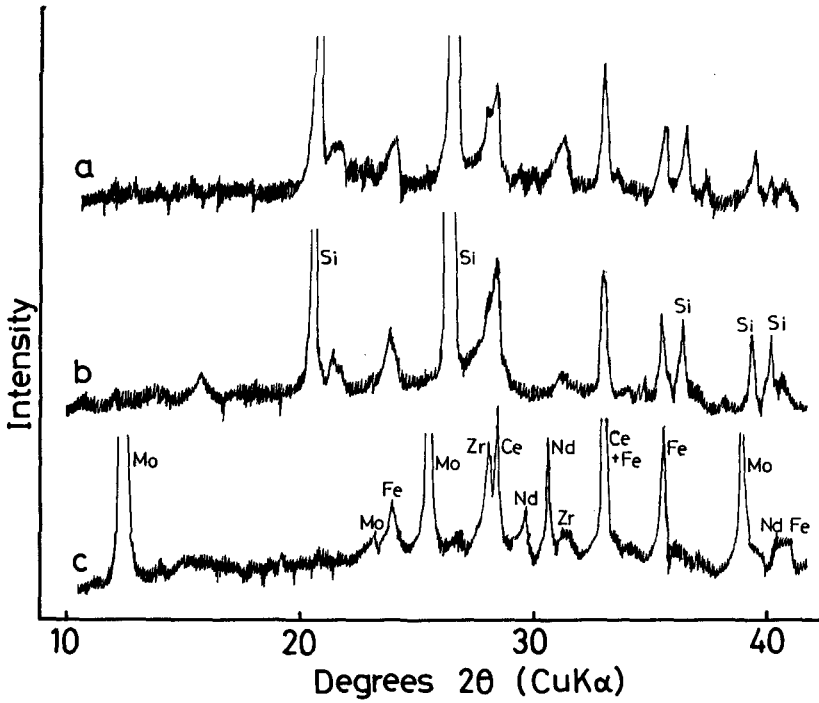
Fig.6 X-ray powder diffraction patterns of the starting simulated waste (a), the waste form produced by hydrothermal hot-pressing (b) and the waste form after heated at 900 ℃ for 6 hours (a).
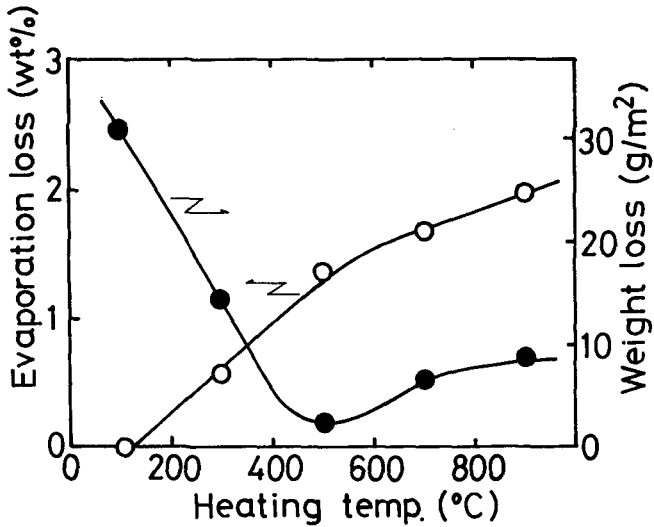

Fig.7 Effect of heat treatment of the waste form on evaporation loss and weight loss by Soxhlet leach tests for 1 day.
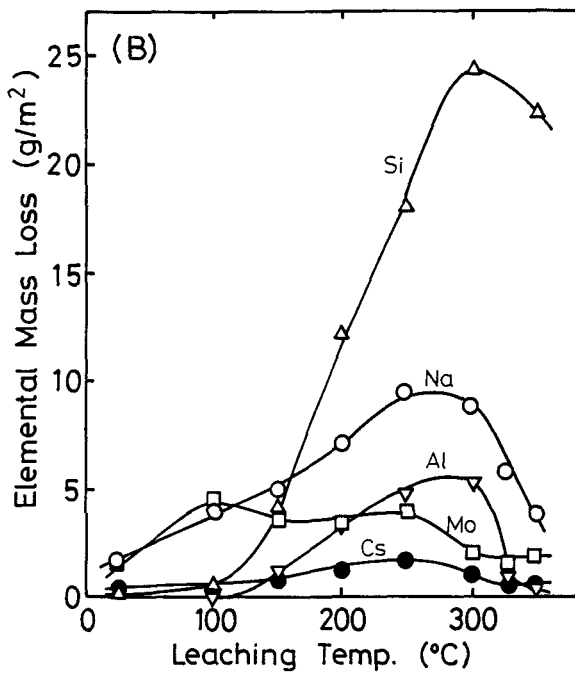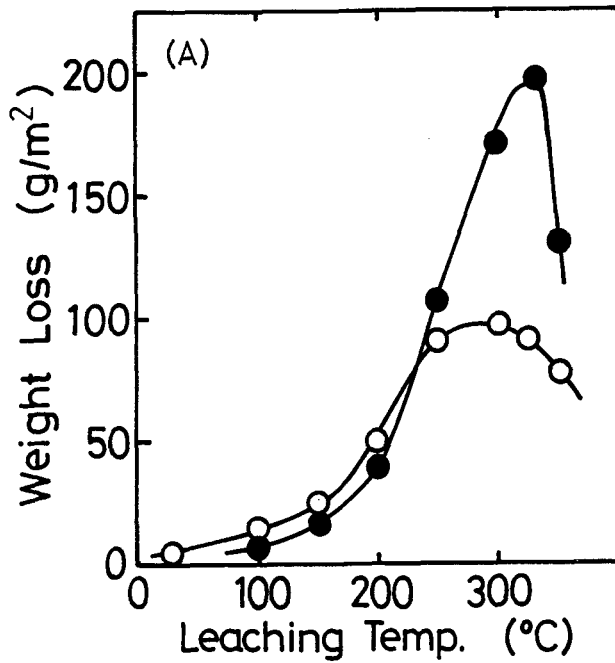
Fig.8 Results of leach tests under hydrothermal conditions for 1 day.

(A) Weight loss of the waste form produced by hydrothermal hot-pressing
(○) and of JW-A glass form (●).

(B) Elemental mass loss of the waste form produced by hydrothermal
hot-pressing.

weight loss of the waste form was smaller than that of the glass waste form at high temperatures above 250 ℃, but larger below 200℃. The elemental mass loss showed that release of Na and Mo was large at low temperature below 100 ℃ and the release of Si, Na and Al caused the large weight loss at high temperature. When the glass waste form was leached above 150 ℃, a reaction layer was produced on its surface. The thickness of the layer was increased with the increase in leaching temperature. The glass waste form leached above 325℃ was swelled and surrounded by a yellow reaction layer, about 1 mm in thickness (Fig.9). The waste form produced by hydrothermal hot-pressing had no reaction layer and maintained the shape before leaching.

The results of Soxhlet leach test are shown in Fig.10. The leach rate was remarkably reduced with the increase in leaching time, because the weight loss at initial stage of the leach test up to 6 hours was very large. After the leach test for 29 days, the leach rate reached 5.3 g/$m^2 \cdot$d, which was higher than that of a glass waste form (2 g/$m^2 \cdot$d [38]). It may be reduced by further long-time leach tests. In leachants, Sr was not detected. The amount of each element released from the waste form by the leach test up to 6 hours was very large. The release rate of each element was reduced up to 8 days and was constant over 8 days. The amount of Si was largest in released elements by the leach test for 29 days.

The results of MCC-1 leach test are shown in Fig.11. The weight loss by short-time leach tests up to 3 days was very large, as seen in the results by Soxhlet leach test. The leach rate calculated from the weight loss by MCC-1 leach test at 90 ℃ for 3 days was 7 g/$m^2 \cdot$d and was reduced to 0.9 g/$m^2 \cdot$d after the leach tests for 91 days. According to the elemental mass loss, Na and Mo were easily released by the short-time leach tests. In the waste components, MoO$_3$ might change to sodium molybdate under alkaline hydrothermal conditions. It may be expected that the addition of alkaline-earth metals to the starting powder reduces the leachability because of the formation of alkaline-earth metal molybdate such as CaMoO$_4$ and SrMoO$_4$, which are stable phases with low solubility under repository conditions [39].

The high leach rate of the waste form by the short-time leach tests was explained as follows: The waste forms produced by hydrothermal hot-pressing have many pores, which have been filled with the mineralizer during hydrothermal treatment. The minelralizer may include Na, Si, Al, and soluble elements of the waste components. These elements are not immobilized enough only by drying at 110 ℃ before leach tests and are easily released by an initial washout through porous structure of the waste forms. The same phenomenon was
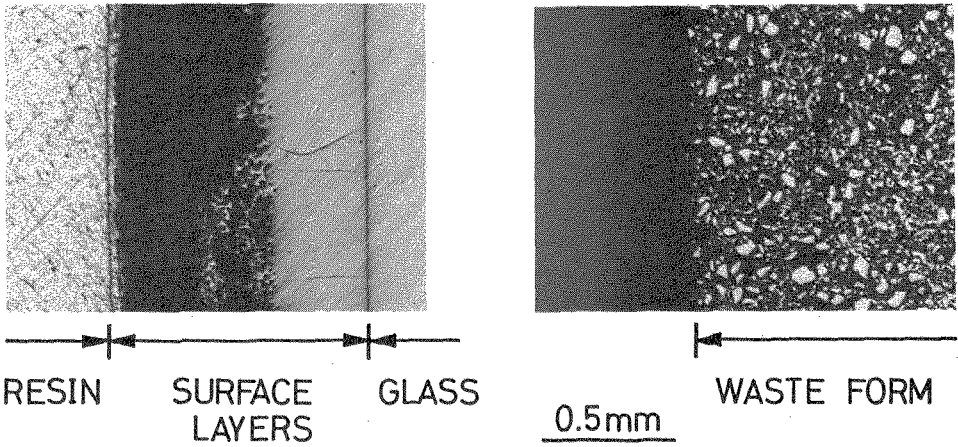
RESIN   SURFACE   GLASS   WASTE FORM
LAYERS   0.5mm

Fig.9 Cross section of specimens leached at 325℃ for 1 day.
JW-A glass form (left) and the waste form produced by hydrothermal
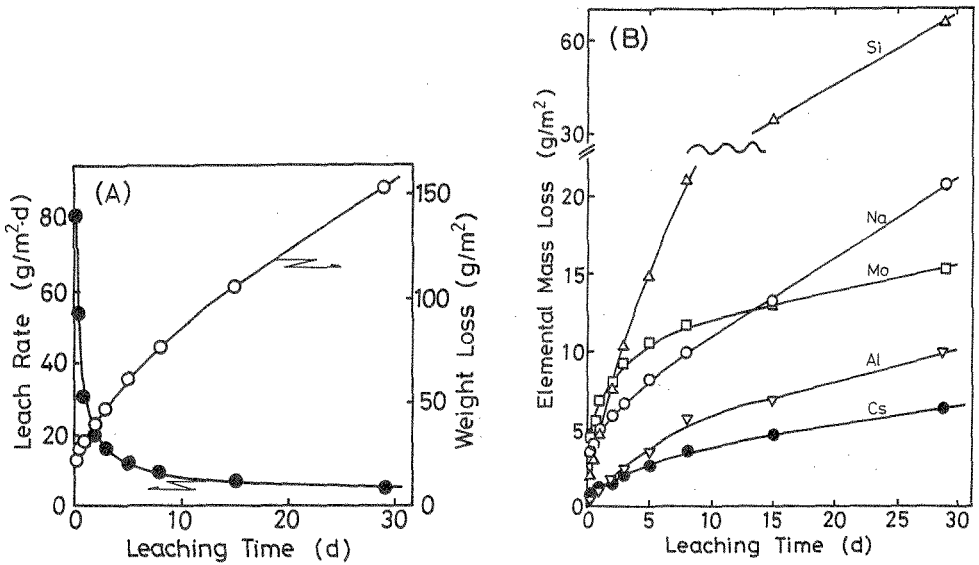hot-pressing (right).

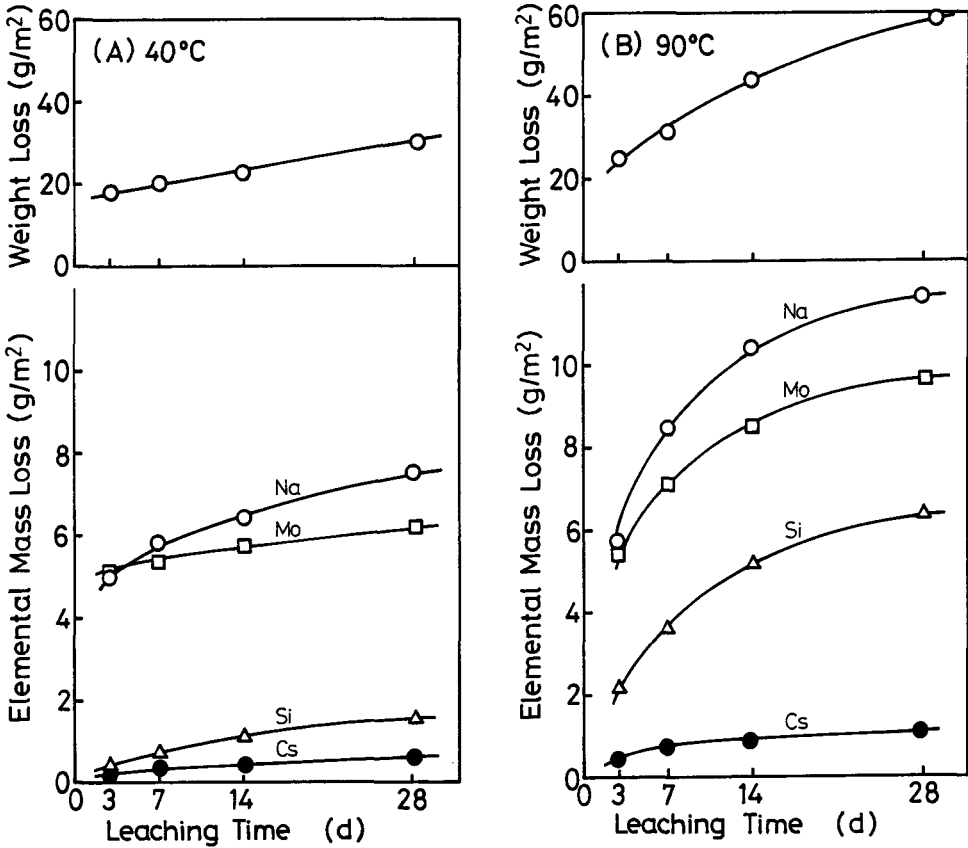Fig.10 Leach rate and weight loss (A) and elemental mass loss (B) by Soxhlet
leach tests.

Fig.11 Weight loss and elemental mass loss by modified MCC-1 leach tests at 40 ℃ (A) and 90 ℃ (B).

found when the FUETAP concretes were leached [29]. Furthermore, selective leaching of glass phases was observed in ceramic waste forms [40,41]. In the case of the waste form produced by hydrothermal hot-pressing, a constant leach rate might be achieved after the initial washout followed by the selective leaching of soluble phases. It took 8 days by the Soxhlet leach test to reach a constant leach rate.

Normalized elemental mass loss is usually given by the following equation [34];

$$NL_i = M_i / F_i / SA$$

where NL_i is normalized elemental mass loss (g/ m^2), M_i mass loss of element "i" in leachant (g), F_i fraction of element "i" in unleached waste form (unitless) , SA specimen surface area (m^2).

Normalized leach rate of each element (NL_i / leaching time) is shown in Table 3, assuming that a batch of the starting powder gaves a waste form of 20g with 21.8wt% waste loading. The leach rate of Sr was not presented bacause Sr was not detected by any leach tests. The leach rate of Na and Mo was large in all leach tests. The leach rate of Cs, Al and especially Si was increased by the Soxhlet leach test more than that of Na and Mo. By further long-time leach tests, the leach rate of all elements would be reduced.

The leach rate of the waste form produced by hydrothermal hot-pressing was compared with that of other waste forms (Table 4). The leach rate of Cs from the waste form was extremely lower than that of the FUETAP concrete waste form but was higher than that of the borosilicate glass waste form. According to the results of Cs immobilization by hydrothermal hot-pressing using the same silica matrix[36], the waste form including 10wt% CsOH produced at 300 ℃ and 49MPa for 24 hours, consisted of pollucite and low-quartz as crystalline phases, and had low leach rate of Cs, 3.15 g/ $m^2 \cdot d$, determined by Soxhlet leach test for 7 days. It suggested the possibility that a high-level radioactive waste form with lower leachability of Cs would be produced by hydrothermal hot-pressing. The waste form produced by hydrothermal hot-pressing had low leach rate of Sr. When a solidified body was produced by hydrothermal hot-pressing from a borosilicate glass powder containing a simulated high-level radioactive waste, its leach rate of Sr was lower than that of the original glass [4]. It is expected that hydrothermal reaction of Sr with silica may immobilize Sr in more leach resistant structure than glass.

Table 3.   Normalized Elemental Leach Rate (g/m^2 · d)

Element	Soxhlet[1]	MCC-1(90℃)[2]	MCC-1(40℃)[2]
Na	24.57	14.64	9.37
Cs	21.47	3.98	2.21
Al	7.11	1.67	0.57
Si	7.76	0.77	0.19
Mo	38.87	27.42	17.56

[1]: Soxhlet leach tests at 97 ℃ for 29 days.

[2]: Modified MCC-1 leach tests for 28 days in
   distilled water.

Table 4.   Comparative Leach Data (g/m^2 · d; Modified MCC-1
           leach tests at 90 ℃ in distilled water for 28 d.)

Element	HHP	BSG *	SYN *	TC *	FUE *
Cs	3.98	1.12	0.75	0.45	48
Sr	<0.09	<0.001	0.33	0.0011	0.27

HHP: Waste Form Produced by Hydrothermal Hot-Pressing,
BSG: Borosilicate Glass,   SYN: Synrock (Titania Ceramics),
TC: Tailored Ceramics,   FUE: FUETAP Concrete (Formed under
Elevated Temperatures and Pressures)
           (* Bernadzikowski et al. [19])

4. Conclusion

The simulated high-level radioactive waste was immobilized in the silica matrix by hydrothermal hot-pressing technique. The high compressive strength of the waste forms was achieved by the use of 10N NaOH solution. The high reaction temperature and pressure increased the strength and decreased the leach weight loss. The consolidation of the waste forms was achieved in 30 minutes; however, longer reaction times reduced the weight loss. The addition of 10wt% $Al(OH)_3$ to the starting material improved the leachability of the waste forms but also reduced the compressive strength. The waste loading of about 20wt% gave the high compressive strenght. The optimum conditions to produce waste forms with the high compressive strength and the resistance to leaching were as follows within the conditions used in this study; addition of 10wt% $Al(OH)_3$, 21.8wt% waste loading, 10N NaOH solution, 350℃, 66MPa, and 6 hours.

The waste form produced under the optimum conditions was characterized as follows;

(1) Porous structure: The density of the waste form was 2.3 g/cm^3 with porosity over 20% and specific surface area 10 m^2/g.

(2) Silica rich matrix: The waste form was mainly composed of low-quartz, the main consituent of the silica matrix, and included the waste components such as Fe_2O_3, CeO_2 and ZrO_2.

(3) High mechanical strength: The compressive strength was 200MPa, higher than that of a concrete waste form.

(4) Stability at high temperatures: It was not melted even at 900 ℃ and the heat treatment above 300 ℃ improved the leachability. The compressive strength of the waste form after quenched from 500℃ was 120 MPa.

(5) Medium thermal conductivity: The thermal conductivity of the waste form was about 0.01 J/cm·sec·K, a similar value of that of a glass waste form.

(6) Stability under hydrothermal conditions: The leach weight loss of the waste form was lower than that of JW-A glass waste form above 250 ℃ and maintained the shape before the leach tests.

(7) High leach rate by short-time leach tests: The weight loss by short-time leach tests was large, but reduced remarkably with the increase in leaching time. The release of Na and Mo was major by low temperature and short-time leach tests.

(8) Low leach rate of Sr and Cs: By any leach tests, Sr was not detected in leachant. The leach rate of Sr and Cs determined by MCC-1 leach tests at 90 ℃ for 28 days was 0.09 and 3.98 g/ m^2·d, respectively, and much smaller than that of a concrete waste form.

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