DEVELOPMENT OF THE WASTE SOLIDIFICATION PROCESS UTILIZING HYDROTHERMAL REACTION

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ABSTRACT

For the purpose of developing the solidification system which is able to transform the powdery wastes such as calciner products and/or incinerator ashes in the nuclear plant to the long-term stable and rigid form, the development test of the hydrothermal solidification system was performed, which succeeded the fundamental test presented in the Symposium on Waste Management '85.[1] In the development test, selection of the preferable solidification conditions, scale-up of the solidified product, evaluation of the properties of the solidified product, etc. were performed. The results are presented in this paper. From these results fair prospect of the practical use of this system was obtained.

INTRODUCTION

Now, calciner (or dryer) system of liquid wastes in the nuclear plant is being put into practical use with a view to realizing its high volume reducibility. Products from the calciner system are powdery form as well as incinerator ashes, therefore they are to be solidified to ensure the safe storage or disposal.

The powdery products generated from calciner (or dryer) and incinerator can be solidified by means of conventional solidification technologies (i.e. asphalt, cement and polymer). The hot-press solidification process utilizing alkaline hydrothermal reaction has been developed, aiming at further improvement in long-term stability and high volume reducibility of the product compared to the conventional technologies. Hydrothermal reaction is characterized by the extremely active water at relatively higher pressure and temperature than the normal condition. By this reaction, radioactive wastes are solidified with natural solidification material to synthesized rock.

For the purpose of developing this process to the practical stage, various tests and studies were performed which succeeded the fundamental test presented in this conference last year. The results of these tests and studies are presented in this paper.

SOLIDIFICATION PROCESS - HYDROTHERMAL REACTION -

Solidification process utilizing hydrothermal reaction is generally shown in Fig. 1. After mixed with natural solidification material (e.g. silica stone etc.), alkali and water, radioactive wastes such as calciner product, incinerator ashes, etc. are solidified by being kept in the hydrothermal condition (high temperature and pressure condition of water). The principle of this solidification is inferred as the following. By this process the radioactive wastes are solidified to the stable and rigid form, where the radionuclides are encapsulated with long-term reliability.

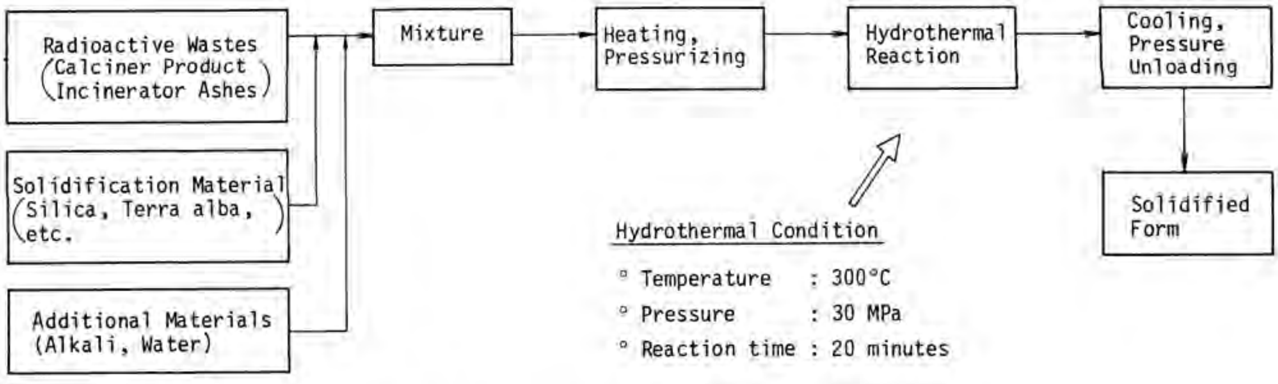


Fig. 1. Hydrothermal Solidification Process.

Ionizing reaction and hydrolysis of water is extremely active on the condition of high pressure and temperature (e.g. 30 MPa, 300°C). By the medium of this water dissolution and eduction (recrystalization) of matrix and waste are accelerated highly. As a result of this reaction, each particle is agglomerated into rock structure solid. (Refer to Fig. 2)

Conceptual figure of hot-press cell is shown in Fig. 3. The cell is cylindrical type. Material to be solidified is compressed by the upper and lower pistons and heated from outside. Reaction pressure is kept by the upper and lower gland packings.

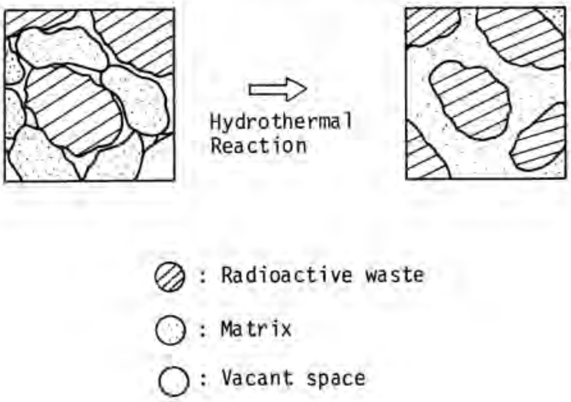


Fig. 2 Conceptual Figure of Hydrothermal Solidification

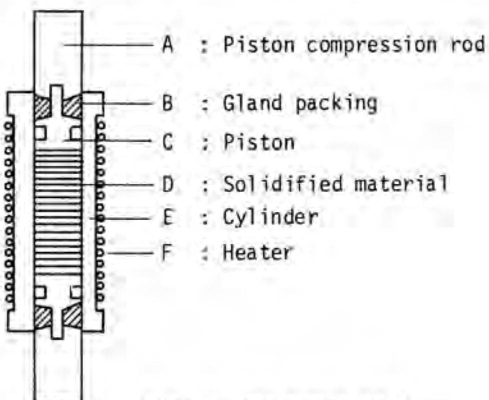


Fig. 3 Hot-press cell

DEVELOPMENT TEST

Selection of the Preferable Solidification Conditions

Factors influenceing the properties of the solidified product is as follows.

(1) Solidification matrix and additives.

(2) Process conditions. (Reaction pressure, temperature and time, waste content, etc.)

(3) Dimension.

Parametric survey on the factor (1) and (2) was performed here. As the test sample solidified form of 20 mm diameter x 30 mm height was used. As solidification matrixes seven kinds of materials consisting mainly of silicon dioxide (SiO_2) and their combinations were selected. (Refer to Table I.)

As additives combinations of calcium hydroxide ($Ca(OH)_2$), barium hydroxide ($Ba(OH)_2$), sodium alminate ($NaA\ell O_2$) and sodium phosphate (Na_3PO_4) were selected. As simulated wastes borax ($Na_2B_4O_7$) and sodium sulphate (Na_2SO_4) were used. And solidification was performed on the typical conditions. (i.e. 30 MPa, 300°C). Compressive strength and leachability were evaluated as the typical properties of the solidified product. It was found from these results that volcanic ashes or powdered glass as matrix and sodium phosphate (Na_3PO_4) + calcium hydroxide ($Ca(OH)_2$) as additives are superior to the others for solidification of borax ($Na_2B_4O_7$). The superiority was considered to be owing to the fact that volcanic ashes and powdered glass consist mainly of amorphous silica which is very active in chemical reaction. Concerning sodium sulphate (Na_2SO_4), it was found that volcanic ashes or powdered glass as matrix and calcium hydroxide ($Ca(OH)_2$) or barium hydroxide ($Ba(OH)_2$) as additive are preferable.

Besides the effects of process conditions (i.e. reaction temperature, pressure and time, waste content, etc.) on the properties of the solidified product were surveyed on the above preferable conditions of matrix and additive.

TABLE I

Solidification Matrixes for Optimization Test

(a)	Silica stone
(b)	Terra alba
(c)	Volcanic ashes
(d)	Clinoptilolite
(e)	Mordenite
(f)	Granulite
(g)	Powdered glass

From the above surveys on solidification matrix, additives and process conditions, preferable conditions of hydrothermal solidification were found to be as follows.

- Solidification matrix ; Volcanic ashes or powder glass
- Additives ;
  - Calcium hydroxide ($Ca(OH)_2$) + sodium phosphate (Na_3PO_4) for borax ($Na_2B_4O_7$) generated from PWR.
  - Calcium hydroxide ($Ca(OH)_2$) or barium hydroxide ($Ba(OH)_2$) for sodium sulphate (Na_2SO_4) generated from BWR.
- Reaction temperature; 300 ∿ 350°C
- Reaction pressure ; over 200 kg/cm^2
- Reaction time ; over 20 minutes
- Waste content ; 30 ∿ 50 wt%

Scale-up of Solidified Product

Study and test on the scale-up of solidified product necessary for practical use of this process were performed. Scale-up of solidified form up to 300 mm diameter was accomplished in this test, where data concerning thermal conduction and axial and radial homogeneity of the solidified product were obtained. From these results the scale-up to 300 mm diameter was successful and fair prospect to the scale-up to DOT 55 gallon drum size (550 mm diameter x 800 mm height) was obtained. Specification of the test device utilized in this scale-up test is shown as follows.

- . Compression cylynder ; 2 MN
- . Heater ; 20 kW, (Low frequency induction type).
- . Solidified product ; 300 mm diameter x 400 mm height (Max).
- . Attachment ; High speed mixer, slide base, heater/solidification lifting cylynder.

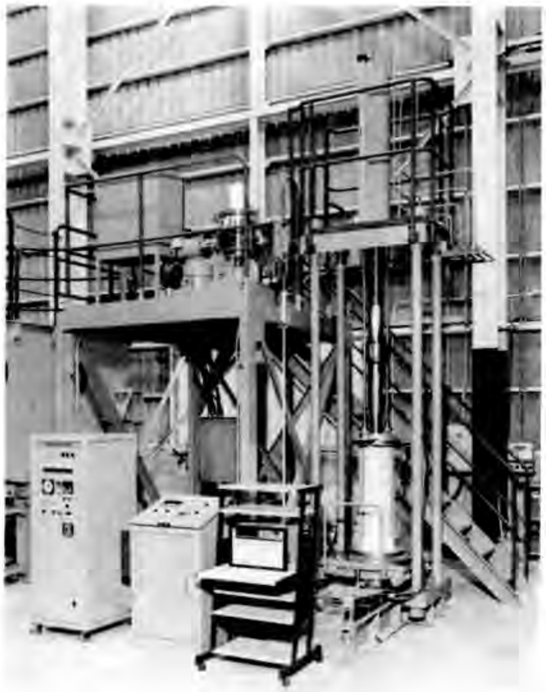


Fig. 4 Scale-up Test Device

Fig. 5 Scale-up Solidified Product (180 mm diameter x 350 mm height)

The test device and scale up solidified product are shown in Fig. 4 and 5. Smooth solidification operation was successfully demonstrated by this test device. Thermal conduction data of the solidified product of 180 mm diameter during the heating, reaction and cooling process and result of numerical analysis on them are shown in Fig. 6. Test data of thermal conductivity of solidified product is shown in Table II. This value is similar to that of glass which is the main composition of solidification matrix. The numerical analysis of two dimensional unsteady thermal conduction model was performed by utilizing this value, and calculated result agreed to the test data closely. Therefore this numerical analysis on the thermal conduction of solidified form is applicable to the evaluation on the practical solidification process.

The homegeneity of solidified product is as follows. Distribution of various chemical elements existing in the solidified product, i.e. Si, Ca, C, Na, B, O, was surveyed by EPMA(Electron Probe Micro Analysis). As an example the distribution of B and O is shown in Fig. 7. It is found from this survey that the solidified form is homogeneous as a whole in spite of some maldislribution of each element. Also test on the properties of the core sample from the solidified product was performed. Properties of the solidified product was almost free from difference between each sample location.

TABLE II

Thermal conductivity of solidified product

Temperature (°C)	60	150	250	400
Thermal conductivity (w/m°C)	1.3	1.3	0.7	0.5

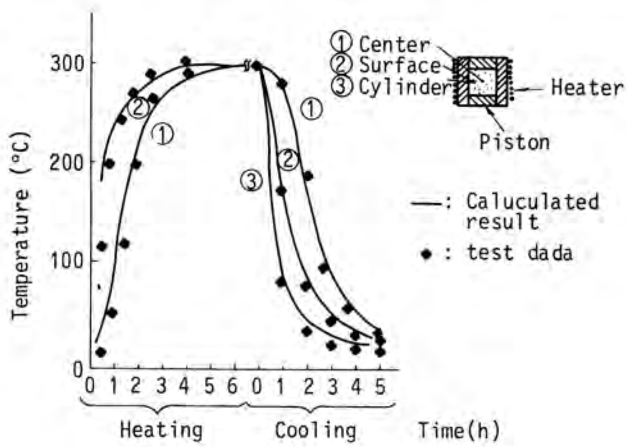


Fig. 6 Thermal Conduction Test Data (180 mm Diameter Solidified Product)

Properties of Solidified Product

Physical and chemical properties of solidified product which was produced on the above preferable condition were evaluated concerning the following items, which is generally required in practical application of solidification system. In this test borax ($Na_2B_4O_7$) as simulated waste and volcanic ashes as matrix were used.

(1) Appearance

Appearance of hydrothermal solidification form is like fine rock. The color is dark gray.

(2) Compressive strength and density

Compressive strength and density of solidified product are shown in Table III.

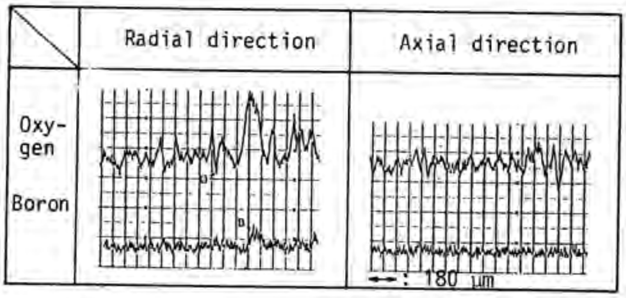


Fig. 7 Distribution of Chemical Elements of the Solidification Form.

TABLE III

Compressive Strength and Density

Waste \ Properties	Compressive Strength (MPa)	Density (kg/m^3)
Borax($Na_2B_4O_7$)	230	2400
Sodium sulphate (Na_2SO_4)	130	2300
Ashes	150	2300

(3) Leachability

In according with the ANS 16.1 procedure, leaching rate of simulated radionuclide was tested. The results are shown in Table IV.

TABLE IV

Leaching Rate

Waste \ Radionuclide	Cs (g/cm^2d)	Co (g/cm^2d)
Borax($Na_2B_4O_7$)	$10^{-4} \sim 10^{-6}$	$< 10^{-6}$
Sodium sulphate (Na_2SO_4)	$10^{-4} \sim 10^{-6}$	$< 10^{-6}$
Ashes	$10^{-4} \sim 10^{-6}$	$< 10^{-6}$

(4) Thermal stability

In accordance with ASTM B553 procedure, heat cycle test (-40°C ∿ 60°C) was performed. No significant change of the properties of the solidified product was found.

(5) Radiation stability

Radiation test up to 10^9 Rad (Co-60, γ-ray) was performed. No change of the properties of the solidified form was found.

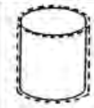
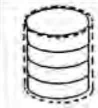
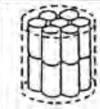
Study of Practical Use.

Conceptual study on the practical hydrothermal solidification system is introduced here. Fundamental comparison and evaluation on typical three kinds of solidified products is shown in Table V. Capacity of a solidification equipment is evaluated from the relation between weight of a solidified product and time for producing a solidified product which is calculated by the above mentioned numerical analysis. From this table it is obvious that solidified product of Dot 55 gallon drum size is preferable as far as the size is evaluated by the criteria shown in the table.

An example of the drum size solidification process is shown in Fig. 8. By the combination of the

TABLE V

Comparison and Evaluation of Solidified Products

Evaluation item \ Form			
Dimension (mm)	550ø×800h	550ø× 50 ∿ 200h	180ø 200 ∿ 800h
Mass of a product (kg)	420	26 ∿ 105	11 ∿ 45
Filling up efficiency (%)[a.b]	B (95)	B (95)	C (70)
Capacity of a solidification equipment[a]	A (1)	B(1/2∿6)	C(1/3∿9)
Scale of a equipment	B	B	A
Handling of product	A	B	C
Total evaluation	A	B	C

a. ( ) Value indicates the relative value.

b. A :Preferable exceedingly, B:Preferable

C :Not preferable

movement of the slide base and the lift of heater, material charge and product discharge can be made automatically. Product is removed from the solidification vessel into drum by being pushed out by the compression cylynder.

Table VI shows the operational condition of the drum size solidification equipment. From this study it is found that capacity of drum size solidification equipment is nearly one drum per day (24 hours).

Table VII shows the study on the application to the nuclear power plant, which are twin 1200 MWe Class PWR plants and 1100 MWe Class BWR plants with calciner and incinerator facility.

The waste volume generated from the both twin plants is approximately 20000 kg/year of the calciner product and 2500 kg/year of the incinerator ashes for PWR and 40000 kg/year of the calciner product and 1500 kg/year of the incinerator ashes for BWR respectively. The solidification product generation is estimated as approximately 100 drums/year for PWR and approximately 250 drums/year for BWR. Therefore in twin PWR plants and twin BWR plants, it is reasonable to assume the practical system will be conservatively designed to produce one DOT 55 gallon drum size product a day, and the generated wastes can be processed by one equipment each.

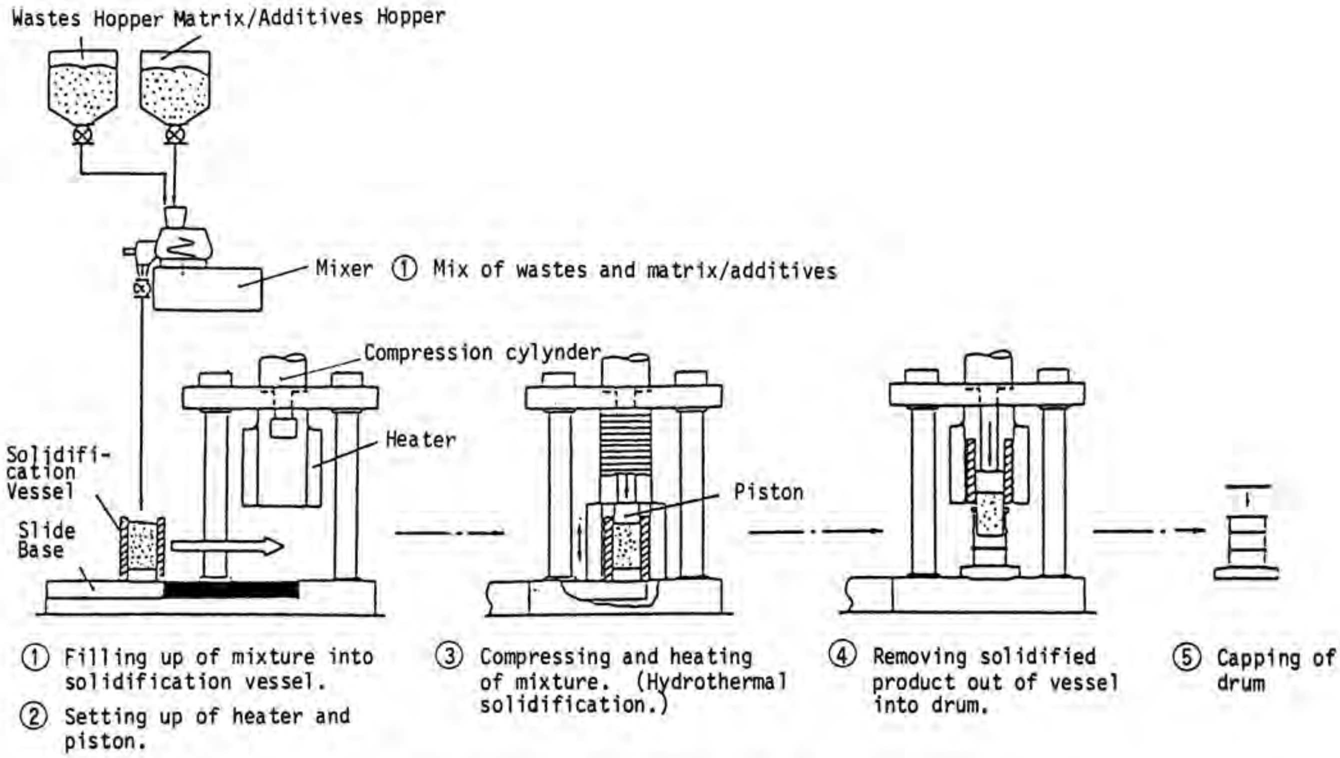


Fig. 8. Example of Solidification Process Flow.

TABLE VI

Operational Condition of Solidification Process

Condition \ Form(mm)	550ø x 800h (Drum size)	550 x 400h
Reaction temperature (°C)	300	300
Reaction pressure (kg/cm^3)	300	300
Operation time(hour)		
Heating	10 ∿ 12	6 ∿ 8
Reaction	∿ 1	∿ 1
Cooling	12 ∿ 14	10 ∿ 12
Total	22 ∿ 26	16 ∿ 20

a. Bulk density of wastes are 1000 kg/m^3 for caliciner products and 500 kg/m^3 for incinerator ashes.

b. Solidified product is 550 mm outer diameter with 800 mm height. Waste content is 50 wt%. Density of solidified product is 2200 kg/m^3.

c. Operation days are 300 days/year.

d. Including waste supply system and drum handling system.

TABLE VII

Study on the Application to the Plant

Study item \ Plant	PWR × 2 units	BWR × 2 units
Waste generation		
· Calciner products	20000	40000
· Incinerator ashes	2500	15000
Waste generation of drum base[a] (drum/year)	125	350
Solitified product generation of drum base[b] (drum/year)	100	250
Solidification capacity[c] (form/day)	1/2	1
Number of solidification equipment	1	1
Total instlation space[d] (m^2)	150 ($15m^w \times 10m^\ell \times 6m^h$)	150 ($15m^w \times 10m^\ell \times 6m^h$)

CONCLUSIONS

It was verified that stable and rigid solidification product with high volume reducibility could be produced by the hydrothermal solidification process under the relatively mild conditions, e.g. 30 MPa reaction pressure and 300°C reaction temperature.

Optimization of the hydrothermal process conditions and various physical and chemical properties of solidified product were obtained. The scale up of the solidified product to 300 mm diameter x 400 mm height, and the fair prospect of the scale-up up to DOT 55 gallon drum size (550 mm diameter x 800 mm height) was obtained.

REFERENCE

1. Y. Nishihara, T. Kashiwai and N. Yamazaki, "Stabilizing Solidification II ; Fundamental Test of the waste Solidification Process Utilizing Hydrothermal Reaction, "Proc. of the Symposium on Waste Management '85, Tucson Arizona, March 24-28, 1985, Vol. II , p177 ∿ 180. (1985).