PNCT 841-79-56

SOLIDIFICATION OF HLLW INTO SINTERED CERAMICS

Nov. 10, 1979

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POWER REACTOR & NUCLEAR FUEL DEVELOPMENT CORPORATION

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SOLIDIFICATION OF HLLW INTO SINTERED CERAMICS

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Nov. 10, 1979

Presented at the International Symposium on Ceramics in Nuclear Waste Management Sponsored by the Nuclear Division of the American Ceramic Society and the U.S. DOE, on April 30 - May 2, 1979, Cincinnati, Ohio.

ABSTRACT

Simulated HLLW from reprocessing plant of PNC at Tokai was solidified into sintered ceramics by normal-sintering or hot-pressing with addition of some oxides. Among various ceramic products obtained so far, the most preferable one was Nepheline type sintered solids formed with addition of SiO_2 and Al_2O_3 to the simulated waste calcine. The solid shows advantageous properties in leach-rate and mechanical strength, which possively comprise the ceramic product be a promising solid waste form.

Other type of ceramic solids were prepared with addition of ZrO_2 or MnO_2, and some of them showed preferable characters.

1. Introduction

The most advantageous solid form of HLLW is vitrified product which is currently accepted as the solid form of the highly radioactive waste for long term storage. It is desirable, however, to develop alternative solid waste form with more stable properties than the vitrified form, since the diffusion of radio-nuclides should be minimized by all means.

One of the alternatives which one may expect the long term stability is ceramic form, as reported as "Supercalcine" or "Synroc", although the characters of those products were not well estimated so far.

On the other hand, the solidification process of the highly radioactive waste is expected to be simple and convertible to the continuous production. On above basis, authors have made some preliminary investigations to produce solidified ceramics of HLLW from the reprocessing plant of PNC at Tokai by normal-sintering of the simulated waste calcine with addition of several oxides. At the same time, some sintered ceramics were fabricated by hot-pressing as references for the comparison of the properties.

2. Design of the Composition of Ceramic Products

The major constituents in the waste are, as oxides, Na_2O of process inert in reprocessing, MoO_3, ZrO_2, CeO_2 and Lanthanide oxides represented as Nd_2O_3 among fission products. Simulated waste was prepared for the present experiments as mixture of chemicals of carbonates, nitrates and oxides of every constituent elements except actinides. Particle size of each chemicals was arranged to be around one micron by grinding.

Prior to the sintering tests, the compositions of ceramic solids were designed on the mineralogical considerations. In order to immobilize each constituents, various refractory crystals containing them were first selected and properties of those crystal phases were investigated.

Especially, crystal phases of the major constituents such as Na_2O, MoO_3 and Nd_2O_3 were carefully checked from the mineralogical points of view. For example, melting temperatures, thermal expansions, heat of formation and lattice parameters of crystals relevant to the capability of involving ions were of importance with respect to the fixation of the nuclides.

A few candidate compositions were elaborated by combining the refractory crystals containing constituent elements. The representative composition designed is shown in Table 1. The main crystal of the composition is, as shown, Nepheline and other elements are immobilized as aluminates or alumino-silicates. The additives required to form those crystals can be calculated, therefore, as shown in the table. In the case of A, 146.51 g of additives is mixed with 98.1 g of the simulated waste, thus content of the waste in the ceramic solid renders about 50 wt %.

Other candidates are Zirconia and Manganate ceramics with addition of ZrO_2 or MnO_2 and SrO to the simulated waste. The contents of the waste of the Zirconia ceramics may rise to 60 wt %.

Chemicals with grain size of around 1μm were used as additives.

3. Sintering of the Ceramics

The simulated waste and additives were weighed and mixed in a ball mill with or without binder. The mixtures were then put into the mold and preforms were fabricated for normal sintering. The size of the preform was 50 mm in diameter and 10 to 15 mm thick. Normal sintering was performed in an electric furnace at temperatures from 1000 to 1400°C.

For comparison, content of the waste in the ceramics was varied from 10 to 40 wt % for Nepheline type and from 30 to 60 wt % for Zirconate and Manganate ceramics.

Dense ceramic solids were obtained by sintering at temperature range around 1200 - 1300°C for 60 minutes in each type of solids providing the content of the waste is properly adjusted.

Ceramic solids were also fabricated by hot pressing for the composition which brought dense ceramics by normal sintering. Hot pressing was performed at around 1200 - 1300°C and at pressure of 300 kg/cm^2 in the alumina mold.

Sintering tests of a few type compositions gave the following results.

a) Dense Nepheline type ceramic solids were obtained from the composition of 30 - 40 wt % waste oxides by normal sintering at temperature around 1300°C for 60 - 90 minutes. Hot-pressing also gave dense Nepheline ceramics at 1250 - 1300°C for 30 minutes.

b) Good Zirconate ceramics in appearance were fabricated by normal-sintering or hot-pressing when the waste content is around 40 - 50 wt %. The operational data are similar to those for Nepheline type ceramics.

c) Manganate type ceramics were fabricated by similar operations with

Nepheline type of ceramics when the waste content is around 50 wt %.

d) Minor additives have considerable effects on the densification of ceramic solids. Addition of increased amounts of SrO to Nepheline type ceramics and addition of SiO_2 and increased amount of SrO to Zirconia and Manganate types are effective to the densification of the ceramics.

e) Addition of vinyl-acetate binder to the mixture of chemicals is also effective for the densification.

f) When the temperature of sintering is high, e.g. at 1400°C, some are half melted, and when the temperature is low, almost all are left as preforms.

Titanate type of ceramics were fabricated by sintering the simulated waste with addition of TiO_2, SrO, Al_2O_3 and in some cases SiO_2 some look well sintered.

4. Characterization of Ceramic Solids

Characterization of the sample ceramics obtained in the above sintering tests was carried out from various view points.

First, crystal phases of the sample ceramics were analyzed by X-ray diffraction. Figure 1 illustrates X-ray diffraction patterns of ceramic solids obtained from Nepheline type composition. Main crystal phase, Nepheline is clearly identified in diffraction peaks, and other crystals expect, such as Ba, $SrMoO_4$, $NdAlO_3$, $FeAlO_3$, $ZrSiO_4$,etc are detected. Figure 2 illustrates X-ray diffraction patterns of other types, such as Zirconia, Manganate and Titanate compositions. ZrO_2 and Fluorite crystals were detected in Zirconia ceramics, but many unidentified peaks remain. Diffraction peaks observed in Manganate and Titanate ceramics were unidentified except a few peaks of $SrO \cdot MnO_2$ in Manganate and $SrO \cdot TiO_2$ and beta-alumina in Titanate.

Second, bulk densities of sample ceramics were measured. Although theoretical densities of respective ceramics are hard to calculate, they are tentatively estimated from those of composite crystals. Estimation shows that theoretical densities are 3.2 g/cm^3 for Nepheline type when the waste content is 40 wt %, 4.4 for Zirconate containing 50% waste, 3.9 and 3.5 for Manganate and Titanate with 40% waste.

Bulk densities of ceramics obtained by hot-pressing were more than 95% to the theoreticals when the temperature during processing is appropriate. Temperature range for proper hot-pressing for each types lies from 1200 to 1300°C. Normal-sintered ceramics, on the other hand, showed that their bulk densities are dependent not only on temperature and time for sintering but also on composition of additives.

Dense Nepheline ceramics, that is bulk density is more than 90% of theoretical, is obtained only when the sintering was performed at temperature of 1300°C for 90 minutes or more on the composition containing excess SiO_2. Zirconate ceramics need higher temperature and longer time for densification than Nepheline ceramics, that is, temperature of 1350°C or more and 200 minutes.

Bulk densities of Manganate and Titanate samples showed that densification was initiated at lower temperature around 1100°C. Bulk density reaches 90% level at that temperature.

Figure 3 illustrates change of bulk density of Nepheline ceramics with sintering temperature as an example.

Third, leach-rates of dense samples were measured. Sample disks were cut and polished, and after the measurements of surface area, sample pieces were immersed in boiling distilled water. The weight loss of the pieces after 24 hours immersion gives the leach-rates.

Dense Nepheline type ceramics, hot-pressed at 1250°C or more and some normal-sintered at 1300°C, showed leach-rates of 5×10^{-5} to 5×10^{-6} $g/cm^2\cdot day$. Zirconate ceramics sintered at 1300°C had leach rate of 5×10^{-4}, and those of Managanate and Titanate types were as low as 10^{-3} order, even for samples sintered at 1300°C.

Ceramic solids usually include pores, especially when they are made by normal-sintering process. Since the leach test was performed as bulk, open pores directly affect on the leach-rates. Thus, the production of sintered ceramics should elliminate open pores by strict process control. Nepheline type ceramics with appropriate additives and with 30 - 40 wt % waste may constitute a solution to the ceramic solidification of HLLW.

Fourth, thermal expansion coefficients of the samples were measured. Nepheline types have the coefficients of $90 - 105 \times 10^{-7}/°C$, for solids containing 30 - 40 wt % waste. Zirconia types have higher values of 130 to 160×10^{-7}, Manganate types have 110 to 150×10^{-7}, and Titanate have values of 80 to 120×10^{-7}, for solids containing 30 - 50 wt % waste respectively. Thermal expansion coefficients of the solids increase with increasing amount of the simulated waste, because of the content of Na_2O.

Thermal expansion of the ceramics is possibly estimated, if the density be as high as the theoretical value, by the additive law of the composite crystals, and that of main crystals is dominating.

Fifth, thermal conductivities of the ceramic products were measured. Dense ceramics of every types showed the value of 0.01 - 0.015 w/cm.°K. Thermal conductivities of natural rocks are around 0.02 and those of the solids obtained in the present tests are a little smaller.

Sixth, the mechanical strength of the ceramic solids were measured as bending strength with polished samples of 5×5×30 mm. The values obtained for dense Nepheline ceramics are in the range of 300 to 700 kg/cm^2, which resembles with values of sintered bricks of clay minerals.

5. Process Evaluation

Normal sintering is simple and productive process and it is preferable to intermittent and time consuming hot-pressing. Authors took above in minds and intended to fabricate the waste incorporated ceramics by simple normal-sintering process. Although the answer is not quite clear yet, the results were encouraging, especially when the waste was sintered with Al_2O_3 and SiO_2 to form Nepheline type ceramics.

The other points to consider is the form of the waste. High level waste from reprocessing plant is in liquid phase, so that it is desirable to use HLLW as the starting material and put the additives in it, which will be carried out in our next experiment.

6. Summary and Further Development

Tests were performed to develop alternative solidification process of HLLW from reprocessing plant of PNC. Since the properties of ceramics are expected to be appropriate as solid form of the radioactive waste, ceramic solids were made with the simulated waste powder and additive chemicals by normal-sintering and hot-pressing. Compositions of the waste incorporated ceramics were designed from mineralogical considerations. Four types of compositions were tested, they are Nepheline type with additives of Al_2O_3 and SiO_2, Zirconia type with ZrO_2, Manganate and Titanate types with MnO_2 and TiO_2. The contents of the simulated waste were varied from 20 to 60 wt %, normal 40 wt %. Sintering tests and characterization of the ceramic samples reveal the following.

a) Dense ceramics were obtained by normal sintering at 1300°C and by hot-pressing at 1200 to 1300°C for Nepheline type ceramics and for Zirconate ceramics. Bulk densities of the solids were more than 90% to the ceramic samples reveal the following.

b) Bulk densities of Manganate and Titanate reach to 90% level at sintering temperature of 1100°C.

c) Minor additives such as SrO or NiO have considerable effects on the densification and properties of the ceramic solids.

d) X-ray diffraction analysis showed that the expected crystals were formed in Nepheline type solids either by normal sintering or by hot-pressing. X-ray diffraction peaks of other type of solids are not well identified.

e) Leach rates of Nepheline type solids are in the order of 10^{-5} to 10^{-6}

g/cm^2·day, as far as the samples were sintered at 1300°C. No other samples were fabricated which have leach rates of less than 10^{-4} g/cm^2·day at 100°C.

f) Thermal expansion coefficients, thermal conductivities, and bending strength were measured. Bending strength of the solids was as high as that of the fired clay bricks.

Further development is necessary in order to adopt the ceramic solidification as an alternative for the solidification of HLLW. One of the main subjects is to improve the properties of the waste incorporated ceramics, especially the chemical durability. Operation of sintering and composition of the additives should be refined. At the same time, for the simple solidification process, HLLW and liquid additives will be examined in the near future.

List of Figures and Tables

Figure Captions

Table Caption

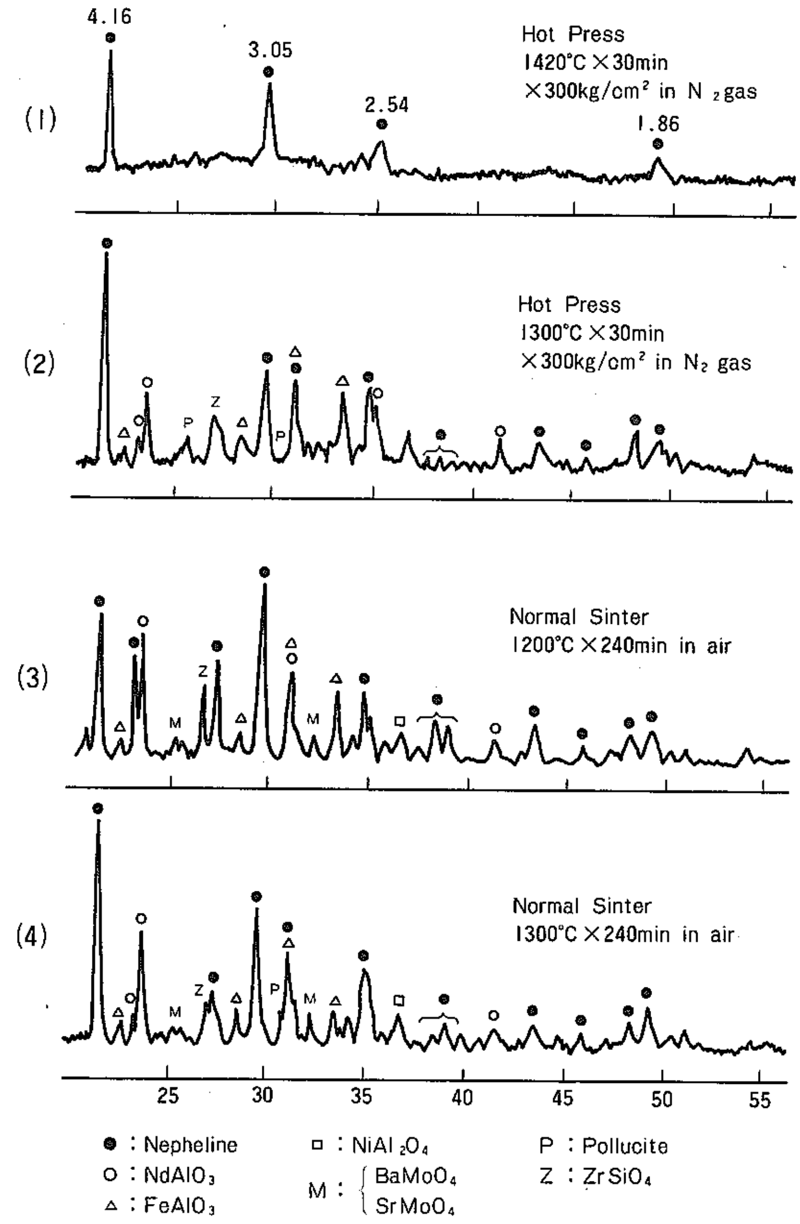

Fig. 1 X-ray diffraction patterns of solidified Ceramics.

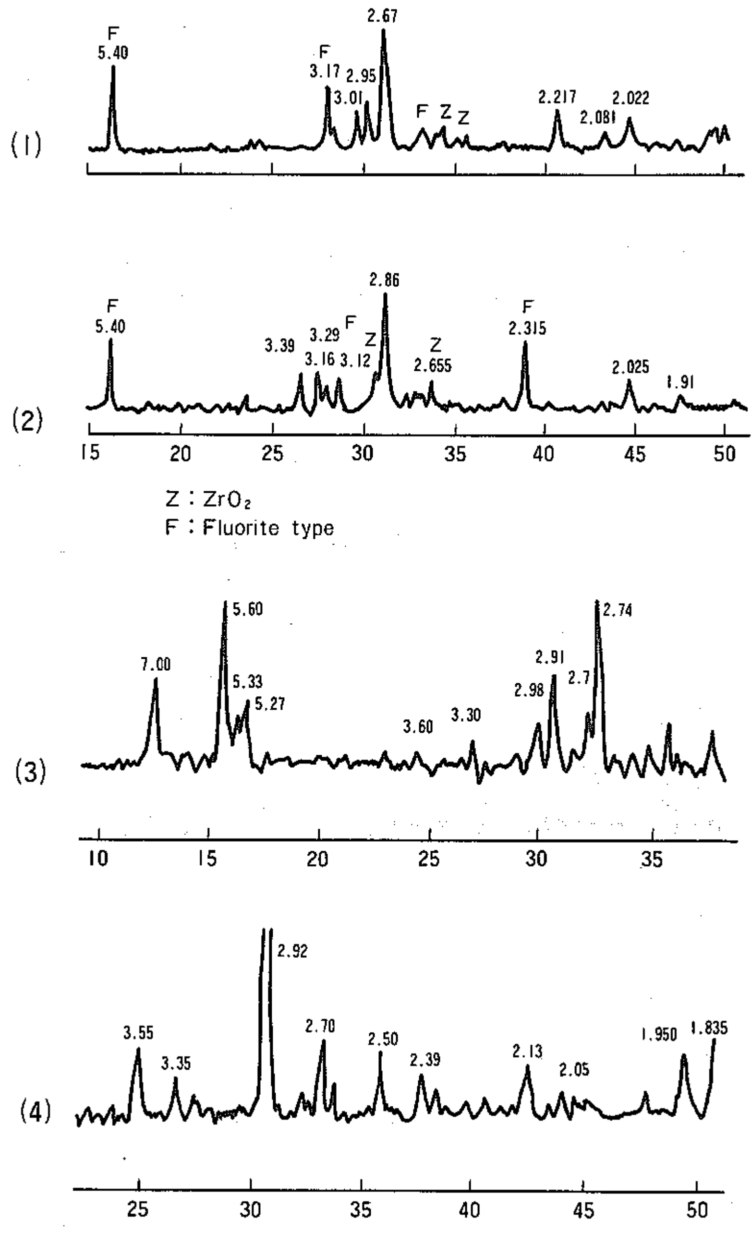

Fig. 2 X-ray diffraction patterns of ceramics solids.
1),2) Zirconate (normal sinter)
3) Manganate (normal sinter)
4) Titanate (normal sinter)

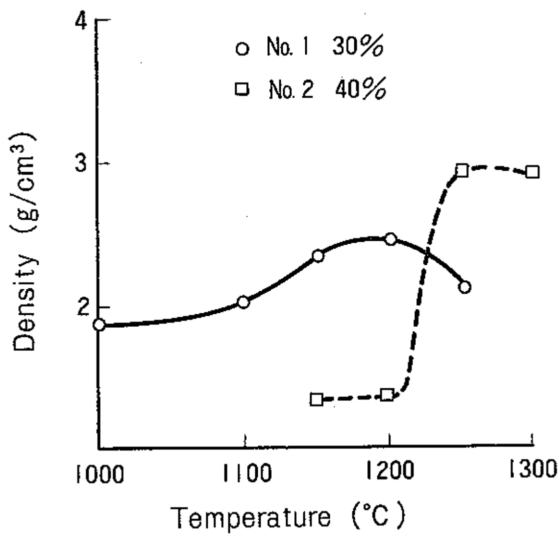

Fig. 3 Change of density with temperature during normal sintering.
Nepheline type ceramics with 30 or 40% waste.

Table 1. First Candidate Composition

- Nepheline Type Ceramics -

Waste Oxides		Compounds	Additives(wt%)		
Constitutents	(wt%)		Al_2O_3	SiO_2	SrO
Na_2O	33.8	$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$	56.14	65.54	
ZrO_2	9.9	ZrO_2			
		$ZrO_2 \cdot SiO_2$		(4.83*)	
Cs_2O	5.1	$Cs_2O \cdot Al_2O_3 \cdot 4SiO_2$	1.85	4.35	
Y_2O_3	1.3	$Y_2O_3 \cdot Al_2O_3$	0.59		
La_2O_3	3.0	$La_2O_3 \cdot Al_2O_3$	0.94		
Nd_2O_3	14.1	$Nd_2O_3 \cdot Al_2O_3$	4.27		
CeO_2	5.7	$CeO_2 \cdot Al_2O_3$	3.38		
NiO	1.9	$NiO \cdot Al_2O_3$	2.89		
Fe_2O_3	6.7	$Fe_2O_3 \cdot Al_2O_3$	4.36		
BaO	3.3	$BaO \cdot MoO_3$			
SrO	2.0	$SrO \cdot MoO_3$			
MoO_3	10.0	$SrO \cdot MoO_3 + BaO \cdot MoO_3$			2.2
Cr_2O_3	0.6	Dispersed			
Rb_2O	0.7				
	98.21		74.42	69.89	
				(74.72*)	2.2
Total of Additives			146.51 = A	(151.34*) = B	

* Numbers in parentheses indicate additive and totals for composition B.