

AN ALTERNATIVE PROCESS TO IMMOBILIZE INTERMEDIATE WASTES FROM LWR FUEL REPROCESSING

Yasuo Hirose,
Hitachi Works, Hitachi, Ltd., Ibaraki-ken, Japan

Tetsuo Fukasawa
Power & Industrial Systems R&D Division, Hitachi, Ltd., Ibaraki-ken, Japan

Dinesh K. Agrawal, and Barry E. Scheetz
Materials Research Laboratory, The Pennsylvania State University, University Park, PA, USA

Rama Nageswaran, Jay A. Curtis, and Santosh Y. Limaye
LoTEC, Inc., Salt Lake City, UT, USA

ABSTRACT

A new concept for converting the intermediate wastes which result from light water reactor (LWR) fuel reprocessing into a single phase material, sodium zirconium phosphate ([NZP]), has been established. This conversion utilizes such waste materials as metals (zirconium alloy, stainless steels, and nickel alloy), spent solvent tri-butyl phosphate (TBP), and concentrated solution of sodium nitrate, and is accomplished using a minimum amount of additional chemicals. The resulting multi-component [NZP] material is homogenous, and has a high mechanical, physical and chemical stability. In addition, the [NZP] can accommodate almost all kinds of fission product cations in the crystalline structure without significant change in its stable lattice structure; as a result, the [NZP] has a high leach resistance appropriate for geological disposal, eliminating the need for additional barrier materials. Taking into account of the equal contribution by boiling water reactors (BWR) and pressurized water reactor (PWR), the amount of immobilized intermediate wastes is predicted to be 1110 kg/MTU (metric ton of uranium before irradiation). After compositional formulation and synthesis of this mineral-like material, X-ray analysis was conducted to ensure single-phase and was followed by processing, microwave-sintering and characterization to demonstrate the fundamental technical feasibility of this concept.

INTRODUCTION

Much public concern has been directed towards waste management, and extensive research and development efforts have been undertaken in an effort to justify the reliability of technological concepts aimed at reprocessing wastes. Further study of these and other new concepts is necessary to steer efforts toward examining such concepts, and establishing a plan for decreasing the volume of waste. This research is aimed at converting existing waste into a stable, single-phase material which can also be utilized for auxiliary purposes.

The sodium zirconium phosphate structural family [NZP], of which $\text{NaZr}_2(\text{PO}_4)_3$ is the parent composition, is well known for its ionic conductivity, low thermal expansion, and structural flexibility to accommodate a large number of multivalent ions. The unique properties of [NZP] materials are attributed mainly to (a) an open framework structure with strongly bonded polyhedra, (b) flexibility with regards to ionic substitution, and (c) anisotropic lattice thermal

expansion under thermal stress. In addition, this material has been extensively researched for use as a host ceramic for highly radioactive nuclear waste immobilization.[1] Furthermore, being the only known single phase host structure, with structural stability at high temperatures (even under radiation exposures), and low solubility in water over a substantial pH range, [NZP] has been evaluated as a potential alternative to borosilicate glass and the poly-crystalline Synroc systems.

The reprocessing of LWR fuel produces not only highly radioactive waste, including almost all fission product nuclides, but also various types of lower radioactive alpha-contaminated wastes. The major components of such LWR fuel reprocessing waste include metals (zirconium alloy, stainless steels, and nickel alloy) composing the LWR fuel assembly (including channel box of BWR fuel), concentrated solutions of sodium nitrate (NaNO_3), and waste solvent tri-butyl phosphate(TBP). The above waste components are currently treated separately, and are combined in a cement matrix to form an immobilized nuclear waste form appropriate for geological disposal. Of major concern is not only the volume of the waste produced, but also the long term stability of the cement matrix. An innovative approach which utilizes all of the components of alpha-contaminated LWR fuel reprocessing waste for the synthesis of a mineral-like material, which is a structural analogue of [NZP] with the least addition of inactive chemicals may provide the waste management alternative with lower volume and higher long term stability. The present study aims to demonstrate the feasibility of this unique approach.

Advantages of the approach are:

- unified and homogenous immobilized waste form,
- small volume of immobilized waste,
- fabrication of single phase material with higher mechanical, physical, and environmental stability,
- conversion of materials using established ceramic technologies.

The approach suggested above has the capability of aiding waste management for a selection of light water reactors and should be seriously investigated for providing a waste management solution.

DESIGN OF [NZP] WASTE FORMS

The standard structural formula for [NZP] is described as $[\text{M}'][\text{M}'']_3[\text{A}^{\text{VI}}_2][\text{X}^{\text{IV}}_3]\text{O}_{12}$ with the structure containing a three-dimensional network of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra. Structural units consisting of two octahedra and three tetrahedra ($[\text{Zr}_2(\text{PO}_4)_3]^-$) are connected to form ribbons parallel to the c-axis of the unit cell; these ribbons are linked by PO_4 tetrahedra normal to the c-axis to generate the three-dimensional network illustrated in Figure 1.[1] The conjunction of units $[\text{Zr}_2(\text{PO}_4)_3]^-$ parallel to the c-axis of the unit cell creates two interconnected interstitial sites, M' and M'' , whose occupation determines the symmetry of the [NZP] structure. The M' site, a strongly distorted octahedral site, is located between each $[\text{Zr}_2(\text{PO}_4)_3]^-$ unit comprising the ribbons. M'' sites are structural holes that separate the ribbons.

In the prototypical structure, the M' site is occupied by sodium ions (Na^+), whereas the M'' site remains vacant. The M' sites can accommodate the larger alkaline (and silver) or alkaline earth cations. This arrangement maintains the rhombohedral symmetry of the unit cell and the

structure belongs to the $R3c$ space group with lattice constants of $a = 8.804\text{\AA}$ and $c = 22.759\text{\AA}$. The cell volume is $1528\text{\AA}^3$ with a density of 3.20 g/cm^3 based upon $Z=6$. [2]

The NZP skeleton is strong and flexible, adjusting its dimensions in response to changes in the sizes of its constituents. The ability of [NZP] compounds to incorporate the ionic species of approximately two-thirds of all known elements has been well documented in literature. Partial and complete isovalent, heterovalent, and coupled substitutions are summarized in Figure 2. It can be noted that not only monovalent alkaline cations, divalent alkaline earth cations, and some large mono- or divalent cations, but also large trivalent rare earth cations can be assigned on M' sites. The three-dimensional skeletal structure of [NZP] offers three distinct crystallographic sites that permit the accommodation of a variety of cations. These sites include the A^{VI} site (an octahedral site normally occupied by Zr^{4+}), the X^{IV} site (a tetrahedral site normally occupied by P^{5+}) and two interstitial sites, M' and M'' , where M' is usually occupied, but M'' becomes populated only when additional Na^+ is needed for charge compensation with polyvalent cations other than zirconium. The occupation of M' sites is based upon equivalent charge.

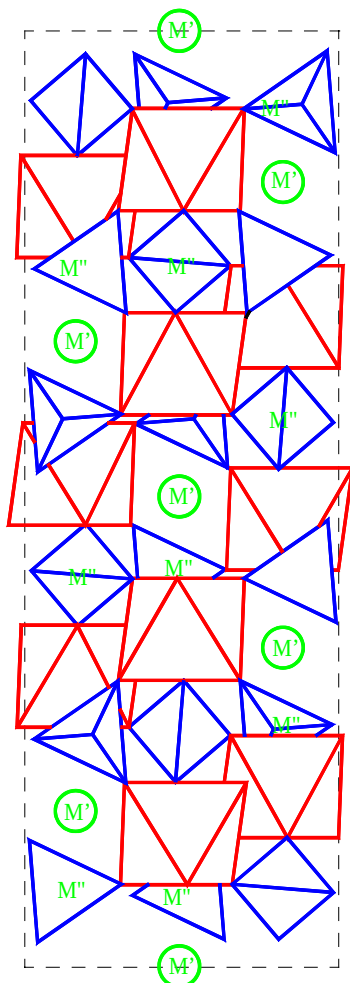


Figure 1. Projection of the $NaZr_2(PO_4)_3$ structure on $[110]$ of the $R3c$ unit cell.

Partial occupation of the M'' sites by Na⁺ caused by the substitution of lower valent cations (such as Fe³⁺ or Cr³⁺) or larger cations (such as Ce⁴⁺ or Th⁴⁺) on A site results in a loss of symmetry and conversion of the rhombohedral unit cell to a monoclinic form, C2/c. In the monoclinic modification of the [NZP] structure, the coordination of the M', M'', and X sites is the same as in the rhombohedral cell, but the coordination of the A site is nine-fold. This arrangement allows the accommodation of the larger tetravalent and trivalent actinide and lanthanide cations on the A site of the NZP structure. In the case of the trivalent cations, charge balance is achieved through partial occupation of the M'' sites by Na⁺. [3]

An ionic substitution model has been proposed to assign cations to the three distinct crystallographic sites of the [NZP] structure based on their R_c/R_a values.[4] Values for R_c/R_a can be calculated for the constituent cations present in a precursor stream; the ionic radius of each cation (R_c) should be divided by the ionic radius of oxygen (R_a). Because the values of R_c and R_a vary with predicted coordination number (ionic radii tend to increase with increasing coordination number), one must make initial assumptions regarding the coordination of the anions and the cations in a given crystal structure and use appropriate ionic radii to calculate R_c/R_a . The radius ratios of cations capable of substituting into the octahedrally coordinated A site fall in the range of (0.414-0.732); in the monoclinic [NZP] structure, cations with radius ratios greater than 0.732 may occupy the nine-fold A site. The radius ratios of cations capable of occupying the tetrahedrally coordinated X site fall in the range of (0.225-0.414).[5] The M' interstitial sites can accept a variety of cations. Thus, almost all cationic constituents contained in the reprocessing waste, including fission product and actinide species, can be immobilized effectively as shown in Table I where (CN) is the coordination number, with much more flexibility than anticipated from the literature.[6]

Table I. Model for ionic substitution in the [NZP] structure

Cations	Oxidation State	Rc/Ra (CN)	Assign-ment	Cations	Oxidation State	Rc/Ra (CN)	Assign-ment
Se	6+	0.20 (IV)	X	La	3+	0.87 (IX)	A
Rb	1+	1.09 (VI)	M'	Ce	4+	0.62 (VI)	A
Sr	2+	0.84 (VI)	M'	Pr	4+	0.61 (VI)	A
Y	3+	0.77 (IX)	A	Nd	3+	0.83 (IX)	A
Zr	4+	0.51 (VI)	A	Pm	3+	0.82 (IX)	A
Mo	6+	0.30 (IV)	X	Sm	3+	0.81 (IX)	A
Tc	7+	0.27 (IV)	X	Eu	3+	0.80 (IX)	A
Ru	4+	0.44 (VI)	A	Gd	3+	0.79 (IX)	A
Rh	3+	0.43 (VI)	A	Tb	3+	0.66 (VI)	A
Pd	2+	0.61 (VI)	M'	Dy	3+	0.65 (IX)	A
Ag	1+	0.82 (VI)	M'	U	4+	0.75 (IX)	A
Cd	2+	0.68 (VI)	M'	Np	4+	0.62 (VI)	A
In	3+	0.57 (VI)	A	Pu	4+	0.61 (VI)	A
Sn	4+	0.49 (VI)	A	Am	3+	0.70 (VI)	A
Sb	3+	0.54 (VI)	A	Cm	3+	0.69 (VI)	A
Te	4+	0.31 (IV)	X	Na	1+	0.73 (VI)	M'/M''
Cs	1+	1.19 (VI)	M'	Fe	3+	0.46 (VI)	A
Ba	2+	0.96 (VI)	M'				

FORMULATION OF [NZP] WASTE FORMS

Table II shows the mass compositions of an LWR fuel assembly, according to a typical design of boiling water reactor (BWR) and pressurized water reactor (PWR). Table III shows elemental compositions (g/MTU) for the assembly metal waste, under an assumption that equal amounts (in terms of MTU) of BWR and of PWR fuels are to be processed together. In this case, the channel box of BWR fuel was also assumed to be the same category as fuel cladding hulls. It is assumed that 0.05% of uranium is attached to the cladding hulls, however this amount to uranium is too small to be accounted in the compositional formulation. Tables IV and V provide typical elemental compositions for LLW concentrate, and waste solvent, respectively. The actual yield of wastes, however, is highly dependent on process variables.

Table II. Mass compositions of an LWR fuel assembly

	BWR (kg)	PWR (kg)
UO ₂ Pellets	198.0 (174.5 U)	510.1 (449.6 U)
Stainless Steels	8.25	22.2
Nickel Alloys	0.73	7.2
Zircaloy-2	53.5	-
Zircaloy-4	49.6	124.7

*Channel Box

**Table III. Typical elemental composition of the LWR fuel assembly metal waste per MTU
Including channel box of BWR fuel assembly**

	Total Mass (g)	Zr (g)	Fe (g)	Cr (g)	Ni (g)	Sn (g)
Stainless Steels	4.84E+04	0	3.58E+04	8.70E+03	3.90E+03	0
Nickel Alloy	1.01E+04	0	7.13E+02	1.51E+03	7.90E+03	0
Zirconium Alloy	4.29E+05	4.21E+05	6.50E+02	4.98E+02	2.13E+02	6.51E+03
Total [kg-mol]	4.87E+05 [5.748]	4.21E+05 [4.620]	3.72E+04 [0.666]	1.06E+04 [0.204]	1.20E+04 [0.204]	6.51E+03 [0.055]

Table IV. Typical elemental composition of LLW concentrate per MTU

	Total Mass (g)	Na (g)	Fe (g)	O (g)
LLW Concentrate [kg-mol]	1.38E+05	9.10E+04 [3.958]	1.05E+04 [0.189]	3.62E+04 [2.263]

Table V. Typical elemental composition of spent solvent per MTU

	Total Mass (g)	P (g)	O (g)
Waste Solvent [kg-mol]	3.80E+04	1.24E+04 [0.400]	2.56E+04 [1.600]

After incorporating the elemental compositions for spent solvent (Table V), LLW concentrate (Table IV) and metallic waste (Table II), an appropriate [NZIP] formula was determined:

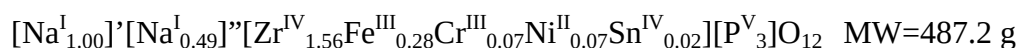


Table VI shows the mass balance for above formulation.

**Table VI. Mass balance for the [NZIP] waste form from reprocessing wastes.
Including channel box of BWR fuel assembly**

Constituent	Mass per MTU (kg)	[kg-mol] per MTU
Fuel Assembly Metal Waste	487.6	5.748
Uranium	0.5	0.002
LLW Concentrate Sodium	91.0	3.958
Iron	10.5	0.189
Oxygen	36.2	2.263
Phosphate in Spent Solvent Phosphorous	12.4	0.400
Oxygen	25.6	1.600
Additives to form [NZIP] Phosphorous	263.5	8.506
Sodium	10.7	0.465
Oxygen	508.1	31.759
Total Additives	782.3	
Immobilized Waste	1446.1	2.968

In the calculation, the assembly metal waste was considered to be a source for A site constituents, whereas the LLW concentrate was considered a source for both M' and A site constituents. The TBP solvent was considered a source for X site constituents and oxygen. In

addition to 1.00 mole of Na^+ in M' site, 0.49 moles of Na^+ are required to occupy M'' site in order to compensate a charge deficiency caused by the heterovalent substitution in A site, such as Fe^{3+} , Cr^{3+} , Ni^{2+} , and Sn^{4+} for Zr^{4+} . Since their concentrations are low, U^{4+} and other minor radioactive elements present in contaminated cladding hulls can also substitute either of the three sites, without disturbing the formulation according to the substitution model shown in Table I. The LLW concentrate occasionally contains 2-3 wt % of sulfates, as well as 3-4 wt% phosphates. As shown in Figure 2, sulfur can heterovalently substitute phosphorous in X site.

In order to accommodate all metallic components of the fuel assembly in the [NZP] waste structure, the amount of sodium present in the LLW concentrate satisfies 89.3% of the requirement for filling the M' site and M'' site (1.00 and 0.49 moles, respectively). The supply of phosphorous from the waste TBP solvent accounted for only 4.5% of the required amount, thus additional phosphorous and oxygen was required; in order to achieve charge and site balance in the proposed formulation of [NZP]. The ratio of the amount of additives to the immobilized waste was 54.1 wt%, yielding a loading factor of wastes to immobilized waste at 45.9 wt %. Total mass of the immobilized waste is 1446 kg/MTU.

Table VII shows another elemental composition for the assembly metal waste, formulated under the same assumptions, except that the channel box of BWR fuel has been excluded (the channel boxes are not likely to be contaminated by alpha activities, and can be thus be disposed separately).

**Table VII. Typical elemental composition of the LWR fuel assembly metal waste per MTU
Excluding the channel box of BWR fuel assembly**

	Total Mass (g)	Zr (g)	Fe (g)	Cr (g)	Ni (g)	Sn (g)
Stainless Steels	4.84E+04	0	3.58E+04	8.70E+03	3.90E+03	0
Nickel Alloy	1.01E+04	0	7.13E+02	1.51E+03	7.90E+03	0
Zirconium Alloy	2.92E+05	2.87E+05	4.42E+02	2.98E+02	1.45E+02	4.43E+03
Total	3.51E+05	2.87E+05	3.70E+04	1.05E+04	1.19E+04	4.43E+03
[kg-mol]	[4.250]	[3.146]	[0.662]	[0.202]	[0.203]	[0.037]

Applying the same elemental compositions for waste solvent and LLW concentrate provided in Tables IV and V, in addition to the those for metallic waste shown in Table III, another [NZP] formulation was given as:

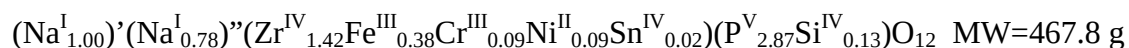


Table VIII shows the mass balance for above formulation.

**Table VIII. Mass balance for the [NZP] waste form from reprocessing wastes.
Excluding channel box of BWR fuel assembly**

Constituent	Mass per MTU (kg)	[kg-mol] per MTU
Fuel Assembly Metal Waste	350.5	4.250
Uranium	0.5	0.002
LLW Concentrate Sodium	91.0	3.958
Iron	10.5	0.189
Oxygen	36.2	2.263
Phosphate in Spent Solvent Phosphorous	12.4	0.400
Oxygen	25.6	1.600
Additives to form [NZP] Phosphorous	184.9	5.970
Silicon	8.1	0.289
Oxygen	390.7	24.420
Total Additives	583.7	
Immobilized Waste	1110.4	2.428

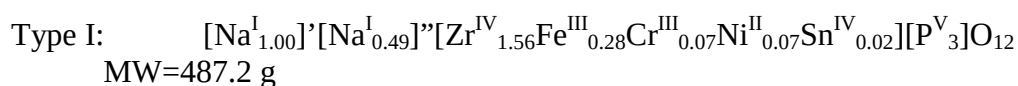
In this case, 0.65 moles of Na^+ were required to occupy M'' sites in order to compensate a charge deficiency caused by the heterovalent substitution in A site. Since the supplied amount of Na^+ was 1.78 moles, and the M'' site requires 0.78 moles of Na^+ in total, 0.13 moles of P^{5+} in the X site were substituted by 0.13 moles of Si^{4+} in order to provide an additional capacity to accommodate all surplus Na^+ in M'' sites. Theoretically, up to three moles of sodium ion can be accommodated in M'' sites using this formulation. The ratio of the amount of additives to the immobilized waste was 47 wt%; and the total mass of immobilized waste is 1110 kg/MTU (see Table VIII).

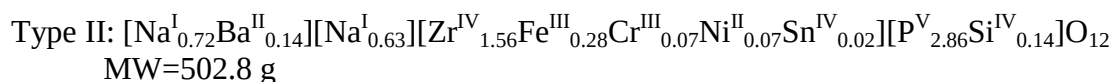
BENCH-TOP SYNTHESIZING OF SINGLE PHASE [NZP] WASTE FORMS

[NZP] compounds can be synthesized using various historical, conventional, and novel ceramic methods, such as single crystal formation method [7], coprecipitation method [8], solid-state reaction method [9, 10, 11], sol-gel method [12, 13], ion exchange method [14], hydrothermal method [15], and self propagating combustion method [16, 17], etc.

The primary objective of this research was to demonstrate the ability to produce single phase [NZP] compositions that are representative of NZPs obtainable through reprocessing waste forms as formulated in Table VI and/or Table VIII. Secondly, the NZP powder synthesis involved a bench-top reaction-precipitation process, proprietary to LoTEC, Inc., that is amenable to the use of waste forms as precursors. (This process has previously been successfully employed for the synthesis of various NZP compositions). Following synthesis of single phase NZP powders, coupons were to be fabricated for further physical and chemical characterization, by means of either the microwave sintering or furnace sintering. Figure 3 illustrates the process steps involved in the synthesis of [NZP] powder that is a waste-form based composition.

Two types of [NZP] waste forms were synthesized. Their compositions were,





The [NZP] composition of type I was exactly the same as shown in Table VI, however type II was not exactly the same as that corresponding to Table VIII. The actual formulation was modified to see the effect of equi-molar substitution of P^{+5} by Si^{+4} as well as Na^{+} by 0.5Ba^{+2} .

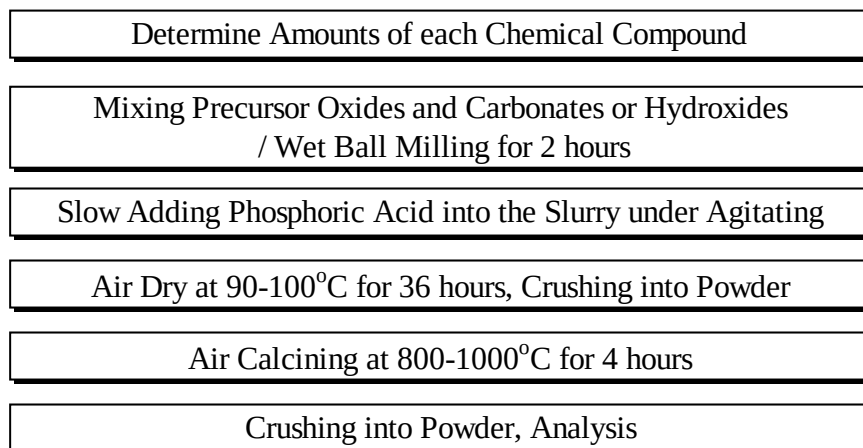


Figure 3. The process steps to synthesize the source powder of [NZP] waste forms

Conventionally, [NZP] materials are synthesized by direct solid-state diffusion reactions of stoichiometric powders at elevated temperatures. Because of the elevated temperatures involved in calcination synthesis using solid state reactions, the resulting NZP powders usually contain trace amounts of unreacted or semi-reacted phases and are characterized by low surface area and low reactivity.

In the reaction-precipitation process of this study, the precursors were wet ball milled in water in order to obtain a fine and homogeneous dispersion of precursors in the mix. However, the selection of chemical compounds to be used as precursors, as well as the procedure for mixing the phosphoric acid with these compounds were the critical issues for achieving single-phase materials at relatively low temperatures. Selected chemical compounds were $\text{Na}_2\text{O}/\text{NaHCO}_3$ for Na, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ or BaCO_3 for Ba, $\text{ZrO}_2 \cdot \text{CO}_2 \cdot 7\text{H}_2\text{O}$ for Zr, Fe_2O_3 for Fe, CrO_3 for Cr, NiCO_3 for Ni, SnO_2 for Sn, SiO_2 for Si, and H_3PO_4 for P. All chemical compounds were at least 99% chemically pure; however, they were still subject to assay or to loss on ignition testing to estimate the exact amounts of elemental constituents, so as to achieve exact stoichiometric compositions.

The wet milled precursor was subjected to pH testing prior to reaction with phosphoric acid. Phosphoric acid was added gradually while stirring the wet slurry. Temperature rise (exothermicity) and the precipitate formation was continuously monitored. The as-reacted precipitates were either semi-crystalline or amorphous (determined by X-ray analysis). After calcination at 925 °C or higher, fully crystalline, phase pure [NZP] was obtained. Table IX compares the X-ray Diffraction Analysis data for the reference NZP, type I [NZP] and type II [NZP]. The type I [NZP] showed a well developed crystalline structure characterized by sharp peaks and equivalent intensities, but with slightly smaller spacing than those of the reference

$\text{NaZr}_2(\text{PO}_4)_3$. The rhombohedral crystalline structure characteristic of $\text{NaZr}_2(\text{PO}_4)_3$ was maintained the type I and type II. There were virtually no indications of extra peaks to show existence of the second phase. The carbonate approach resulted in a lower pH value (7.9) in the slurry after mixing with phosphoric acid, while the hydroxide approach resulted higher pH (11.7). Despite the different pH of the precursor slurries, both types produced identical single-phase [NZP] crystal structures.

Table IX. X-ray diffraction analysis data for the synthesized [NZP]s

Miller Index <i>hkl</i>	Reference NZP		Type I [NZP]		Type II [NZP]*	
	<i>d</i> (Å)	<i>I/I</i> ₀	<i>d</i> (Å)	<i>I/I</i> ₀	<i>d</i> (Å)	<i>I/I</i> ₀
012	6.321	29	6.269	27	6.337	26
104	4.546	84	4.516	68	4.554	74
110	4.390	94	4.374	100	4.410	91
113	3.974	100	3.779	100	3.809	100
024	3.158	52	3.146	46	3.149	5
116	2.863	79	2.851	81	2.871	81
018	2.655	6	2.646	5	2.647	5
214	2.562	21	2.556	22	2.573	22
300	2.533	32	2.530	54	2.546	35
208	2.272	6	2.261	5	2.277	5
220	2.186	7				
306	2.105	11	2.103	11	2.112	8
128	2.018	18	2.012	16	2.023	14
134	1.976	13	1.973	11	1.984	12
0210	1.946	6	1.941	6	1.948	6
226	1.898	20	1.895	20	1.904	27
Cell Parameters	a=8.804Å c=22.759Å		a=8.706Å c=22.549Å		a=8.820Å c=22.688Å	
Cell Volume	1527.7 Å ³		1484.2 Å ³		1528.5 Å ³	
Theoretical Density	3.20 g/cm ³		3.27 g/cm ³		3.28 g/cm ³	

* Sintered specimen

MICROWAVE SINTERING OF [NZP] WASTE FORM

Microwave sintering has been perceived as a unique technique for processing a variety of materials, saving energy and time while improving physical and/or mechanical properties. This type of sintering has been utilized for the sintering of phosphate ceramic, i.e., hydroxyapatite.[18] In this work, microwave sintering was applied for the purpose of obtaining the highest attainable density of [NZP] compacts from type I powders. This technique, however, is still in the exploratory state of development. Commercial application of microwave sintering is particularly promising for radioactive materials, because of its amenability to remote operation.

The source powder was blended with 3 wt % acrolid resin binder. Pellets of 12.7 mm in diameter and 3 mm in thickness were pressed by applying a uniaxial pressure of 152 MPa, using a hydraulic press. Binder was burned off at 550 °C for 3 hours in air. Microwave sintering was carried out using modified multimode microwave industrial furnace (Amana Refrigeration Inc.,

Iowa, USA) operating at 2.45 GHz with a maximum power output of 2 kW. The pellet was placed on a zirconia base plate, enclosed in appropriate insulation. MoSi₂ rods were used as secondary microwave couplant to provide initial heating to the sample. The temperature was continuously monitored using a shielded Pt/Rh thermocouple placed in the vicinity of the pellet. Temperature was controlled within ± 5 °C of the desired value.

A green pellet was heated to a specified temperature typically in 35 minutes, and soaked for a specified period of time. The pellet was allowed to cool to room temperature freely. Density calculations were made based on geometrical sizes and weight.

Table X. Effect of microwave sintering temperature and time on sintered density of the type I [NZP] waste form

Time Temperature	Sintered Density (% T.D.)				
	10 min	15 min	25 min	30 min	60 min
1100 °C		90.5			
1150 °C	92.4	92.4	92.8	93.6	93.6
1200 °C	92.5				
1220 °C	93.0				
1250 °C	93.3				

Theoretical density of the type I [NZP] for XRD = 3.27 g/cm³

The sintering density of the type I [NZP] increased with increased sintering temperature, however specimens which were sintered at 1200 °C or higher showed local flaking on the surface subjected to microwave irradiation. Sintering at 1150 °C for 30 min or longer produced intact specimens with a saturated density of 93.6 % of the theoretical. Since the source powder had been calcined at 1075 °C in this case, temperatures of 1100 °C was not high enough to achieve a high density.

COLD PRESS AND FURNACE SINTERING OF [NZP] WASTE FORM

In this work, a conventional cold press and furnace sintering was applied for the purpose of obtaining the suitable specimens of compacts from the type II [NZP] powders for physical and chemical characterization. The source powder (from oxide and hydroxide precursors) that been calcined at 950 °C, was milled for 30 minutes with zirconia media, mixed with 2 wt% PEG powder binder, uniaxially pressed into square tiles of dimensions 25.4mm x 25.4mm x 8mm (thickness) at 51.7 MPa, and then iso-pressed at 206.8 MPa. The green density was 70 % of theoretical density. The green compact was placed in a zirconia crucible and embedded in the type II [NZP] powder. Debinding and sintering was accomplished in a single heat treatment in air using an electric furnace. The debinding part of the schedule was a ramp-up to 600 °C in 4 hours, followed by an isothermal hold for 2 hours. The sintering phase was a ramp-up to 1075 °C in 2 hours, followed by an isothermal hold for 4 hours. Finally, the sample was cooled to room temperature in 4 hours. The sintered density was consistently 88.4~88.7 % of the theoretical density (3.28 g/cm³). The volume shrinkage was 26%; which translates to 9.5 % linear shrinkage assuming isotropic 3 dimensional shrinkage.

SOLUBILITY OF SINTERED [NZP] WASTE FORM

In general, for heterogeneous dissolution of a mineral is to follow a mechanism which obeys a zeroth order kinetic rate law, as given by Lasaga [19],

$$dC_i/dt = (A/V)(k_{iS})$$

where dC_i/dt is the change in C_i solely due to mineral S and k_{iS} is the dissolution rate constant of species i (in solution) from mineral S. The dissolution rate constant k_{iS} has units of moles per square meter per second. A is the surface area of mineral S, and V is the volume of solution in contact with mineral S. The equation becomes,

$$dC_i/dt = (A/V)(v_i k_{Si})$$

where v_i is the stoichiometric content of species i in mineral S and k_{Si} is the overall dissolution rate constant of mineral S based on the dissolution of species i.

Dissolution was conducted on a sintered tile of the type II [NZP], with surface area to leachate ratio of 4.55×10^{-3} (m^2/L), which was suspended on a nylon string into 1000 mL of deionized water as the leachate. The study was conducted in a high SiO_2 glass flat bottom container (13 cm in diameter) that was surrounded by a mantle heater to keep leachate temperature at $75^\circ C$ and continually stirred at 100 rpm during the course of the experiment. At each sampling interval, appropriate amount of leachate for analysis was extracted from the stoppered container. At the end of the experiment, amount of the leachate was measured, and analytical data were calibrated for any loss of the leachate due to sampling or volatilization. Two consecutive dissolution test runs were performed, using the same sample under an identical experimental set up. No pH adjustment was made during the test runs. During the first run, The final pH was 8.36 for the first run and 8.86 for the second run, meanwhile the initial pH had been 5.99 for the first run and 5.38 for the second run.

Na and P were the predominant components of the type II [NZP] observed in the leachate, but the latter was always in less extent. Figure 4 represents concentration versus time behavior for the leachate recovered at $75^\circ C$. For the first run, the each curve consists of the initial non-linear part, the middle linear part, and the final flat part. Lasaga [19] suggested that the initial non-linear part of the curve would not have been due to the classic leached layer mechanism but to the presence of submicron particles coating the surface of sample. The concentration at the flat part of the curve implies saturation. Thus, the dissolution in the first run did not represent essential property of the material but a transient state. For the second run, the flat part did not exist, and the linear part in each curve was grown up. The second run represented more steady dissolution, however the slopes were still decreasing.

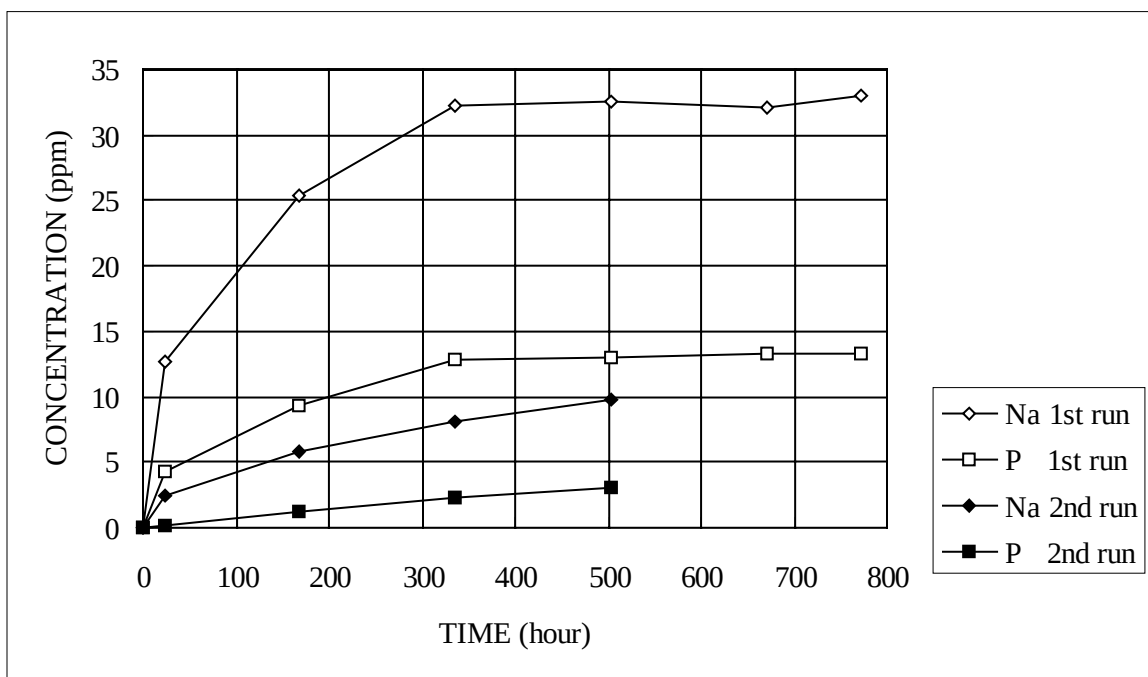


Figure 4. Concentration versus time plots of the raw dissolution data for the type II[NZP] of 88.7 % theoretical density, at 75 °C and pH=5.38~8.86

No other major components, such as Ba, Zr, Fe, Cr or Ni were observed in the leachate. The presence of excess B in the leachate suggested that any Si in the leachate should have been attributed to dissolution of glass ware. The dissolution rate constant of Si ($k_{\text{Si-Glass}}$) from the high SiO_2 glass was $1.16 \times 10^{-09} \text{ mol/m}^2/\text{sec}$, and that of B ($k_{\text{B-Glass}}$) was $1.49 \times 10^{-09} \text{ mol/m}^2/\text{sec}$.

The dissolution rate constant $k_{\text{i[NZP]}}$ and $k_{\text{[NZP]i}}$ were calculated for Na, P using the last linear part of the curves in the second run, and listed in the Table XI. The dissolution rate constants were also calculated for Ba and Zr assuming that the dissolution was linear and taking into account of detection limits of the elements.

Table XI. Dissolution rate constant observed at 75°C and pH=8.86

Species	Dissolution Rate Constant $k_{\text{i[NZP]}}$ mol/m ² /sec	Dissolution Rate Constant $k_{\text{[NZP]i}}$ mol/m ² /sec
Na	1.08×10^{-08}	8.01×10^{-09}
Ba	$<6.33 \times 10^{-11}$	$<4.52 \times 10^{-10}$
Zr	$<2.34 \times 10^{-10}$	$<1.50 \times 10^{-10}$
P	1.02×10^{-08}	3.56×10^{-09}

Lasaga calculated the time required to totally dissolve a spherical particle 10^{-3} m in radius, for various minerals, based upon the relationship between the dissolution rate constant of $\text{Si}(\text{OH})_4$ at 25°C and pH=5, and molar volume. Table XII lists the mean life time of various minerals by Lasaga [19] comparing with those obtained for the type II [NZP] and the high SiO_2 glass at pH=5.99~8.36 assuming the activation energies of 60 kJ/mol for dissolution using the Arrhenius plotting procedure. The molar volume for the type II [NZP] was $172.78 \text{ cm}^3/\text{mol}$ (molecular

weight: 502.8 g/mol, density :2.91 g/cm³). The molar volume for the high SiO₂ glass was 33.32 cm³/mol (molecular weight :74.3 g/mol, density :2.23 g/ cm³).

Table XII. Dissolution rate constant of minerals and the type II [NZP] and mean lifetime of a 1-mm radius particle at 25 °C

Mineral	Chemical Formula	Dissolution Rate Constant mol/m ² /sec	Lifetime
Quartz	SiO ₂	4.1×10^{-14}	34,000,000 y
Muscovite	KAl ₃ Si ₃ O ₁₀ (OH) ₂	2.56×10^{-13}	2,700,000 y
K-Feldspar	KAlSi ₃ O ₈	1.2×10^{-12}	520,000 y
Albite	NaAlSi ₃ O ₈	1.67×10^{-12}	80,000 y
Enstatite	MgSiO ₃	1.19×10^{-11}	8,800 y
Diopside	CaMgSi ₂ O ₆	1.0×10^{-10}	6,800 y
Nepheline	Na ₃ KAl ₄ Si ₄ O ₁₆	2.8×10^{-9}	211 y
Anorthite	CaAl ₂ Si ₂ O ₈	5.6×10^{-9}	112 y
Type II [NZP]	[Na _{1.35} Ba _{0.14}] [Zr _{1.56} Fe _{0.28} Cr _{0.07} Ni _{0.07} Sn _{0.02}] [P _{2.86} Si _{0.14}]O ₁₂	$k_{[NZP]Na} = 2.47 \times 10^{-10}$ $k_{[NZP]Ba} < 1.39 \times 10^{-11}$ $k_{[NZP]Zr} < 4.62 \times 10^{-12}$ $k_{[NZP]P} = 1.10 \times 10^{-10}$	741 y >13203 y >39723 y 1668 y
High SiO ₂ Glass	SiO ₂ 80.9 wt%, B ₂ O ₃ 12.7 wt%	$k_{GlassSi} = 3.58 \times 10^{-11}$ $k_{GlassB} = 3.40 \times 10^{-10}$	26534 y 2802 y

It is obvious that the dissolution mechanism of Na and P was entirely different from that of Ba and Zr. Any components that occupy the octahedral sites in the three-dimensional network of [NZP] structure are demonstrated to be as stable as Si in a high SiO₂ glass, however P in the tetrahedral site is less stable and Na in interstitial sites is least stable. P is more stable than Na by a factor of 2.3. Ba is very stable despite being in an interstitial site. Different dissolution mechanisms as well as different values of lifetime due to preferential dissolution suggests the long term selective changes of [NZP] composition during leaching. Further study of the dissolution mechanism of Na and P from [NZP] material is emphasized in order to verify the potentially high leaching stability of [NZP] waste forms.

THERMAL PROPERTIES OF SINTERED [NZP] WASTE FORM

A cylindrical disc with polished parallel surfaces of 10 mm in diameter and 2 mm in thick machined from a sintered tile of the type II [NZP] material was used to measure the specific heat and thermal diffusivity using a laser flash technique at 20 °C and 300 °C. The thermal conductivity was calculated based on measured data and a geometrical density of a sample disc (2.84 g/cm³). A bar with square cross section of 4 mm x 4 mm and 20 mm long machined from a sintered tile of the type II [NZP] material was used to measure the thermal expansion coefficient between 20 °C and 1000 °C.

Thermal properties of the type II [NZP] material are summarized and compared with thermal properties for typical NZP materials in Table XIII. It is obvious that the type II [NZP] material possesses the characteristic low thermal expansion property of typical NZP materials. This means that the [NZP] waste forms should have very good dimensional stability under severe temperature conditions and therefore thermal shock resistance despite its low thermal conductivity.

Table XIII. Thermal properties of the type II [NZP] and typical NZP materials.

Thermal Properties	Type II [NZP] Material	Typical NZP Materials
Specific Heat	0.59 J/g K 0.73 J/g K	0.5 J/g K
Thermal Diffusivity	$4.2 \times 10^{-7} \text{ m}^2/\text{sec}$ (20 °C) $3.8 \times 10^{-7} \text{ m}^2/\text{sec}$ (300 °C)	$6 \times 10^{-7} \text{ m}^2/\text{sec}$
Thermal Conductivity	0.70 W/m K (20 °C) 0.79 W/m K (300 °C)	~1 W/m K or less with increasing porosity
Thermal Expansion Coefficient	$<1.1 \times 10^{-6}/\text{K}$ (20~1000 °C)	$1 \times 10^{-6}/\text{K}$ or lower
Bulk Thermal Expansion	0.11% (20~1000 °C)	
Thermal Shock Resistance		from 1200 °C to ice water

CONCLUSIONS

1. A new concept for converting the intermediate wastes which result from light water reactor fuel reprocessing into a single phase structural analogue of sodium zirconium phosphate ([NZP]), was investigated.
2. Taking the design basis of [NZP] waste forms into consideration, the [NZP] waste forms could be successfully formulated utilizing such waste materials as metals (zirconium alloy, stainless steels, and nickel alloy), spent solvent tri-butyl phosphate, and concentrated solution of sodium nitrate a minimum amount of additional chemicals.
3. The crystallographic feasibility to form single phase [NZP] materials based on the formulated composition was successfully demonstrated by processing phase pure powders using an innovative precipitation-calcination process.
4. The capability to form high density compacts as a single phase [NZP] material was demonstrated by microwave sintering process as well as by a conventional furnace sintering process.
5. It was emphasized that only repeated dissolution test runs could represent the essential dissolution property, but not by the once-through dissolution test. Although, Na and P exhibited preferential dissolution in water, other major components of the type II [NZP] material, such as Zr, Fe, Cr, Ni and Ba exhibited high dissolution/leaching resistance in an appropriate test.
6. This preliminary study indicates significant potential for in-situ formation of single-phase NZP based immobilized radioactive waste forms that are thermally and environmentally stable.

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