

Microwave-assisted low temperature synthesis of sodium zirconium phosphate (NZP) and the leachability of some selected fission products incorporated in its structure – A case study of leachability of cesium

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Abstract. Microwave-assisted procedure for low temperature solid state synthesis of sodium zirconium phosphate (NZP), a material with the potential for immobilization and disposal of high level nuclear waste, was developed. Three selected fission products, namely, Cesium, Strontium and Tellurium were introduced (substituted) in the NZP matrix during its synthesis at 450°C. Leaching studies were carried out on the fission product substituted NZP sintered at 1000°C, in pure de-ionized water and 80% saturated brine solution at the ambient temperatures of 30°C and 90°C for four weeks. The major part of leaching in all the cases was observed in the first week. The extent of leaching after four weeks was found not exceeded from 12 to 15% of the elements substituted in NZP, which later became negligibly small. The effect of temperature and the nature of leachant on the leaching rate did not indicate any systematic trend. The EDX analysis of the surfaces of the leached NZP pellets showed that the leaching of the dopants is limited mainly to the surface region of the sintered pellets.

Keywords. Microwave aided synthesis; SEM; EDX; XRD; HLW immobilization; leaching.

1. Introduction

Immobilization and safe disposal of highly radioactive waste produced during irradiation of nuclear fuel is a matter of great concern in nuclear power generation. Much of this waste comprising of several radioactive elements remains hazardous for thousands of years, leaving a deadly radioactive legacy to future generations. The most important mandate of the nuclear establishments is therefore, to immobilize this waste and isolate it from the public.

1.1 Immobilization of radioactivity

1.1a *Fixation of radioactivity in glass:* Borosilicate glass^{1–3} is currently used for the fixation of high level nuclear waste (HLW) in several nuclear power generating plants around the world. The procedure involves the concentration of the nitrate waste solution obtained after reprocessing of the spent fuel and

adding it to the mixture of glass forming components, comprising of boric acid, sodium carbonate and silica. This results in the formation of the slurry from which water and other volatile components are removed by slow heating and the resulting oxides from the nitrates are incorporated in the glass matrix by heating the charge to the pouring temperature of glass which could be as high as 1150°C. During this process, oxides of several elements such as those of Cs, Te, Ru, etc. vaporize and get deposited in the ducts and pipelines connected to the processing plant making this area inaccessible for work to the technicians, due to high radioactivity. It is therefore necessary to devise a process by which these elements could be fixed into the solid matrix at temperatures low enough, where the vaporization of these oxides is not significant.

The other disadvantage of fixing the radioactivity in glass is mainly due to its thermodynamically meta-stable nature. The solidified radioactive glass contained in special steel canisters located in the repositories can spontaneously de-vitrify and the

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heat produced due to this transformation could breach the canister and expose its radioactive contents to the environment.

1.1b Potential of ceramic matrices for immobilization of nuclear waste: Several attempts have been made to develop suitable thermodynamically stable solid ceramic matrices with the potential to fix the radio nucleides.⁴⁻¹⁰ Ringwood and co-workers⁴ synthesized several perovskite and pyrochlore structure based ceramic phases which could be used for fixation of number of radioactive elements. But each of these phases could be used for immobilization of only specific elements. They considered the use of the mixture of several phases for the fixation of several nucleides together, and termed this assemblage as SYNROC. Similar attempts were also made by Roy and co-workers.⁶⁻¹⁰ The solid state synthesis routes adopted by these investigators for the preparation of these compounds, particularly in the case of SYNROC, used sophisticated technique such as hot iso-static pressing (HIP) involving the use of very high temperatures and high pressures and were not cost effective.

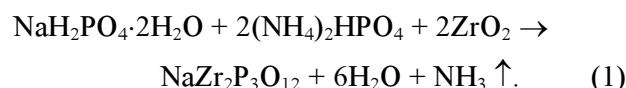
The development of SYNROC was followed by several attempts to prepare thermodynamically stable ceramics which would accommodate large number of fission products in a single ceramic matrix without major structural alteration. Scheetz and co-workers⁷ in their recent review presented the potential of sodium zirconium phosphate (NZN) as the most suitable candidate for the replacement of glass for fixing the high level nuclear waste. They observed that almost all the fission products could be accommodated in NZN owing to its peculiar structure. Few experiments on the fixation and leaching of HLW performed on NZN were promising,^{7,11} but the potential of this material as a substitute for glass however, is yet to be established firmly. The details of the structure and the potential sites for substitution of different fission products based on the ionic size of the substituents and the structure of NZN are presented in several publications.¹¹⁻¹⁴

2. Experimental

2.1 The methods reported for the preparation of NZN

Three different methods have been used by the earlier investigators for the preparation of the com-

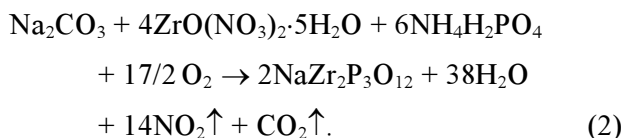
pounds in NZN family. These include: (i) Sol-gel method¹⁵⁻²⁰; (ii) Solid state method²¹⁻²⁶ and (iii) Hydrothermal reactions.^{27,28} Almost all the methods reported for the synthesis of NZN are time consuming, need speciality chemicals like alkoxides^{19,20} and temperatures in excess of 800°C. Breval *et al*¹³ synthesized low-thermal-expansion materials in NZN family by the combustion reaction method using low cost chemicals including urea as a fuel and NH₄NO₃ as an oxidizer, zirconium oxynitrate, and ammonium dihydrogen phosphate. Govindan Kutty²⁹ prepared NZN by heating the mixture of Zirconyl chloride or nitrate, sodium carbonate and ammonium dihydrogen phosphate at temperature as low as 600°C in conventional resistance furnace. Vaidynathan and Rao³⁰ prepared NZN by heating the mixture of NaH₂PO₄·2H₂O, (NH₄)₂HPO₄ and ZrO₂ in stoichiometric proportion in microwave oven. The reaction was represented as



Vaidynathan and Rao³⁰ performed elaborate experiments to prove that among the reaction components used, only NaH₂PO₄·2H₂O remained microwave-active after dehydration and mainly contributed to microwave heating of the reaction mixture. The method proposed by NIST³¹ involved heating of the mixture of ZrO₂, NaHPO₄ and (NH₄)₂HPO₄ in resistance furnace above 1200°C for 12 h with repeated grinding.

2.2 The basis for the procedure adopted in the present work

2.2a Thermal analysis of the reaction mixture: Among the three methods outlined above the method proposed by Kutty²⁹ was adopted in the present investigation, with the difference that the conventional resistance heating of the mixture was changed to microwave heating. The choice was based on the fact that ammonia released in the reaction could be oxidized by nitrate providing the local exothermicity, in addition to the heating provided by the interaction of the reaction components with the microwave radiation. The reaction involved heating of the mixture of Na₂CO₃, ZrO(NO₃)₂·5H₂O and (NH₄)H₂PO₄ in the ratio 1:2:3 at 600°C. The overall reaction could be represented by the equation



The choice of selection of reaction temperature was based on the information provided by thermogravimetry, and differential scanning calorimeter.³² The simultaneous TG-DSC plot recorded employing the SETARAM simultaneously recording TG-DSC unit, for the reaction mixture in argon is shown in figure 1. It is clear from the TG curve that the total mass loss of the mixture resulting due to dehydration, denitration, deammoniation and decarbonation is virtually complete by 500°C, which is expected to be completed at much lower temperature if the mixture is heated isothermally. DSC curve however, shows some interesting features. The first endothermic peak (120°C) which could mainly be attributed to dehydration, was followed by a prominent exothermic peak (300°C) which could involve simultaneous denitration, deammoniation and decarbonation. The exothermicity of this peak could be understood in terms of the oxidation of the evolved ammonia in the mixture by nitrate. Though the decomposition reaction is complete by around 500°C, another conspicuous broad exothermic peak was observed around this temperature. This broad exothermic peak could be understood only if the product formed after the completion of the reaction around 500°C is amorphous. The thermal data in figure 1 provided the guideline for optimizing the temperature of heat treatment of the reaction mixture to obtain pure NZP.

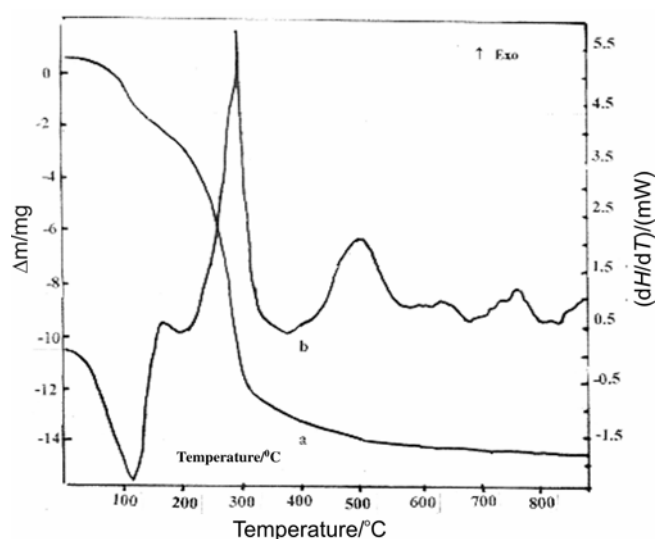


Figure 1. Simultaneous thermogravimetric and differential scanning calorimetry plot for the reaction mixture.

The exothermicity observed in the reaction mixture (DSC peak around 300°C) during the decomposition facilitated the formation of NZP at low temperatures as in the case of self propagating high temperature reactions.^{33–36} Adopting microwave heating was expected to further decrease the reaction temperature,³⁷ which, in fact, was observed in the recent work of Ganesh and co-investigators.³⁸

2.2b Characterization of NZP by X-ray diffraction: X-ray diffraction pattern (figure 2a) of the product obtained by heating the reaction mixture at 450°C in conventional resistance heated furnace for 1 h indicated that the product was indeed partially crystalline. The same mixture heated in microwave oven at the same temperature (450°C) for the same duration yielded highly crystalline NZP (figure 2b) nearly as crystalline as the product obtained by heating the reaction mixture at 650°C (figure 2c) for the same time interval. The highly crystalline nature of NZP obtained from the reaction mixture heated in the resistance furnace at 650°C in air, confirmed that the broad exothermic peak around 500°C (figure 1) was indeed due to crystallization of the partially amorphous NZP formed below 500°C.

2.1c The procedure adopted for the preparation of pure and fission elements doped NZP: In the procedure developed, the stoichiometric (1 : 2 : 3) mixture of sodium carbonate, zirconyl nitrate pentahydrate and ammonium dihydrogen phosphate was thoroughly ground in agate mortar and homogenized in acetone. The mixture frothed and became sticky during grinding, probably due to evolution of carbon dioxide by the reaction of sodium carbonate with highly acidic zirconyl nitrate hydrate. The product obtained was ball milled in presence of acetone and dried in air oven at 90°C till free flowing powder was obtained which was then heated in microwave heating system (MHS), at 450°C. The fission products (Cs, Sr, Te) doped NZP was obtained by adding the appropriate salts or oxides of these elements to the reaction mixture prior to heating.

The quantities of original components in the reaction mixture were appropriately adjusted to accommodate 1 to 2a/0 of the substituted elements. XRD patterns of pure as well as doped NZP samples were found to be identical and yielded the value for the volume of the unit cell within 1% of that reported by Sizova³⁹ for pure NZP. The substitution of selected fission product elements in the parent NZP matrix

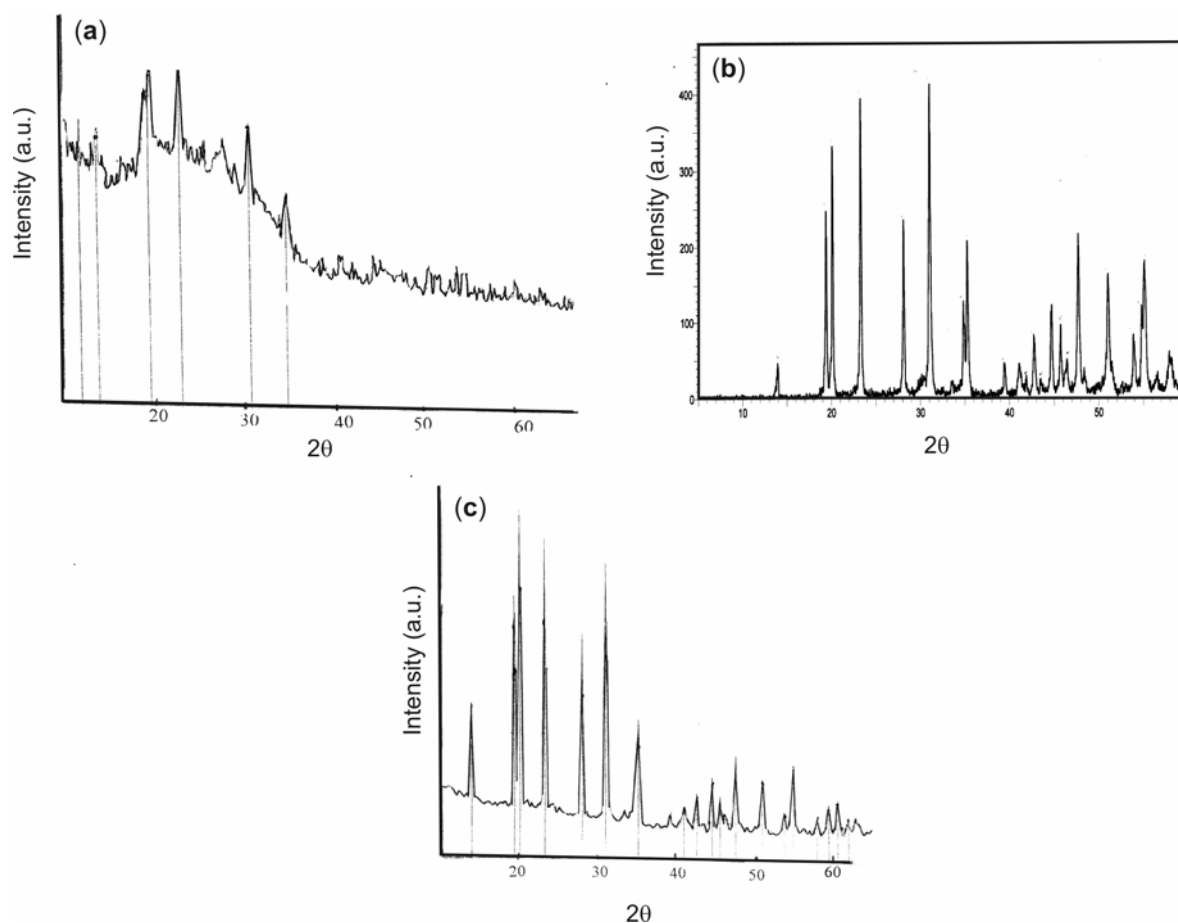


Figure 2. (a) XRD pattern of the product obtained by heating mixture of Na_2CO_3 , $\text{ZrO}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ and $(\text{NH}_4)\text{H}_2\text{PO}_4$ in resistance heated furnace at 450°C for 1 h. (b) XRD pattern of the product obtained by heating mixture of Na_2CO_3 , $\text{ZrO}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ and $(\text{NH}_4)\text{H}_2\text{PO}_4$ in microwave oven at 450°C for 1 h. (c) XRD pattern of the product obtained by heating mixture of Na_2CO_3 , $\text{ZrO}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ and $(\text{NH}_4)\text{H}_2\text{PO}_4$ in resistance heated furnace at 650°C for 1 h.

was confirmed by EDX analysis (table 1). The total concentration of the dopants in the NZP matrix was limited to 2%. The elements were doped either singly, in pairs or triads.

The concentration of the dopants introduced in NZP determined by EDX were based on limited data obtained by scanning the sample at few points on the sample surface and may not be representative of the whole bulk. More accurate results were therefore obtained by chemical analysis which involve dissolution of the samples in HCl, HF mixture in the ratio 85 : 15 at 160°C employing microwave heating. Good agreement was seen in the concentration values of the dopants added to the reaction mixture and those derived from chemical analysis (table 2) indicating that the dopants added in the mixture were retained in the product obtained at 450°C quantitatively. The concentration of the dopant elements in

the solution prepared from doped NZP was determined by flame photometry and ICP-MS.⁴⁰

2.1d Densification of NZP and determination of the concentration of dopants in the sintered compacts: NZP prepared by the above method had to be sintered to high density to minimize the leaching of the doped elements. 2 mm thick, 12 mm diameter green NZP pellets obtained by compacting the powder applying the uniaxial pressure of 2.8 tonnes/sq. inch were analysed dilatometrically in order to optimize the temperature of sintering. The sintering temperature should not be too high in order to prevent the loss of the dopants from NZP. The shrinkage data for the pellets doped with different selected elements are presented in figure 3. It can be concluded from the figure that NZP sinters rapidly above 850°C . Optimum temperature for sintering

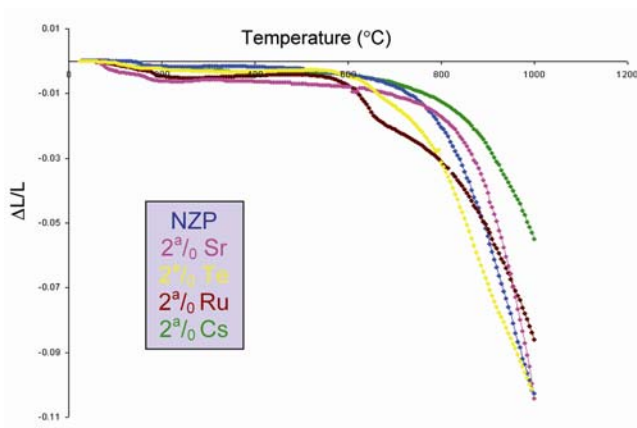
Table 1. Comparison of the amount of dopant added in the reaction mixture with that estimated in the reaction product by EDX.

Combination	Amount of Cs added (atom percentage)	Amount of Cs estimated by EDX analysis (atom percentage)
Cs	2.0	2.87
Sr–Cs	1.0	1.12
Sr–Cs–Te	1.0	1.23

Table 2. Amount of the elements in the doped NZP prepared at 450°C.

Combination	Element	Amount added* (mg)	Amount estimated by MW dissolution (mg)	Amount estimated by flame photometry (mg)
Cs	Cs	12.19	12.25	11.83
Sr–Cs	Sr	4.02	4.50	4.21
	Cs	6.10	6.11	6.02
Sr–Cs–Te	Sr	4.02	4.47	4.15
	Cs	6.10	6.10	6.23
	Te	5.88	4.96	–

*Amount of substituent in 100mg of the doped NZP

**Figure 3.** The shrinkage curves recorded for pure and doped samples.

was fixed at 1000°C where the rate of sintering was fairly rapid. The pellets heated at this temperature for three hours yielded NZP with densities ranging between 85 and 92% of the theoretical value. The values of the concentration of the dopants in the sintered compacts determined by chemical analysis are listed in table 3 which indicate small but significant loss of the dopant during the sintering process. It is reported that NZP does not sinter significantly above 1000°C.⁴¹ Increasing the temperature of sintering above 1000°C would therefore, result only in additional loss of the dopants from NZP.

3 Leaching studies on fission product doped NZP

The most important part of this study was to investigate the leaching behaviour of the dopants immobilized in the NZP matrix and to assess the extent to which these elements would find their way in the environment by the interaction with ground waters under accidental conditions. In the leaching experiments, the sintered pellets weighing between 400 and 500 mg, containing the dopant was leached in 20 to 25 ml ($V/SA = 10$) of the leachant liquid (deionized water or saturated brine solution) at room temperature and at 90°C. The value of volume to surface area ratio (V/SA) was maintained at 10 as required by the procedure recommended by MCC.⁴² The concentration of the elements released in the leachants were estimated after 7, 14, 21 and 28 days. The leachant in the container was replaced by a fresh lot after each time interval. The concentration of elements in the leachant was estimated by ICP-MS after suitable dilution. The rate of leaching was calculated in $gm/m^2/day$ as per the procedure MCC⁴².

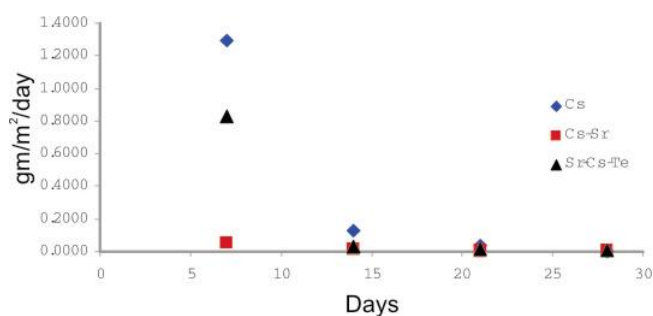
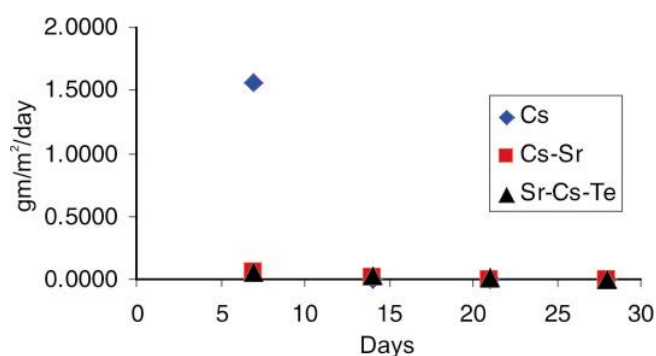
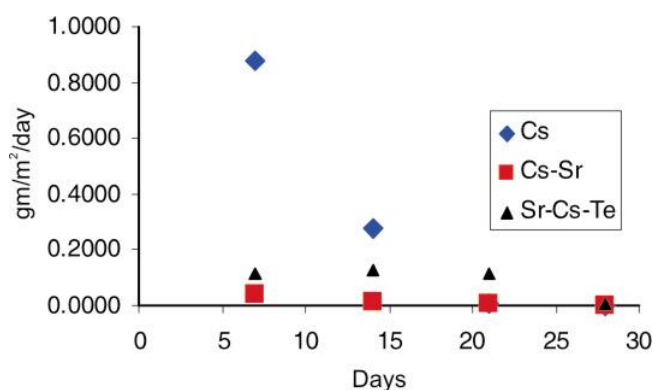
The leaching of dense fission product doped NZP was carried out in pure de-ionized water and 80% saturated brine solution at ambient room temperature and 90°C respectively. The studies were carried out on singly as well as multiply doped NZP pellets.

Table 3. Amount of the elements in NZP matrix before and after sintering.

Mode of doping	Element	Amount estimated at 450°C (mg)	Amount estimated at 1000°C (mg)
Cs	Cs	12.25	10.15
Sr–Cs	Sr	4.50	4.46
	Cs	6.11	6.09
Sr–Cs–Te	Sr	4.47	5.2
	Cs	6.10	6.10
	Te	4.96	4.96

Table 4. Leaching of Cs in deionized water at RT.

Days	Cs–NZP	Amount of Cs leached (gm/m ² /day)	
		Sr–Cs–NZP	Sr–Cs–Te NZP
7	1.2913	0.0533	0.8290
14	0.1286	0.0157	0.0319
21	0.0377	0.0059	0.0160
28	0.0020	0.0047	0.0060

**Figure 4.** Leaching of Cs in deionized water at RT.**Figure 6.** Leaching of Cs in 80% saturated brine solution at RT.**Figure 5.** Leaching of Cs in deionized water at 90°C.

Results are however presented for only few combinations including Cs, Cs–Sr and Cs–Sr–Te. Some data was available in the literature in the case of Cs

and Cs–Sr doped samples for comparison.^{7,11} Each element in these combinations was substituted to the extent of 2^a/₀ when singly doped and 1^a/₀ each when more than one element were substituted in the NZP matrix. Among the doped NZP samples, those doped with Cs and Sr and Cs, Sr and Te simultaneously were found to retain much more amount of Cs in the sintered pellets (table 3). It was therefore, decided to study the leachability of Cs from these samples and compare the results with those obtained on singly Cs substituted NZP sample.

The results obtained for leaching of Cs in the combination involving Cs–Sr and Cs–Sr–Te in pure deionized water and 80% brine solution at room temperature and 90°C are presented in tables 4 to 7

Table 5. Leaching of Cs in deionized water at 90°C.

Days	Cs–NZP	Amount of Cs leached (gm/m ² /day)	
		Sr–Cs–NZP	Sr–Cs–Te NZP
7	0.8816	0.0406	0.1128
14	0.2802	0.0128	0.1305
21	0.0071	0.0096	0.1124
28	0.0029	0.0032	0.0057

Table 6. Leaching of Cs in 80% brine water at RT.

Days	Cs–NZP	Amount of Cs leached (gm/m ² /day)	
		Sr–Cs–NZP	Sr–Cs–Te NZP
7	1.5654	0.0554	0.0628
14	0.0052	0.0141	0.0242
21	0.0000	0.0052	0.0098
28	0.0000	0.0048	0.0039

Table 7. Leaching of Cs in 80% brine water at 90°C.

Days	Cs–NZP	Amount of Cs leached (gm/m ² /day)	
		Sr–Cs–NZP	Sr–Cs–Te NZP
7	0.9870	0.0534	0.1170
14	0.0289	0.0139	0.0920
21	0.0129	0.0051	0.0707
28	0.0012	0.0052	0.0411

Table 8. The pellet leached at 90°C in deionized water.

Mode of doping	Element	Amount estimated at 450°C (mg)	Amount estimated in the pellet sintered at 1000°C (mg) (before leaching)	Amount estimated (mg) in the pellet sintered at 1000°C (after leaching)
Cs	Cs	12.25	10.15	9.72
Sr–Cs	Sr	4.50	4.46	4.21
	Cs	6.11	6.09	5.90
Sr–Cs–Te	Sr	4.47	5.20	4.9
	Cs	6.10	6.10	5.90
	Te	5.88	4.96	4.86

and plotted in figures 4 to 7. These results indicate that the leaching of Cs from Cs–Sr and Cs–Sr–Te combinations is much less compared to that from NZP containing Cs alone and the total amount of the dopant element leached after four weeks in none of the cases exceeded 12 to 15% of the amount originally contained in the sintered pellets. The values of concentration of the dopants in NZP determined before and after four weeks of leaching are listed in table 8.

4 Surface analysis of the doped NZP pellets before and after leaching

4.1 EDX analysis

The results of elemental analysis by EDX of the surfaces and the bulk of Cs–Sr and Cs–Sr–Te doped NZP pellet before and after leaching for four weeks are presented in tables 9–14. The leaching of Cs–Sr, Cs–Sr–Te containing pellet was done in deionized

water and in brine solution at RT and 90°C respectively. The EDX patterns for the surfaces of unleached Cs–Sr substituted NZP and that leached deionized water at 90°C are shown in figures 8 and 9. The similar results for surfaces of Cs–Sr–Te

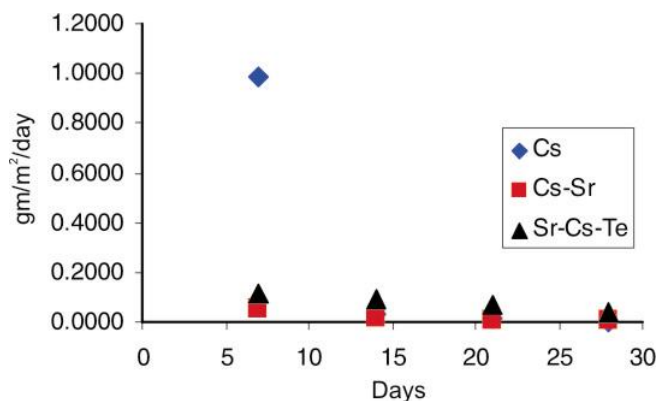


Figure 7. Leaching of Cs in 80% saturated brine solution at 90°C.

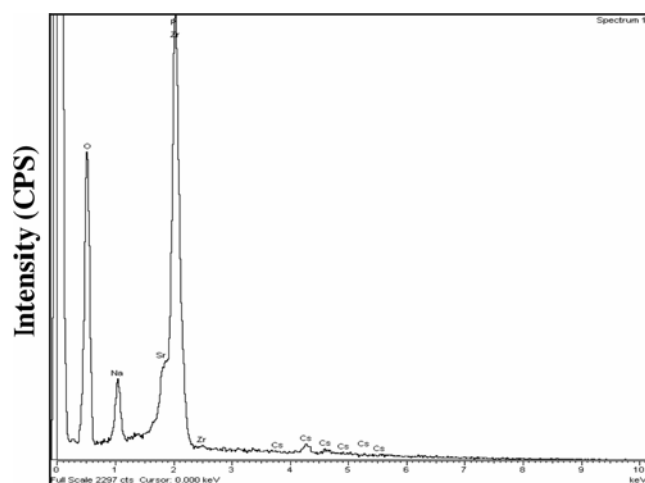


Figure 8. EDX data of unleached Sr–Cs NZP.

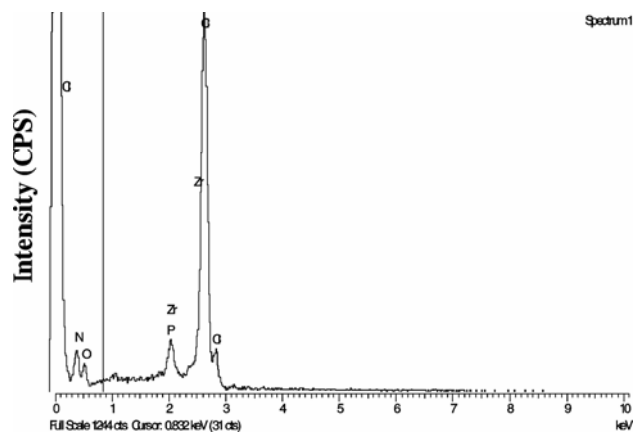


Figure 9. EDX data of Sr–Cs NZP on surface of leached pellet.

doped pellet were obtained after leaching the pellet at 90°C in more chemically hostile environment containing 80% saturated brine solution. The surface of Cs–Sr doped pellet after leaching was virtually

Table 9. EDX data of unleached Sr-Cs NZP.

Element	Weight (%)	Atomic (%)
O K	31.90	62.97
Na K	3.22	4.43
P K	16.04	16.35
Sr L	5.30	1.91
Zr L	36.78	12.73
Cs L	6.76	1.61
Total	100.00	–

Table 10. EDX data of Sr–Cs NZP on surface of leached pellet.

Element	Weight (%)	Atomic (%)
N K	26.55	46.18
O K	6.61	10.07
P K	1.82	1.43
Cl K	59.40	40.82
Zr L	5.61	1.50
Total	100.00	–

Table 11. Sr–Cs NZP at Center of leached pellet.

Element	Weight (%)	Atomic (%)
O K	29.03	62.17
Na K	3.95	5.88
P K	21.45	23.73
Cs L	2.68	0.69
Pt M	32.89	7.53
Sr	10.80	1.60
Total	100.00	–

Table 12. EDX data of unleached Sr–Cs–Te NZP.

Element	Weight (%)	Atomic (%)
Na K	9.86	20.32
P K	32.52	49.77
Sr L	4.75	2.57
Zr L	52.00	27.02
Te L	0.87	1.96
Cs L	7.11	1.23
Total	100.00	–

devoid of Cs (table 10, figure 9). However, in the case of Cs–Sr–Te doped pellet the presence of considerable amount of Cs was observed on the leached

surface (table 14, figure 12). This is contrary to the observation in table 8 in which the amount of Cs leached in pure deionized water from Cs–Sr–Te containing NZP after four weeks of leaching is much higher than that from Cs–Sr containing NZP. This observation suggests that the presence of sodium in the leachant could possibly suppress the dissolution of Cs from Cs–Sr–Te doped NZP. The analysis of the dopants in the center of the section obtained by cutting it perpendicular to the diameter revealed that while there is significant depletion of Cs in the case of Cs–Sr (table 11, figure 10) doped pellet, there is no sizeable variation in the concentration of Cs from surface to center in the case of Cs–Sr–Te (table 13, figure 11) containing NZP pellet after leaching indicating the suppression of leaching of Cs from the pellet. The concentration of Cs in the centre of the CS–Sr doped pellet determined by EDX is however much lower than that expected on the basis of the total Cs estimated in the leached sample (table 3). This could be due to very few data points recorded by EDX for the estimation of Cs. More studies are needed to examine the influence of the presence of NaCl in the leachant on the leaching behaviour of doped elements in the NZP matrix.

5. Conclusions

Pure and fission products (Cs, Sr, Te and Ru) substituted NZP could be prepared in highly crystallined

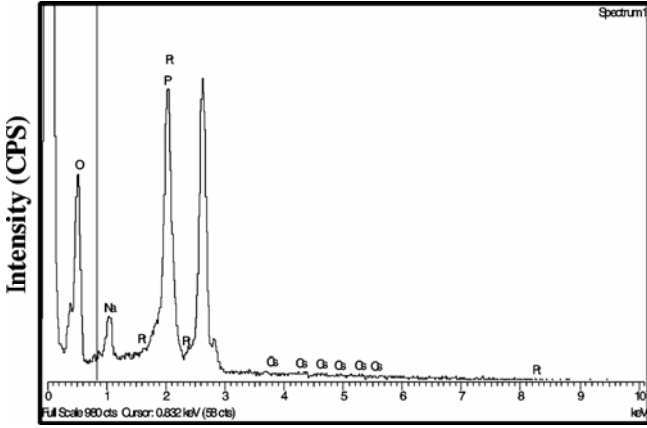


Figure 10. EDX data of Sr–Cs NZP at Center of leached pellet.

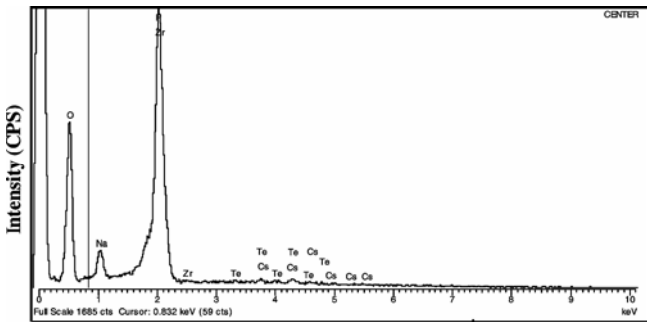


Figure 11. EDX data of Sr–Cs–Te NZP at Center of leached pellet.

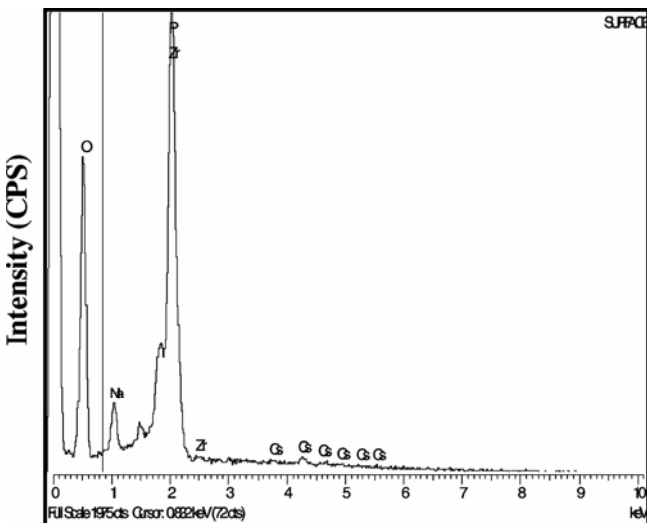


Figure 12. EDX data of Sr–Cs–Te NZP on surface of leached pellet.

Table 13. EDX data of Sr–Cs–Te NZP at center of leached pellet.

Element	Weight%	Atomic%
O K	30.90	62.23
Na K	2.59	3.63
P K	16.72	17.39
Zr L	41.90	14.80
Te L	2.93	0.74
Cs L	4.96	1.20
Totals	100.00	–

Table 14. EDX data of Sr–Cs–Te NZP on surface of leached pellet.

Element	Weight%	Atomic%
O K	34.75	65.46
Na K	2.69	3.53
P K	16.97	16.52
Zr L	40.08	13.24
Cs L	5.51	1.25
Totals	100.00	–

Table 15. Studies on 1a/o Cs-1a/o Sr NZP.

Element	1a/o Cs-1a/o Sr-NZP (our work)		1a/o Cs-1 ^a /o Sr-NZP (Zyrynov) ¹¹	
	Days	Leaching rate (gm/m ² /day)	Days	Leaching rate (gm/m ² /day)
Cs	7	0.04	7	0.02
	28	0.003	28	0.002
Sr*	7	0.015	7	0.01
	28	0.003	28	0.003

*Results to be published separately

Table 16. Comparison of our data with that reported in the literature CsZP.

No. of days	2a/o Cs-NZP (our work)		Cs ZP (Scheetz <i>et. al</i>) ⁷	
	Temperature (°C)	Leaching rate (gm/cm ² /day)	Temperature (°C)	Leaching rate (gm/cm ² /day)
14	RT	1.3×10^{-5}	—	—
14	90	2.8×10^{-5}	110	2×10^{-5}

form at temperature as low as 450°C, at which the volatility of most of the fission products is insignificant, by proper choice of the reactants employing microwave heating technique. The quantitative retention of all the fission products added to the reaction mixture in the resulting NZP could be confirmed by chemical analysis.

Pure and fission product doped NZP could be sintered to nearly 85 to 92% of theoretical density by heating at 1000°C for 3 h. The loss of the dopants due to heat treatment during sintering was limited to 12 to 15% of the amount contained in doped NZP prepared at 450°C.

Leaching of Cs from the sintered pellets of doped NZP containing Cs, Cs-Sr and Cs-Sr-Te indicated maximum leaching in the case where only Cs was doped in NZP. The extent of leaching was much less for other two combinations. The concentration of the dopants determined in the leachant and the doped pellets after leaching confirmed that almost 90% of the elements doped in NZP matrix were retained in most of the cases even after leaching for more than 28 days. Changing of leachant from pure de-ionised water to 80% saturated brine solution in the case of CS-Sr-Te combination resulted in the retention of maximum Cs in the doped NZP.

The temperature had small but significant effect on the leaching rate. The average leaching rates of Cs decreased with increasing temperature in the case of pure Cs and Cs-Sr doped NZP.

The extent of leaching and the leaching rate of the doped fission products from NZP was also influ-

enced by changing the leaching medium from deionized water to 80% saturated brine solution. In case of Cs, there is increase of initial leaching rate; however, the leaching rate after two weeks attains nearly the same value in all the Cs containing samples.

The results obtained in this investigation certainly demonstrate the potential of NZP as a candidate for the fixation of high level nuclear waste. However, the present data cannot be compared with that of leaching from glass matrix due to unavailability of such information from the literature. Most of the studies involving leaching of glass, monitor the loss of sodium from the matrix during leaching. The superiority of NZP for immobilization of HLW over glass however can only be established, when the leaching of the elements selected in the present work is studied from the glass matrix in the same concentration range under the identical set of experimental conditions. The present data obtained for the leaching of fission products embedded in the NZP matrix indicate that the leaching rates of these elements from this matrix is at least two orders magnitude lower than that of sodium from borosilicate based glass.⁴³

There are very limited data in the literature to compare the leachability of fission products from NZP in the present work. The only information available in the literature on this topic^{7,11} is summarized in tables 15 and 16.

Luo *et al*⁴⁴ presented the leaching rate data on 1 atom percent Cs and Sr doped SYNROC at 110°C in pure water (table 17). It is observed that the leaching

Table 17. Comparison with SYNROC (after 7 days of leaching).

Element	1a/0Cs-1a/0Sr-NZP		SYNROC	
	Temperature	Leaching rate (gm/m ² /day)	Temperature	Leaching rate (gm/m ² /day)
Cs	90°C	4×10^{-2}	110°C	5.64×10^{-2}
Sr		1.5×10^{-2}		2.83×10^{-2}

rates of these two elements from SYNROC at 110°C are within the same order of magnitude of that of leaching of Cs from 1 atom percent doped Cs-Sr NZP.

The most important conclusion from the present work is that in the case of immobilization of high level nuclear waste on NZP and its disposal, the leaching of the waste partially from this matrix would provide the barrier for further leaching. The extent to which the dopants are leached do not exceed about 15% of the quantity incorporated in NZP. In the event of exposure of such partially doped material to ground water there will be much less risk of the radioactivity entering the environment. Further, there will be much less leaching of Cs in geological locations containing rock salt in the event of accidental exposure of the material to the underground hot water sources. Much data however need to be collected to justify the claim based on few observations reported in this investigation.

More data on leaching of Sr and Te under the set of conditions identical to those in the present work will be published separately.

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