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COMPARISON OF SODIUM ZIRCONIUM PHOSPHATE AND SYNROC MATRICES FOR IMMOBILIZATION OF HIGH-LEVEL WASTE

V. N. Zyryanov,* Institute of Experimental Mineralogy, Russian Academy of Sciences, 142432, Chernogolovka, Russia, and E. R. Vance, Materials Division, Australian Nuclear Science and Technology Organization (ANSTO), Menai, NSW 2234, Australia

The aims of the present work were to investigate possible compatibility between sodium zirconium phosphate (NZP) and Synroc titanate phases, to prepare NZP-based waste forms by hot-pressing rather than sintering, and to investigate the incorporation in NZP of (a) Cs/Sr as simulated heat-generating nuclides; (b) simulated actinides; and (c) simulated Purex waste. The NZP samples were prepared by methods similar to those used for Synroc. The precursor NZP phase was formed from tetrabutyl zirconate $Zr(OC_4H_9)_4$, sodium nitrate, and 85% orthophosphoric acid. Simulated waste nitrate solutions were then mixed with the liquid precursor. After stir drying of the precursor, calcination was carried out at 700°C to remove nitrates and organics. In preliminary work, the calcine was sintered in air at 1000 to 1200°C. Subsequent preparations were hot-pressed uniaxially or isostatically in metal bellows at 1100°C. Uniaxial hot-pressing was not very successful because of the low tap density of the calcine. This caused the bellows to collapse completely on hot-pressing, thereby producing significant resistance to densification in the final stages of the pressing. Severe layering of the pressings occurred, although densities of 92 to 94% of theoretical values were obtained. These problems did not occur in hot isostatic pressing. For this purpose, an EAGLE hot isostatic press (manufactured by International Pressure Systems) was used.

The phases present in the hot-pressed samples were characterized by scanning electron microscopy (JEOL JXA-480 instrument run at 15 keV) and powder X-ray diffraction (Siemens D500). Archimedes' method was used for density determinations, with the samples under vacuum in l-octanol. Leaching tests of 7 and 28 day duration were performed on 0.1 g powder samples (particle sizes of 37-63 μm where the fines were removed by acetone washing), and on ~1-cm sized cubes. The ratios of sample surface area to leachant volume were about 1 and 0.2 cm^{-1}, respectively. The samples were immersed in 20 mL of water at 90°C held in a sealed 50 mL TEFLON jars. The leachate from the cube sample was sampled periodically. No intermediate leachate sampling was done for the powders.

The NZP was found to be incompatible with all the Synroc titanate phases, viz. zirconolite, perovskite, hollandite, and rutile. However, the titanium analogue of NZP may have some potential for compatibility.

*Present address: Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

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Calcination at 700°C led to essentially fully crystalline NZP. The densities of cold-pressed pellets that were sintered at ~1100°C reached 90% of theoretical values without taking special precautions.

In sintering studies, substitutions of rare earths (surrogates for actinides) into NZP were attempted. Limited solid solubility of rare earths and molybdenum on the order of 0.2 formula units appeared to exist. However, it was difficult to draw definite conclusions because of sodium volatilization and the very fine grain size, which precluded SEM microanalysis of the NZP grains. From XRD, it was clear that monazite and xenotime phases were present after the solid solubility limits had been attained. Table 1 shows the densities, porosities and phase assemblages of samples made by hot isostatically pressing of NZP with different types of simulated wastes.

TABLE I. Densities, Porosities, and Phases Present in Hot Isostatically Pressed Preparations

Sample Composition	Waste Ions	Density (g/cm^3)	Porosity (%)	Phases
$Na_{0.5}Cs_{0.2}Sr_{0.15}Zr_2(PO_4)_3$	Cs, Sr	3.23	3.6	NZP + tr ZP
NZP*	-	3.09	3.6	NZP + tr ZP
NZP + 20 wt% PW-4b	Purex	3.23	1.5	NZP + M + ZP
$Na_{0.5}YZrGd_{0.5}(PO_4)_3$	Actinides (simulated)	3.76	3.3	NZP + X + ZP
$Na_{0.5}Ca_{0.5}Gd_{0.5}Zr_{1.5}(PO_4)_3$	Actinides (simulated)	3.43	3.8	NZP + M + ZP

M= monazite; X= xenotime; ZP = ZrP_2O_7; tr = traces

* theoretical density = 3.19 g/cm^3.

The solid solution strategies were simple replacement of Na with Cs, 2Na for Sr; substitution of Y for Na and a coupled substitution of Gd for Zr; and a coupled substitution of Ca for Na and Gd for Zr. The appearance of monazite and xenotime was not unexpected from the above substitutions for rare earths in NZP done for the preliminary sintering studies, and both monazite and xenotime are durable phases in water. The sodium leach rates for all preparations were typically 0.01 to 0.1 $g/m^2/d$ except when Purex waste (PW-4b) was simply added to NZP, for which the leach rate was ~1 $g/m^2/d$. The release into solution of other elements from the hot pressed samples was generally lower than that of sodium. However, the weight losses of these samples were typically 10 to 20 wt% in the first 7 days, corresponding to bulk leach rates of ~1 $g/m^2/d$. Moreover the weight losses in 28 day experiments were less than those in the 7 day experiments, indicating that substantial reprecipitation and hydroxylation were taking place. On the basis of the current work, it is clear that dense NZP-based waste ceramics have chemical durabilities within an order of magnitude of Synroc.