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LANTHANIDE ORTHOPHOSPHATES AS A MATRIX FOR SOLIDIFIED RADIOACTIVE DEFENSE AND REACTOR WASTES

M. Petek, M. M. Abraham, And L. A. Boatner

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SOLID STATE DIVISION
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LANTHANIDE ORTHOPHOSPHATES AS A MATRIX FOR SOLIDIFIED RADIOACTIVE DEFENSE AND REACTOR WASTES*

M. PETEK, M. M. ABRAHAM, AND L. A. BOATNER
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830

INTRODUCTION

Previous investigations have shown that the lanthanide orthophosphates (i.e., analogs of the mineral monazite) are promising candidate waste forms for the storage of high-level actinide or TRU wastes [1]. In the present work, the properties of lanthanide orthophosphates loaded with simulated Savannah River defense wastes and simulated reprocessed light water reactor wastes have been investigated with the goal of evaluating the potential of these materials as advanced primary waste forms.

Pure $LaPO_4$ was selected as the host matrix for the incorporation of either Savannah River defense waste (SRW), or reprocessed reactor fuel waste as represented by the PW-4b composition. Mixed rare-earth phosphate is more economical than any of the pure lanthanide phosphates and was also used as a host for SRW. The formation and precipitation of the composite phosphates was accomplished by adding ammonium hydrogen phosphate and urea to nitric acid solutions of combined rare-earth and calcined oxides of the respective simulated waste form [2]. The compactability of the resulting product was studied as a function of the metal-to-urea ratio during precipitation, waste content and composition, and sintering temperature. Selected properties such as density, particle size, crystallographic phases, and leachability of the resulting materials were examined.

MATERIALS AND METHODS

Powdered, solidified waste phosphate samples were prepared by first combining the simulated waste form and the corresponding rare-earth oxides or nitrates in a nitric acid solution. Ammonium hydrogen phosphate and urea were added, and the mixture was calcined to form a fine powder as described by Abraham et al. [2]. The resulting powder was either hot-pressed, or cold-pressed and sintered, and the density of the compacted cylindrical bodies was determined from their geometrical dimensions and weight.

Lanthanum phosphate was used as the host material for incorporating the simulated PW-4b waste form and for the simulated composite SRW without aluminum removal [3]. In addition, a commercially-available lanthanide nitrate solution** was used to prepare waste forms with a mixed rare-earth phosphate matrix for the composite SRW. The composition of the solid material contained in this nitrate solution was 66% La, 24% Nd, 8.2% Pr, 0.7% Ce, and 1.1% other rare earths.

X-ray diffraction measurements were used to determine the presence of phases other than the monoclinic monazite phase in the compacted material. Scanning electron microscopy with an X-ray energy spectroscopy capability was used to examine the relative distribution of various elements within different phases.

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**Rare-earth nitrate solution was supplied by Molycorp Inc., White Plains, NY, product code No. 5247.

Dilatometry measurements were performed on $LaPO_4$:SRW and $LaPO_4$:PW-4b composite powders to establish the sintering behavior of the waste forms.

The leachability of Cs, Sr, and U was examined using several selected solidified waste samples in distilled water at 90°C. The ISO recommended leachant exchange schedule [4] was followed, and the waste form samples were suspended by a 5 mil Teflon FEP monofilament fiber in standard 90 cm^{-3} Teflon containers (Saville Corp., part No. 0103-53 MOD). Ratios of the sample surface area to the volume of the leachant were maintained at 1:10 cm^{-1}. Immediately following the removal of the sample and cooling to room temperature, the leachate pH was determined. Routinely, the leachate was acidified with 0.5 ml of concentrated HNO_3 prior to atomic absorption analysis. The leachability of the matrix was examined by determining the La content in the leachate by means of neutron activation analysis.

RESULTS AND DISCUSSION

$LaPO_4$:10 wt. % PW-4b. The effect of varying the amount of urea used in the precipitation process on the particle size and the associated compaction properties was studied. The quantity of urea was varied between 0 and 270 moles of urea per mole of lanthanum. Waste form pellets with 92 ± 2% of the theoretical density of pure $LaPO_4$ were formed with urea ratios between 20:1 to 200:1 by cold-pressing (1000-5000 psi) followed by sintering (1200°C). Electron microscope examination of the precipitated powders with 70:1, 100:1, 140:1, and 270:1 urea-to-La ratios revealed that the resulting particles were oblong and 0.1 to 0.2 microns in size.

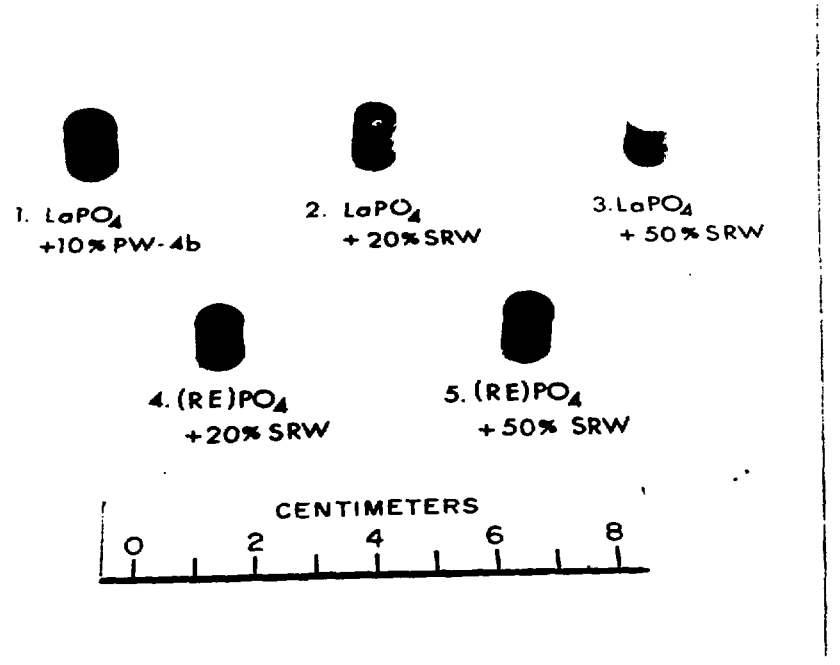

Fig. 1. Cold-pressed and sintered pellets of lanthanum and mixed rare-earth phosphate doped with simulated nuclear waste. Sintering temperature: 1. 1200°C, 2. and 3. 1000°C, 4. 950°C, and 5. 1050°C.

No significant differences for various urea-to-La ratios were found. Hot-pressing of $LaPO_4$:10% PW-4b powders at 4000 psi and 1050°C, resulted in the formation of pellets with a density of 96% of the theoretical value for pure $LaPO_4$ (5.1 g cm^{-3}). No phases other than the monoclinic monazite phase were detected in either hot-pressed, or cold-pressed and sintered samples. Representative samples of compacted bodies of $LaPO_4$:10% PW-4b waste are shown in Fig. 1. The sintering properties were investigated by continuous reading dilatometry, and a typical curve is shown in Fig. 2. It can be seen that the sintering occurs between 800 and 1200°C. The sample was held for only 2 h at 1200°C, and the sintering process still appeared to be in progress when the cooling cycle was initiated.

A direct comparison of the leaching behavior of cold pressed, sintered $LaPO_4$:10% PW-4b pellets and PNL 76-68 glass was carried out using the previously noted conditions. For PNL 76-68 glass, the strontium leach rate remained constant at $\sim 10^{-4}$ g-cm^{-2} day^{-1} during the 60 day duration of the leach test. Although the initial Sr leach rate for $LaPO_4$:10% PW-4b was only about a factor of 2 lower than that of PNL-76-68 glass, the leach rate for the monazite waste form decreased rapidly and, at the end of 60 days, was lower than that of PNL 76-68 by a factor of $\sim$ 100. An extrapolation of the leach rate versus time curve for the $LaPO_4$:10% PW-4b pellets indicates that the Sr leach rate would be lower than that of PNL 76-68 by a factor of 1,000 at the end of one year. For PNL 76-68 glass, the cesium leach rate was found to remain constant at $\sim 3 \times 10^{-6}$ g-cm^{-2} day^{-1} during the two month leaching period. For $LaPO_4$:10% PW-4b, however, the amount of cesium leached from the compacted bodies was below the analytical detectability limit. The Cs leach rate from $LaPO_4$:10% PW-4b is so low that radioactive tracer techniques will be required in order to make any meaningful quantitative measurements.

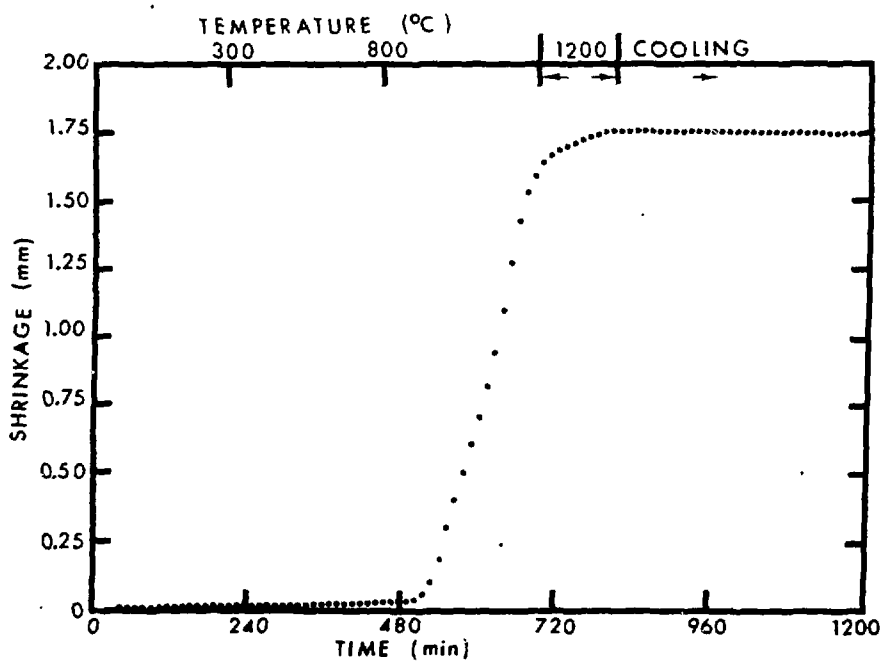

Fig. 2. Sintering of cold-pressed $LaPO_4$ pellet doped with 10% PW-4b. The samples were heated at a rate of 100°C/h to 1200°C, and held at 1200°C for 2 h before cooling down.

$LaPO_4$ with various loadings of composite SRW. The effect of waste loading of simulated SRW without aluminum removal on the compaction and sintering properties of the composite $LaPO_4$ waste material was investigated. In this case the composite powder preparation procedure was modified. The calcination temperature had to be decreased from 800°C to 650°C, since the onset of sintering took place at temperatures above 700°C. This low sintering temperature was attributed to the relatively high aluminum and iron content in the waste.

Waste loadings from 10 to 50 wt. % relative to La_2O_3 were used, and a 100:1 urea-to-metal molar ratio was employed in all of the powder preparations. For loadings up to 20 wt. %, no additional phases were detected by X-ray powder diffraction techniques. At higher loadings, however, an extra phase, identified as an orthorhombic form of $AlPO_4$ was detected. The relative fraction of this phase increased proportionally with increased waste loadings. Dilatometry measurements on 20 wt. % waste loaded pellets showed that sintering occurs in the range from 700 to 1000°C. Increasing the sintering temperature above 1100°C resulted in a decrease in density that was apparently caused by the formation of new phases. Accordingly, the sintering temperatures for these composites should be held below ∿ 1050°C. The SRW:$LaPO_4$ pellets produced by cold pressing and sintering had densities of 3.2 to 3.9 g-cm^{-3} (i.e., 63 to 76% of the theoretical density for $LaPO_4$) depending on the waste loading. It was anticipated that replacing the pure lanthanum with a mixture of rare earths would more readily accommodate foreign ions with different ionic sizes and thereby increase the pellet densities. This was indeed the case as can be seen in Fig. 3.

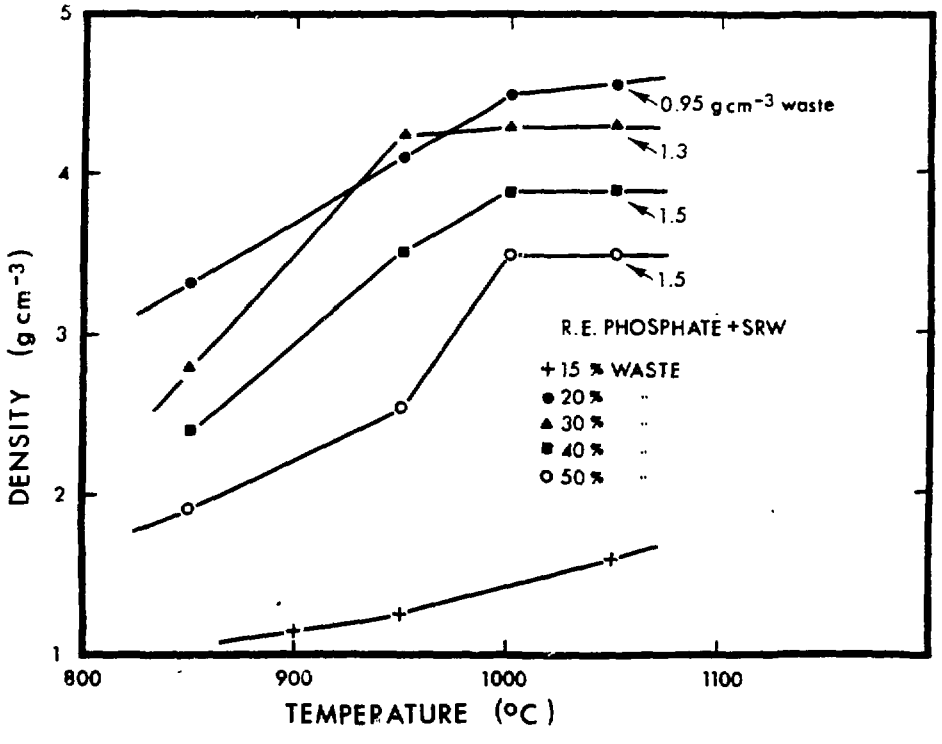

Fig. 3. Density of cold-pressed and sintered rare-earth phosphate pellets, containing SRW without aluminum removal, as a function of the sintering temperature. The maximum waste densities are shown and expressed in g-waste per cm^3 of the composite.

A direct comparison of the leaching properties of $LaPO_4$:SRW and PNL 76-68 glass was also carried out under the previously described conditions. Pellets loaded with 20 and 50 wt. % SRW without aluminum removal were used in these tests. The pH of the leachate for the pellets was constant at pH = 4.5 ± 0.5, whereas for the glass sample, the pH increased with leaching time as follows: 6-7, 9.0, 9.2, 9.4 for 1, 3, 7 and 30 day leaching periods, respectively. While the strontium leach rate for PNL 76-68 remained constant at 10^{-4} g-cm^{-2} day^{-1} during the 60 day duration of the test, the rate for the monazite waste form decreased by an order of magnitude during the first 10 days (i.e., from approximately 10^{-4} to 10^{-5} g-cm^{-2} day^{-1}) and continued to decrease until it was $\sim$100 times lower than the glass leach rate at the end of two months. The cesium leach rate for the $LaPO_4$:50 wt. % SRW material was also two orders of magnitude lower than that of PNL 76-68 at the end of the 60 day period and it continued to decrease relative to the constant Cs leach rate for glass. An extrapolation of the Cs leach rate vs. time curve for the $LaPO_4$:50 wt. % SRW waste form shows that its leach rate should be lower than that of PNL 76-68 by a factor of 3000 at the end of one year.

Mixed rare-earth phosphate with various loadings of SRW. The effect of loading of simulated SRW on the compaction and sintering properties of the composite material was investigated using mixed rare-earth phosphates as the host. The composite powders were prepared by the same procedure used to prepare the $LaPO_4$:SRW powders - including a calcination at 650°C instead of the usual 800°C. The waste loading was varied between 0 and 50 wt. % waste relative to the rare-earths and the cold-pressed pellets were sintered for 60 h at temperatures between 850 and 1200°C.

The resulting pellet densities for different waste content and sintering temperatures are given in Fig. 3 for the composite SRW without aluminum removal. The waste loading is expressed as the percentage of calcined waste oxides relative to the combined rare-earth and calcined waste oxides. A more meaningful measure for the capacity of the waste form to contain radioactive waste is the "waste density" expressed as g-waste/cm^3 of the composite. The "waste density" values are shown in Fig. 3 for the highest compaction obtained with each waste loading. Increasing the waste loading lowers the absolute pellet density since there is an increasing proportion of low molecular weight components in the composite. The waste density increases, however, with waste loading to an optimum value of 1.5 g-waste/cm^3 at a 40% load. No sintering was obtained with waste loadings of zero to 15%. Good sintering was obtained, however, with 20% and higher loadings at sintering temperatures above 950°C. At 1200°C the pellet density decreased apparently because of the formation of new phases. The behavior of the rare-earth phosphate mixture loaded with composite SRW with aluminum removal, was similar to that described previously, except that the sintering process began at lower temperatures, and the maximum densities for the 40 and 50% waste containing pellets were reached at 950°C. Increasing the temperature to 1000°C resulted in reduced densities. Scanning electron microscope observations of a pellet containing 40% SRW without aluminum removal sintered at 950°C indicated the existence of two different phases. Although the sensitivity for all elements was not equal, X-ray energy spectroscopy revealed that one of the phases has increased amounts of Fe, Ni, Ca, P, and Mn relative to the other.

CONCLUSIONS

Lanthanum phosphate is a promising host material for reprocessed light water reactor wastes (e.g., PW-4b). This is demonstrated by the high density of the composite waste form and by the low leach rates of both Cs and Sr.

Additionally, crystallographic data on $LaPO_4$ pellets loaded with 10 wt. % simulated PW-4b indicate the presence of only one phase, i.e., monoclinic monazite.

The rare-earth orthophosphates have also been shown to be a viable waste form for SRW defense wastes. Compaction and sintering studies indicate that the rare-earth phosphate mixture employed here is preferable to pure $LaPO_4$ for containing SRW. Higher density and more homogeneous samples were obtained by using the mixed phosphates as compared to pure $LaPO_4$ as the host material. It is shown that aluminum removal from the composite SRW is not necessary when incorporating this type of waste into a rare-earth phosphate host.

The current results support the view that lanthanide orthophosphate waste forms (i.e., monazite) are potentially superior to borosilicate glasses in the following respects: 1. Lower processing temperatures ($\sim$ 1000°C versus 1160°C for glass). 2. Significantly higher "waste per volume" loadings for a given wt. % of waste for monazites relative to glass. 3. The current leaching data show that monazite-type waste forms are clearly superior to glass in retaining Sr, and, in particular, Cs.

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