ANL/ET/CP--88412

CONF- 9604124--6

ZIRCONIUM PHOSPHATE WASTE FORMS FOR LOW-TEMPERATURE STABILIZATION OF CESIUM-137-CONTAINING WASTE STREAMS*

Dileep Singh, Arun S. Wagh, and Marcin Tlustochowicz
Energy Technology Division
Argonne National Laboratory
9700 S. Cass Avenue, Argonne, IL 60439

April 1996

ZIRCONIUM PHOSPHATE WASTE FORMS FOR LOW-TEMPERATURE STABILIZATION OF CESIUM-137-CONTAINING WASTE STREAMS

Dileep Singh, Arun S. Wagh, and Marcin Tlustochowicz
Energy Technology Division, Argonne National Laboratory
9700 S. Cass Avenue, Argonne, IL 60439

ABSTRACT

Novel chemically bonded phosphate ceramics are being developed and fabricated for low-temperature stabilization and solidification of waste streams that are not amenable to conventional high-temperature stabilization processes because volatiles are present in the wastes. A composite of zirconium-magnesium phosphate has been developed and shown to stabilize ash waste contaminated with a radioactive surrogate of ^{137}Cs. Excellent retainment of cesium in the phosphate matrix system was observed in Toxicity Characteristic Leaching Procedure tests. This was attributed to the capture of cesium in the layered zirconium phosphate structure by intercalation ion-exchange reaction. But because zirconium phosphate has low strength, a novel zirconium/magnesium phosphate composite waste form system was developed. The performance of these final waste forms, as indicated by compression strength and durability in aqueous environments, satisfy the regulatory criteria. Test results indicate that zirconium-magnesium-phosphate-based final waste forms present a viable technology for treatment and solidification of cesium-contaminated wastes.

INTRODUCTION

The estimated volume of high-level waste (HLW) and low-level waste (LLW) across the DOE complex is several hundred thousand cubic meters and occurs in a variety of forms, including solids, sludges, salt cakes, and liquids [1]. Because

the physical and chemical compositions of these wastes are diverse, no single solidification and stabilization technology can be successfully used to treat and dispose of all such wastes.

The presence of fission products such as radioactive cesium-137 and strontium-90 causes a myriad of problems in the safe disposal of HLW and LLW. Cesium and strontium are volatile and may escape to the off-gas system during vitrification of the waste. In addition, these contaminants are heat generators that increase the effective heat load of the vitrified waste form. Currently, various separation technologies are being developed to remove the volatile fission products from HLW streams. This removal is expected to reduce the overall radioactivity of the HLW and simplify waste-handling operations. However, it will also create a secondary waste stream that is rich in fission products. Therefore, a low–temperature treatment and stabilization technology is critically needed to effectively stabilize the partitioned waste stream, along with other low-level waste streams that contain fission products and that are not amenable to treatment by current technologies. To this end, we are developing and demonstrating a low–temperature stabilization technology based on chemically bonded zirconium phosphate ceramics for the stabilization of ^{137}Cs.

CHEMICALLY BONDED PHOSPHATE CERAMICS AND THEIR WASTE FORMS

Chemically bonded phosphate ceramics are dense and hard materials that can be processed at low temperatures [2]. The phosphates generally exhibit high solid-solution capacity for incorporating heavy metals, actinides, and rare-earth contaminants [3]. Also, the very low solubilities of heavy metal, actinide, and rare earth phosphates [4] indicate that phosphate-bonded ceramics should be effective in stabilizing these contaminants. In addition, monazite and apatite minerals are durable natural analogs of phosphate-bonded ceramics [5], suggesting that phosphates are good hosts to radionuclides. The present developmental program on phosphate waste forms is being conducted to utilize their attractive properties in solidifying and stabilizing wastes that contain volatile radioactive contaminants such as fission products. Fabrication of phosphate ceramics can be achieved at room temperature or slightly elevated temperatures, thus minimizing off-gassing of contaminants.

Zirconium Phosphate Ceramic

The rationale for using α-zirconium phosphate [$Zr(HPO_4)_2 \cdot H_2O$] ceramic for the stabilization of fission products such as ^{137}Cs and ^{90}Sr is based on this phosphate's ability to accommodate the radionuclides in its lattice structure by intercalation reactions [6]. Because α-zirconium phosphate is two-dimensional and layered, it is easily deformable along its third dimension. Thus, a wide range of ions and molecules can be incorporated in such a material system by ion exchange and then chemically bound. In addition, α-zirconium phosphate is refractory, has high radiation stability, and can tolerate structural changes caused by decay of radioactive contaminants because of its unique layered crystal structure [6].

Fabrication of phosphate ceramics such as zirconium phosphate is achieved by an acid-base reaction route [2]. The starter powder used in this study was zirconium hydroxide (Magnesium Elektron, Inc., Flemington, NJ), with an average particle size of $\approx$10 μm. This powder was reacted with a phosphoric acid solution (85 wt.% concentrated), producing a slurry that was subsequently poured into a plastic mold. Time required for complete hardening was 2 to 3 weeks. Figure 1 shows X-ray diffraction of the fabricated material; the peaks correspond to the α-zirconium phosphate ceramic phase, which is desired for the containment of cesium.

Waste Stream Composition

A simulated ash waste stream was selected to demonstrate solidification and stabilization of cesium with zirconium phosphate binder. Composition of the surrogate waste stream is given in Table I. This waste was modeled after typical ash wastes present at various DOE sites [7]. To simulate radioactive ^{137}Cs, stable cesium chloride was added to establish cesium metal content in the ash waste at 10,000 ppm. Details of the mixing sequence for preparing the simulated waste stream are given in Ref. 4.

Fabrication of Waste Forms

Figure 2 is a flow sheet for fabricating final waste forms with phosphate ceramics, based on acid-base reactions. Both solid and liquid wastes can be treated by this process. Solids, such as contaminated ashes, may be crushed and
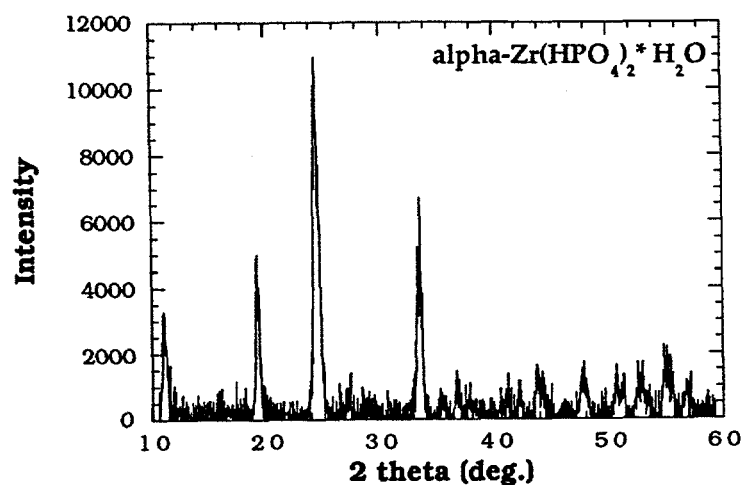
Fig. 1.   Typical X-ray Diffraction Pattern Fabricated
α-Zirconium Phosphate.

Table I. Composition of Surrogate Ash Waste Stream

Bulk Ingredients	wt.%
Activated carbon	4.7
Fly ash	37.5
Coal ash	30.9
Vermiculite	18.7
Radionuclide surrogate	
CsCl	1.3

mixed with a zirconium hydroxide starter powder and then reacted with the liquid acid solution. On the other hand, if the waste is a liquid, it may be mixed with the liquid acid component and the resulting solution then reacted with a base powder. Thus, submitting both solid and liquid waste to acid-base reactions to form phosphate ceramics widens the applicability of this technology. In addition, because this process is based on the reaction between an acid and a base, it can occur over a wide pH range.
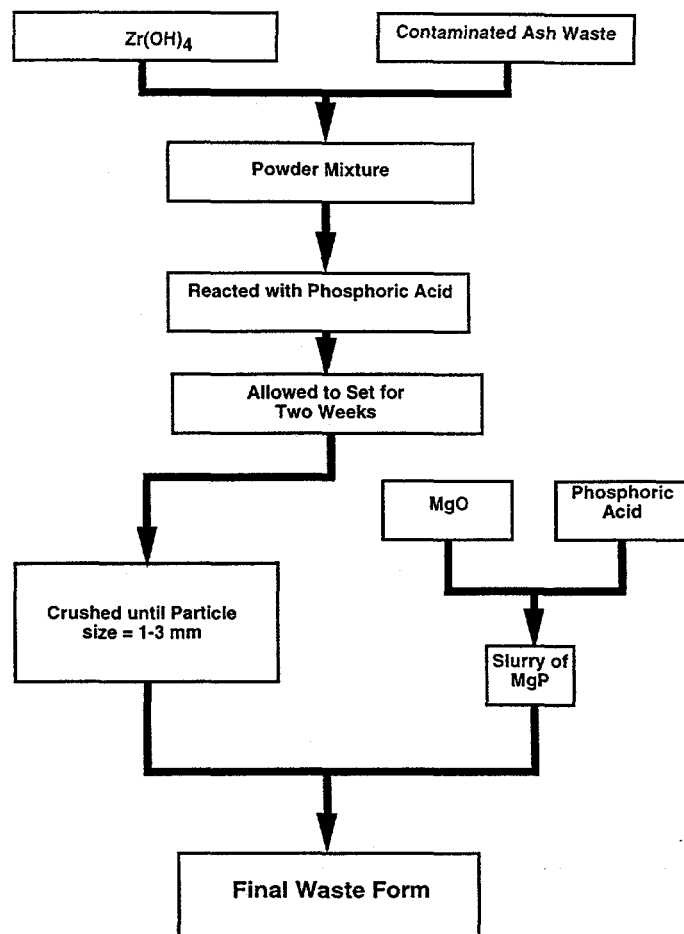
Fig. 2. Flow Sheet of Fabrication Process of Zirconium/Magnesium Phosphate Composite Final Waste Forms.

As shown in Fig. 2, zirconium hydroxide powder and ash waste, spiked with 10,000 ppm of Cs, were mixed such that the waste was 70 wt.% in the powders. Subsequently, the powder mixture was reacted with 85% phosphoric acid solution. The slurry was allowed to cure for two weeks under ambient conditions. The resulting product sets into a homogeneous product that has significant porosity (as shown in Fig. 3) and low strength. Therefore, it was necessary to improve on the structural integrity of the waste form. This was achieved by further crushing the zirconium phosphate-ash waste product to particle sizes of 1 to 3 mm. The crushed pieces were mixed in a slurry of magnesium phosphate and allowed to set for another week to produce a dense
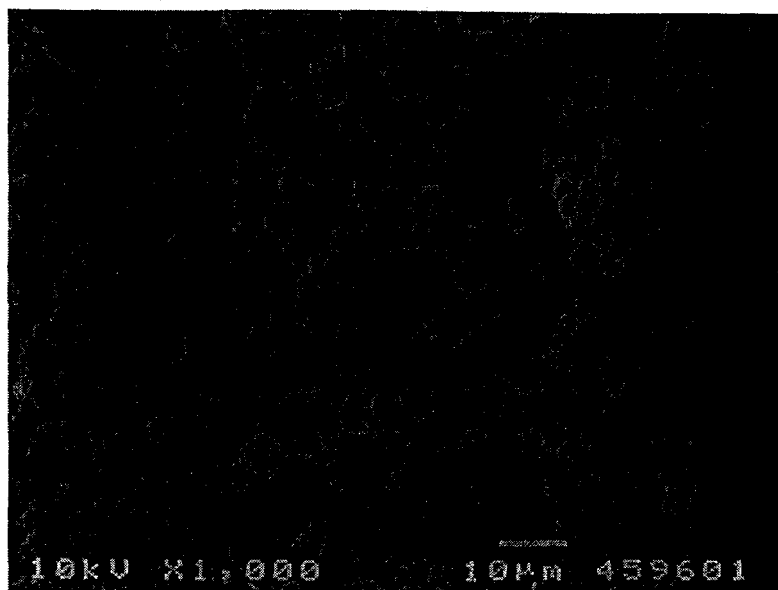
Fig. 3. SEM Photomicrograph of Fracture Surface of
Zirconium Phosphate-Ash Waste Forms.

final waste form. The purpose of magnesium phosphate is to bind the zirconium
phosphate-ash waste into a structurally durable form. Relative fraction of
magnesium phosphate binder in the composite waste form is ≈0.5.

Physical and Mechanical Properties of Waste Forms

The density of the final fabricated waste forms was 1.6 g/cm^3; corresponding
porosities were ≈15%. Average compression strengths of fully cured waste
form samples, as measured with an Instron machine, were 1557 ± 68 psi. These
strengths are significantly higher than the regulatory requirements and are of the
same order as those of other room-temperature-setting waste forms such as those
based on grout cement. We expect that the open porosity of the waste forms
could be further decreased by application of pressure on the waste form during
its curing period. This will also lead to higher strength of the waste form.

Phase and Microstructural Characterizations of Waste Forms

The X-ray diffraction pattern (Fig. 4) on the final waste form shows phases of
zirconium phosphate, as well as of magnesium phosphate. This implies that the
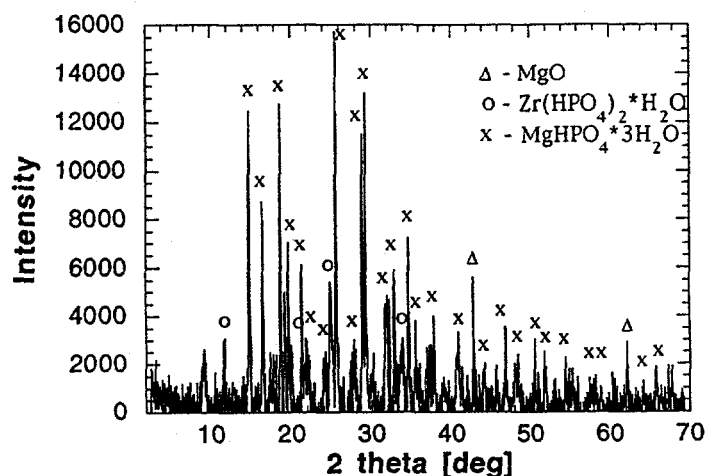zirconium phosphate phase, which entraps cesium, is not degraded during the

Fig. 4. X-Ray Diffraction Pattern of Zirconium/Magnesium
Phosphate Composite Waste Form.

magnesium phosphate binding step. The major phase in the Mg–phosphate
system is newberyite (MgHPO$_4$·3H$_2$O), an insoluble phase that further helps to
encapsulate the contaminants in the final waste form [8].

Scanning electron microscopy (SEM) was conducted on final waste forms to
identify and establish the various phases and the fate of the contaminants in the
waste form. Figure 5 is a photomicrograph of a fracture surface on a composite
final waste form. We believe that both crystalline and noncrystalline binding
phases are present. The fracture surface of the waste form, which appears to be
quite dense, thus confirming the high compressive strength and low porosity
measurements obtained for these waste forms. It is clear that in the final
product, magnesium phosphate completely coats and binds the reacted
zirconium phosphate and ash waste. We believe that this microencapsulation of
cesium in the zirconium/magnesium phosphate matrix, along with chemical
stabilization by ion exchange, leads to excellent performance of the phosphate
systems in preventing leaching of the contaminants, as discussed below.

Leaching Properties of Fabricated Waste Forms

Leaching studies on the fabricated waste forms were conducted according to the
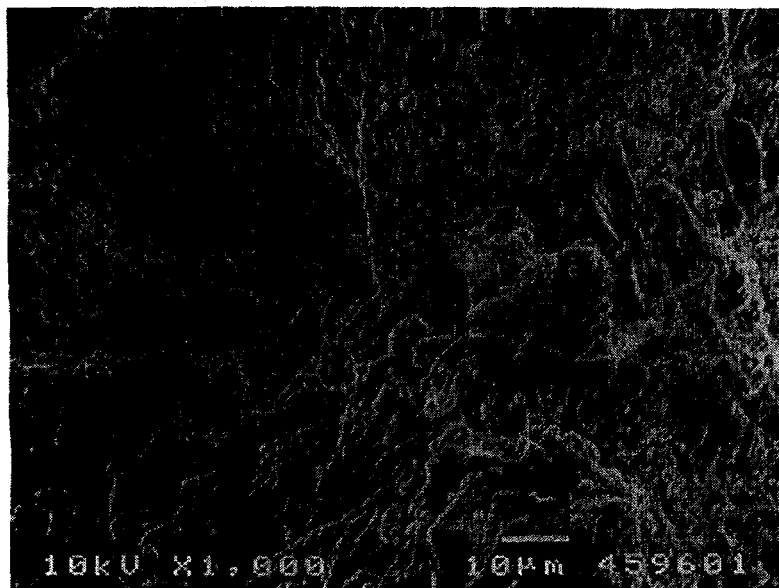standard Toxicity Characteristics Leaching Procedure (TCLP) of the U.S.

Fig. 5. SEM Photomicrograph of Fracture Surface of
Zirconium/Magnesium Phosphate Waste Form.

Environmental Protection Agency (EPA) [9]. Results (Table II) show the net contamination level in the specimen that underwent TCLP testing, the level of contaminant in the leachate, and the retainment efficiency (which is defined as the ratio of the contaminant in the leachate to the original contamination level in the specimen).

Untreated surrogate waste with 10,000 ppm of cesium, when exposed to TCLP testing showed 340 ppm of Cs eluting; retainment efficiency was 3.4%. However, when the same waste was treated with zirconium phosphate, retainment efficiency decreased by two orders of magnitude to 0.01%. This clearly suggests that zirconium phosphate helps to capture and stabilize cesium. Further, when the zirconium phosphate-ash waste was crushed to about 1-3 mm particle size and subsequently bonded by magnesium phosphate, the retainment efficiency did not change; this implies that the composite fabrication process does not degrade Cs stabilization in zirconium phosphate. However, when the zirconium phosphate-ash waste was crushed to a fine powder and then bonded by magnesium phosphate, the retainment efficiency increases to 0.33%. This is believed to be due to exposure of Cs as a result of fine crushing. Therefore, for an optimum waste form extensive crushing may not be required.

Table II. TCLP Results for Cs Stabilization

Sample Specification	Contaminant Level in Specimen (ppm)	Contaminant Level in Leachate (ppm)	Retainment Efficiency (%)
Unstabilized ash waste	10,000	340	3.4
Zr phosphate with ash waste	3,740	0.382	0.01
Mg-Zr phosphate with ash waste (large particles)	1,450	0.234	0.016
Mg-Zr phosphate with ash waste (fine particles)	1,450	4.8	0.33

The TCLP results show that all of the zirconium phosphate and magnesium-zirconium phosphate composite waste forms are very effective in stabilizing cesium at room temperature. A comparison between the leaching levels of untreated waste and stabilized samples shows that the levels of the stabilized waste are two orders of magnitude lower than those of the untreated waste. Further, they are much lower than those reported for other immobilization systems such as glass where the retainment efficiency is $\approx 0.05\%$ [10]. The reason for the superior immobilization in our process is the chemical stabilization of the contaminants in the matrix due to capture of cesium ions in zirconium phosphate by intercalation reaction, followed by physical encapsulation within the dense phosphate matrix.

Durability Studies

To study durability of the final waste forms in an aqueous environment, long-term water immersion studies were initiated. Samples were immersed in deionized water that was periodically changed to compensate for evaporation loss. Samples were taken out of the water at regular intervals, dried and weighed to observe weight loss. The procedure was similar to that outlined in

ANS 16.1 [11]. This is an on-going study for 90 days; the results reported here are for first nine weeks of testing. Figure 6 shows percentage weight change of a zirconium-magnesium phosphate composite waste form with ash waste. The percentage weight change is computed with respect to the weight of the waste form at the beginning of the immersion study. Over nine weeks the waste form has shown excellent durability, with a weight change <= 2%. This small weight loss is believed to be due to the initial loss of weight because of the release of free phosphoric acid and/or unreacted hydroxide/oxide powders from the surface of the waste form when immersed in water.

SUMMARY

The overall aim of these studies was to develop a low-temperature phosphate stabilization technology for immobilizing ash waste containing cesium as a fission product. This investigation reveals the suitability of zirconium/magnesium phosphate composite as a durable binder system to stabilize cesium contaminant both chemically and physically in a very effective and economical way. Because this process needs no thermal treatment,
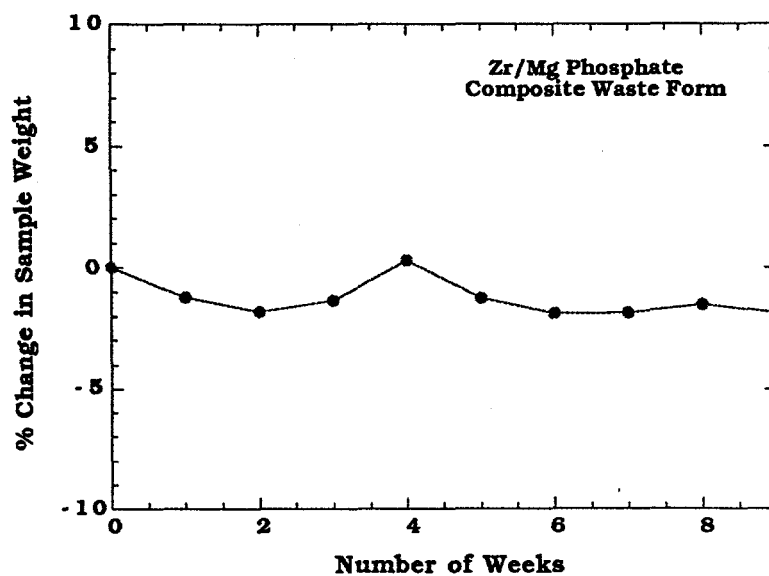

Fig. 6. Variation in Weight of Final Waste Form during Long-Term Water Immersion Test.

stabilization may be performed economically on site without capital–intensive equipment and high transportation costs. Based on our other work, this technology is also applicable for stabilizing fission products in other bulk compositions such as sludges and salts. Our investigations demonstrate only the potential of these materials. A wider scope of applicability may be revealed in the future with further research and development.

ACKNOWLEDGMENTS

REFERENCES

1. M. J. Kupfer, "Disposal of Hanford Site Tank Waste," Report WHC-SA-1576-FP, published by Westinghouse Hanford Co., Sept. 1993.

2. W. D. Kingery, "Fundamental Studies of Phosphate Bonding in Refractories, II., Cold-Setting Properties," J. Am. Ceram. Soc., 33 (1950) 242-247.

3. D. D. Double, "Chemically Bonded Ceramics: Taking the Heat Out of Making Ceramics," J. Mater. Educ., 12 (1990) 353-381.

4. A. D. Wilson,, and H. W. Nicholson, Acid-base cements, Cambridge Univ. Press (1993) p. 222.

5. G. J., McCarthy, W. B. White, D. K. Smith, A. C. Lasaga, R. C. Ewing, A. W. Nicol, and R. Roy, "Mineral Models for Crystalline Hosts for Radionuclides in Radioactive Waste Disposal," Vol. 1, The Waste Package, ed. R. Roy, Pergamon Press (1982) 184-232.

6. T. Kanazawa, Inorganic Phosphate Materials, Elsevier, New York (1989) p. 131.

7. W. D. Bostick, D. P. Hoffman, J. M. Chiang, W. H. Hermes, L. V. Gibson, Jr., A. Richmond and J. Mayberry, "Surrogate Formulations for Thermal Treatment of Low-Level Mixed Waste: Part II: Selected Mixed Waste Treatment Project Waste Streams, DOE/MWIP-16 (1994).

8. C. Palache, H. Berman, and C. Frondel, The Sytstem of Mineralogy, Seventh Edition, Vol. II, John Wiley and Sons, Inc. , New York (1951) p. 771.

9. Environmental Protection Agency Method 1311, Toxicity Characteristic Leaching Procedure (TCLP), March 15, 1992, Revision II.

10. Vortec Corp., "TSCA Incinerator Ash Surrogate Pilot-Scale Vitrification Tests," presented at Mixed Waste Integrated Program Review, Gaithersburg, MD, April 19, 1994.

11. American Nuclear Society, "American National Standard Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure," Method ANSI/ANS 16.1-1986, American Nuclear Society, La Grange Park, IL, 1986.

DISCLAIMER