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Model Apatite Systems for the Stabilization of Toxic Metals: I, Calcium Lead Vanadate

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Apatites of composition $(\text{Ca}_{10-x}\text{Pb}_x)(\text{VO}_4)_6\text{F}_2$ with $0 \leq x \leq 9$ were synthesized by sintering in air at 800 °C the oxides of calcium, lead, and vanadium that were mixed with calcium fluoride. Variations in lattice parameters, grain size, and durability were monitored as a function of composition. The expected dilation in unit cell edges with increasing replacement of calcium (IR = 1.26 Å) by lead (IR = 1.45 Å) was observed. The a cell edge (in angstroms) varied linearly $(0.0458x + 9.7068)$ with x , while c followed the binomial function $0.0018x^2 + 0.0279x + 7.0118$. Average grain sizes increased from approximately 5 μm ($x = 0$) to 25 μm ($x = 9$) as grain growth was enhanced due to incipient melting of the lead-rich compositions. For $x < 5$ the materials were biphasic. Overall dissolution, as determined by the toxicity characteristic leaching procedure (TCLP), was faster in calcium-rich apatites. Etching of well-crystallized apatite grains occurred preferentially on $\{10\bar{1}0\}$ faces. These leach losses were augmented through the more rapid removal of cryptocrystalline regions and intergranular thin films.

I. Introduction

Synthetic apatite minerals have long been candidates for the immobilization of nuclear waste because of their chemical stability and radiation resistance.¹ More recently, waste form apatites has gained prominence due to their applications in the stabilization of contaminated soils² and hazardous industrial wastes.³⁻⁷ Evaluation of the performance of these waste forms has, in large part, relied solely on the determination of leach rates using standard test methods, especially the

toxicity characteristic leaching procedure (TCLP),⁸ in which the absolute concentration of metal extracted into acetic acid solutions over an 18 h period is measured. The quantity of metal extracted when compared with accepted loss rates determines whether the waste form is acceptable for landfill disposal. While TCLP is a useful screening method, the scientific limitations of the approach are well known,^{9,10} especially the short duration of the test that precludes an estimation of long-term durability. Moreover, in its standard form, TCLP results do not convey information concerning the mechanism of dissolution, including the contribution of precipitates or passivation layers to the overall leach rate. Consequently, there remains some uncertainty as to the longevity of waste form apatites, the precise mechanism of immobilization (crystallochemical incorporation or absorption), and the manner in which apatite-related phases may enhance or degrade performance. Further, almost all studies have focused on the use of phosphate-based compounds, although the apatite family of minerals encompasses a rich and diverse solid-state chemistry. Other potentially useful formulations for hazardous waste management have to date received less attention.

Incinerator ashes generated by the combustion of municipal and industrial wastes can contain high concentrations of toxic metals.^{11–15} In countries with limited access to landfills and/or high landfill charges there is considerable incentive to stabilize ash before disposal or reuse without excessive bulking. As part of a wider-ranging study of alternative methods of ash stabilization, we report the preparation and characterization of the apatite series $(\text{Ca}_{10-x}\text{Pb}_x)(\text{VO}_4)_6\text{F}_2$ with $0 \leq x \leq 9$ as simplified surrogates for apatites derived from the stabilization of certain waste oil ashes. The aims of this work were to establish the continuity of the lead vanadate solid solution series, investigate the relationship between chemistry and waste form durability, and seek a clearer understanding of apatite dissolution, specifically under TCLP-like conditions.

II. Crystal Chemistry

Apatites (somewhat simplistically) conform to general formula $\text{A}_{10}(\text{BO}_4)_6\text{X}_2$ where A includes larger mono-, di-, and trivalent cations, B are metalloids, and X represents halides and anion radicals. All apatites adopt hexagonal (or pseudohexagonal) symmetry, the most common space group being $P6_3/m$. The ability to tolerate so many cation matchings arises from three

crystallochemical features peculiar to the apatite structure (Fig. 1).¹⁶ First, there are two crystallographically distinct A-sites. The anion coordination of the A(1)-site is AO_6 and metaprismatic, lying between perfect octahedral and trigonal prismatic coordination. The anion coordination of the larger A(2)-site is irregular with bonding to between seven and nine oxygens. Such ill-defined coordination enhances the capacity to immobilize cations of different sizes. The A(2)-site lies adjacent to a continuous “tunnel” within the structure which is partially filled with X anions and provides a location for lone-pair electrons (which enlarge the radius of Pb^{2+}). A second source of structural flexibility arises because BO_4 tetrahedra are the only rigid polyhedra. Minimal rearrangements in the topology of these structural units can adjust apatite dimensions to accommodate cations with quite disparate crystal radii. Third, apatites may display X-site nonstoichiometry that facilitates charge balance in chemically complex wastes.

Natural varieties of apatite are remarkably accommodating to a wide variety of cation substitutions.¹⁷ The apatites of the present study are fluorine analogues of the rare mineral vanadinite $\text{Pb}_{10}(\text{VO}_4)_6\text{Cl}_2$, which forms as a secondary product in oxidized lead ore deposits. It is known that phosphate apatite minerals can survive unaltered in limestones and calc-silicate rocks;¹⁸ however, the longevity of nonphosphate apatites has not been reported on extensively. Although apatites are often sparingly soluble in water, they can present enhanced solubility in oxalic, citric, tartaric, and salicylic acids.¹⁹ This will evidently be deleterious when acetic acid based TCLP testing is used.

III. Experimental Procedure

(I) *Fabrication*

Fresh CaO (prepared by firing AR grade CaCO_3 at $900\text{ }^\circ\text{C}$), CaF_2 , V_2O_5 , and PbO powders were mixed in the appropriate proportions and fired at $800\text{ }^\circ\text{C}$ in alumina boats at ambient atmosphere for 10 h. Ten compositions of $(\text{Ca}_{10-x}\text{Pb}_x)(\text{VO}_4)_6\text{F}_2$ with $x = 0, 1, 2, \dots, 9$ were prepared. These precursor powders were then ball-milled and treated again at $800\text{ }^\circ\text{C}$ for about 2.5 days to allow the reaction to proceed to completion. The powders were subsequently pressed into pellets ($10\text{ mm} \times 3\text{--}4\text{ mm}$) and sintered at $800\text{ }^\circ\text{C}$ for 15 h. Each pellet had a total weight of $\sim 1.5\text{ g}$. The firing temperature chosen was just below the melting point of lead end member $\text{Pb}_{10}(\text{VO}_4)_6\text{F}_2$.

(2) *Characterization*

Powder X-ray diffraction patterns were collected using a Siemens D5005 X-ray diffractometer (XRD) fitted with a Cu tube that was operated at 40 kV and 40 mA. Scans were collected from 10° to $140^{\circ} 2\theta$ with a scanning rate of $0.12^{\circ} 2\theta/\text{min}$. Under these conditions the intensity of the strongest peak was 1500–2000 counts. Before collection, the pellets were mechanically ground to powder to minimize preferred orientation effects and mixed with a small quantity of standard silicon powder with $a_0 = 5.43088 \text{ \AA}$ (NIST 640c) to allow internal calibration of d -spacings. The data were analyzed using the Rietveld method.²⁰ A two-step procedure first fixed the zero-shift parameter against the Si reflections, followed by refinement of the apatite phase. For each compound four polynomial background coefficients, peak half-widths V and W , and an asymmetry parameter were refined. A Pearson VII peak shape was corrected for asymmetry. As no crystallographic data could be located for $\text{Ca}_{10}(\text{VO}_4)_6\text{F}_2$, the starting model for refinement used the atomic positions for $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ²¹ and the unit cell dimensions of vanadinite.²² For each model the occupancy of the calcium/lead was fixed at the assumed composition and not refined. As the focus of this study was confirmation of the solid solution, no attempt was generally made to refine atomic positions or thermal parameters (which were fixed at $0.5 \text{ \AA}^2$). Although the final matches of diffracted intensities were not optimized, this did not compromise the determination of lattice parameters. Patterns were analyzed systematically from the calcium to lead end members. In a single case of a two-phase apatite powder, complete structure refinement was undertaken.

Scanning electron microscopy (SEM) (Model JSM-5310LV) was conducted at 20 keV and a low vacuum of $\sim 29 \text{ Pa}$ to minimize the effects of charging. Pellets were polished to $1 \text{ }\mu\text{m}$ using diamond paste. The polished disks were studied before and after TCLP testing by backscattered electron (BSE) imaging to more readily differentiate second phases. Quantitative microanalysis (Oxford Link Si(Li) X-ray detector and associated software) was conducted using the K -lines of calcium, vanadium, and fluorine while the L -lines were used for lead.

Analytical transmission electron microscopy (TEM) of thin sections was used to investigate the crystallinity of apatite crystals and search for the presence of amorphous phases. Electron-transparent specimens were prepared from 3 mm diameter trepanned disks cut from the central part of each pellet. After being polished with emery paper to a thickness of $<50 \text{ }\mu\text{m}$, the

samples were ion milled to perforation at 4.5 kV with double argon guns at a glancing angle of 7°. TEM was performed at 300 kV (Model JEOL JEM-3010). Specimens were studied before and after leaching by orienting with a double tilting holder.

(3) *Leach Testing*

Extractions were conducted on individual sintered pellets using a modified TCLP method to determine the losses of calcium, lead, and vanadium. The leach solution used was the prescribed acetic acid of pH 2.88 prepared by diluting 5.7 mL of glacial acid with deionized water to a volume of 1 L. However, because of the small quantity of material available for test purposes a single sintered pellet (<9.5 mm diameter) was tested while maintaining a solid:extraction-fluid weight ratio of 1:20. After 30 mL of leach solution was added to the extractor bottle and the 1.5 g pellet was immersed in the liquid, the bottle was tightly closed and kept to rotate at about 30 rpm on the leaching machine. The concentrations of lead, vanadium, and calcium released into leach solution were measured after leach periods of 72, 120, and 168 h with a Bruker 3500 wavelength dispersive X-ray fluorescence spectrometer (XRF). Quantitation was completed using manufacturer software and calibrated against standard solutions.

IV. Results

(1) *Microstructural Features*

Backscattered electron micrographs for a representative selection of pellets are shown in Fig. 2. Overall image contrast decreases across the series as the average atomic number decreases from 23.4 to 17.5 in passing from the $x = 3$ to $x = 7$. Grain growth was less pronounced in calcium-rich samples (with mean diameters < 10 μm) as compared with lead-rich compositions (diameter > 20 μm). This is to be expected as increasing concentrations of lead systematically depress the melting point of the pellets, such that a firing temperature of 800 °C is just below the solidus of $\text{Pb}_{10}(\text{VO}_4)_6\text{F}_2$. While the melting point of each composition was not determined, it is clear that for the calcium-rich compositions with $x < 4$ reaction was incomplete as two-phase assemblages resulted (see Fig. 1(c)). Semiquantitative microanalysis showed that the apatite phases were of similar composition; for illustration, Table I summarizes the data (normalized to reflect the presence of 10 cations on the A-site) for the $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ pellet.

The difference in the Ca/Pb ratio is evident, and within the accuracy of the analysis, the concentration of vanadium is fixed. The analysis of fluorine is clearly high and should not be regarded as especially reliable; nonetheless, confirmation of its presence excludes the possibility of significant volatilization losses during synthesis or the existence of fluorine-free phases such as $\text{Ca}_3(\text{VO}_4)_2$.

(2) *Crystallography Analysis*

The preliminary analysis of the X-ray diffraction patterns assumed the samples to be single-phase apatite (Fig. 3). Cell parameters as a function of composition (x) could be well fitted ($R > 99\%$) to the functions

$$a = 0.0458x + 9.7068$$

$$c = 0.0018x^2 + 0.0279x + 7.0118$$

Indeed, inspection of the X-ray patterns did not obviously indicate peak splitting or significant line broadening that might have led to a supposition of disequilibrium and phase separation. This could only be recognized from the BSE images.

In a single case, a trial Rietveld analysis of $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ was conducted starting with two apatite phases, the unit cells of which bracketed the average cell edge (Fig. 4). In addition, the calcium and lead contents over the two A-sites were refined in a coupled fashion with the total occupancy (k) for each site constrained such that $k_{\text{Ca}} + k_{\text{Pb}} = 1$. This yielded lead-rich (35 wt%) and lead-poor (65 wt%) phases with unit cells slightly deviating from the average unit cell. These data are summarized in Table II. The residuals for the two-phase model are marginally better than for the single-phase model, and the overall composition, derived from the refined structures, is in reasonable agreement with the bulk composition. However, there is substantial disagreement ($\sim 0.5\% - 1\%$) between the observed unit cells and the chemical compositions derived algebraically using the fitted formula above. Certainly the algebraic deviations would have been sufficient to result in clear splitting of reflections arising from the two compounds. Furthermore, in work still in progress, it has been shown that even for single-phase apatites (as confirmed by SEM), longer-term annealing at 800°C leads to significant deviations from these relationships. It is believed that this is due to differences in Ca/Pb partitioning over the cation acceptor sites; however, this remains the subject of a current investigation.

(3) *Disequilibrium Structures*

The majority of apatite crystals were well developed and perfect, in the sense that no extended defects were observed. Figure 5 shows the high-resolution $[011] \equiv [1\bar{2}13]$ images of $\text{Ca}_{10}(\text{VO}_4)_6\text{F}_2$ and $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ collected near the Scherzer defocus. While the contrast in calcium-pure apatite was uniform, that in the Ca/Pb mixed crystal displayed contrast domains and reversals. While these differences may be attributable to electron beam etching leading to pitting of lead-rich apatite surfaces, it is suggested that disorder of lead and calcium may be responsible, as a relatively small variation in lead content would have a sizable impact on the projected electron potential of the crystal.

Cryptocrystalline regions were also found as shown in Fig. 6, where a disordered crystal was located between two relatively perfect crystals. High-resolution lattice images from the ordered crystal (A) and disordered crystal (B) revealed the presence of domains ~ 10 nm in diameter. Chemical analysis of the two regions showed that although the vanadium content was uniform, the Pb-*L* and Ca-*K* X-ray intensities were reversed with the cryptocrystalline region being far richer in lead.

In addition to these larger-scale disequilibrium structures, thin grain boundary phases were commonly observed. Figure 7 is a typical example where a Clarke through focal series was collected under overfocus, focus, and underfocus conditions.²³ The reversal of contrast from white in the overfocus condition to dark at underfocus indicates that the intergranular film has a higher mean inner potential than the surrounding crystals. This is believed to be consistent with the accumulation of lead at the interface.

(4) *Dissolution Mechanisms*

The most direct identification of the contributions various microstructural features make to overall dissolution rates can be derived from transmission electron microscopy, especially with respect to the relative dissolution of different crystalline surfaces and nonequilibrium components. Examples of STEM/BSE images of a two-phase $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ pellet before and after 90 h TCLP testing are shown in Fig. 8. After immersion in the leach solution many grain boundaries have been altered and appear more prominent. More careful inspection using a combination of bright-field TEM and SAD showed that dissolution occurred preferentially along

$\{10\bar{1}0\}$ crystallographic planes (Fig. 9). This result was confirmed on a larger scale by SEM where grains with faces close to $\{10\bar{1}0\}$ were covered by long etch channels, while those near to (0001) were covered by numerous small etch pits (Fig. 10). SEM of two-phase $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ apatite (Fig. 11) showed that the lead-rich bright regions dissolved more slowly than the darker calcium-rich regions. While the former displayed pit morphology, it appears that in the calcium regions complete grains had been dislodged.

Although TCLP data are usually reported as the quantity of metal extracted in 18 h (in the case of lead the regulatory limit is 5 ppm in 18 h), our data are reported as a leach rate (or 6.6 ppm/day), so that the trends in leachability can be followed (Fig. 12).[†] The leach rates for calcium and vanadium accelerated after 6 days, possibly because of the gradual exposure of more cryptocrystalline regions that were rich in these metals and were likely to have relatively poorer durability. Lead, on the other hand, appeared to have a falling leach rate after 6 days, possibly due to the removal of near-surface grain boundary lead.

V. Discussion

The trend toward treating toxic industrial effluents as a resource for recycling into nonstructural building materials, rather than a waste, requires unequivocal assurances that secondary products will maintain their design specifications, if not indefinitely, then certainly throughout their useful life. Consequently, there is a growing need for more complete understanding of the crystal chemistry, microstructure, and longevity of industrial waste-bearing ceramics. Such knowledge is essential, as unexpected phases, even when present in low concentration, can have lower durability and limit chemical and/or physical properties. Given that large volume usage of recycled industrial waste is anticipated, even slight degradations in performance could have a profound effect on toxic metal loads in certain built environs or ecosystems.

This work has confirmed that for a simplified vanadinite waste system complete solid solution exists between $\text{Ca}_{10}(\text{VO}_4)_2\text{F}_2$ and $\text{Pb}_{10}(\text{VO}_4)_2\text{F}_2$ with lattice parameters dilating continuously and regularly as lead ($\text{IR} = 1.45 \text{ \AA}$) replaces calcium ($\text{IR} = 1.26 \text{ \AA}$). In detail, complexity arises due to disequilibrium partitioning of lead over the two possible cation acceptor sites. The trend lines shown in this study were achieved by firing all compositions for the same

times and temperatures (Fig. 2). However, a reconnaissance investigation, the details of which will be published separately, has shown that apatites fired for longer times (an additional 72 h at 800 °C) adopt cell edges that deviate from these data. It is believed that this is due to the tendency of lead to enter the larger A(2)-site—as has been observed in lead-substituted hydroxyapatite²⁴—via a diffusion process which may be quite slow in the subsolidus condition. Indeed, such preferred partitioning was confirmed for the two-phase apatite of average composition $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ where the Rietveld convergence required significantly greater scattering from the A(2)-site than anticipated from an even equimolar cation distributions over the A crystallographic sites (Table II). On the nanoscale, disequilibrium is even more complex as the HRTEM shows microdomains a few tens of angstroms in extent that may be attributed to different proportions of lead and calcium. For the calcium-rich material ($x < 5$) the synthesis conditions yielded assemblages far from equilibrium as evidenced by the coexistence of two apatites adopting similar, but clearly distinct, chemical compositions. It is anticipated that longer firing times or higher temperatures would have resulted in single-phase ceramics. Of particular significance is the observation that XRD analysis alone would not necessarily have detected the two-phase nature of these preparations as the unit cells were essentially indistinguishable. Nonetheless, the strong dependence of the backscattered electron coefficient on small changes in lead content made them readily visible by SEM (Fig. 1(c)).

Regions of partially crystalline apatite, which were enriched in lead relative to surrounding crystals, were present, as were thin intergranular films believed to accumulate lead. These microstructural features will play a dominant role in determining the short-term leach rates of metals from the ceramic, as their dissolution as demonstrated by TEM proceeds more quickly than from the fully crystalline material. In the longer term, losses will be determined by metals solubilized directly from apatite crystals, especially along the susceptible $\{10 \bar{1} 0\}$ crystallographic planes, especially so in calcium-rich compositions. Short-term leach tests conducted according to a modified TCLP method showed lead losses to be within regulatory limits in this trial apatite system, which is not yet optimized in terms of immobilization.

VI. Implications for Immobilization

It is clear that even this relatively simple apatite system containing only three toxic

elements (lead, vanadium, and fluorine) displays considerable crystallochemical and microstructural complexity, which will have a direct bearing on the long-term performance of the waste form. First, the solubility of the apatite is strongly dependent on overall composition, with lead-rich material being substantially more durable. This result might have been anticipated, for while no published solubility for lead vanadium apatites could be found, it has been reported that lead phosphate apatites are less soluble than their calcium-rich counterparts.²⁵ This is a positive result in terms of stabilization of lead-rich wastes. It would be of interest to establish whether chemically similar toxic metals (e.g., cadmium or mercury) behave similarly in calcium vanadium apatite. Second, in common with wasteform ceramics generally, grain boundary phases and other imperfections will reduce chemical and mechanical durability. The present system could be enhanced through the inclusion of additives that would improve sinterability and to yield denser and more homogeneous ceramics. Finally, while the synthesis conditions used apparently resulted in negligible volatilization of lead (as evidenced by the formation of near stoichiometric apatite), further emphasis should be given to validating that the losses are minimal and within regulatory guidelines.

The procedures to validate the suitability of apatite-based ceramics for the immobilization of inorganic industrial wastes are, in most respects, completely analogous to the mature methods used to develop crystalline nuclear waste forms.²⁶⁻²⁸ Key technical demonstrations include the capacity to incorporate waste at high loadings, an ability to accept variations in waste composition and resistance to alteration under a range of conditions. Similarly, the effectiveness of both nuclear and industrial waste ceramics can be limited through the formation of less durable secondary phases (especially at higher loadings), volatilization of components, and intergranular solubility.²⁹ It would be efficacious for future studies of apatite ceramics for industrial waste treatment to adopt the same rigor as routinely applied to nuclear waste materials, especially where transformation into voluminous secondary products is envisaged.

References

- [1] G. J. McCarthy, "High-Level Waste Ceramics: Materials Considerations, Process Simulation, and Product Characterization," *Nucl. Technol.*, **32**, 92–105 (1977).
- [2] P. Zhang and J. A. Ryan, "Formation of Pyromorphite in Anglesite–Hydroxapatite Suspensions under Varying pH Conditions," *Environ. Sci. Technol.*, **32**, 3318–24 (1998).
- [3] J. Neubauer and H. Pöllmann, "Solid Solution Series of Silico-Sulphate-Chloride Apatites," *Neues Jahrb. Mineral., Abh.*, **168** [3] 237–58 (1995).
- [4] J. V. Bothe and P. W. Brown, "Apatite Formation in the CaO–PbO–P₂O₅–H₂O System at 23° ± 1°C," *J. Am. Ceram. Soc.*, **83** [3] 612–16 (2000).
- [5] Q. Y. Ma, S. J. Traina, T. J. Logan, and J. A. Ryan, "In Situ Lead Immobilization by Apatite," *Environ. Sci. Technol.*, **27**, 1803–10 (1993).
- [6] S. Furuta, H. Katsuki, and S. Komarneni, "Removal of Lead Ions Using Porous Hydroxyapatite Monoliths Synthesized from Gypsum Waste," *J. Ceram. Soc. Jpn.*, **108** [3] 315–17 (2000).
- [7] Y. Xu and F. W. Schwartz, "Lead Immobilization by Hydroxyapatite in Aqueous Solutions," *J. Contam. Hydrol.*, **15**, 187–206 (1994).
- [8] J. R. Conner, "Toxicity Characteristic Leaching Procedure (TCLP)"; pp. 638–51 in *Chemical Fixation and Solidification of Hazardous Wastes*. Van Nostrand Reinhold, New York, 1990.
- [9] P. L. Bishop, "Leaching of Inorganic Hazardous Constituents from Stabilized/Solidified Hazardous Wastes," *Hazard. Waste Hazard. Mater.*, **5** [2] 129–43 (1988).
- [10] V. Albino, R. Cioffi, B. de Vito, and L. Santoro, "Evaluation of Solid Waste Stabilization Processes by Means of Leaching Tests," *Environ. Technol.*, **17** [3] 309–15 (1996).
- [11] T. Lind, T. Valmari, E. I. Kauppinen, G. Sfiris, K. Nilsson, and W. Maenhaut, "Volatilization of the Heavy Metals During Circulating Fluidized Bed Combustion of Forest Residue," *Environ. Sci. Technol.*, **33**, 496–502 (1999).
- [12] L. Paya, M. V. Borrachero, J. Monzo, and M. Bonilla, "Properties of Portland Cement Mortars Incorporating High Amounts of Oil-Fuel Ashes," *Waste Manage.*, **19**, 1–7 (1999).
- [13] T. T. Eighmy, B. S. Crannell, L. G. Butler, F. K. Cartledge, E. F. Emery, D. Oblas, J. E. Krzanowski, J. D. Eusden, E. L. Shaw, and C. A. Francis, "Heavy Metal Stabilization in

Municipal Solid Waste Combustion Dry Scrubber Residue Using Soluble Phosphate,” *Environ. Sci. Technol.*, **31**, 3330–38 (1997).

[14] S. Iretskaya, A. Nzihou, C. Zahraoui, and P. Sharrock, “Metal Leaching from MSW Fly Ash before and after Chem. and Thermal Treatments,” *Environ. Prog.*, **18** [2] 144–48 (1999).

[15] C. C. Wiles, “Municipal Solid Waste Combustion Ash: State-of-the-Knowledge”; pp. 171–90 in *Municipal Solid Wastes: Problems and Solutions*. Edited by R. E. Landreth and P. A. Rebers. Lewis Publishers, New York, 1997.

[16] M. O. O’Keeffe and B. G. Hyde, “An Alternative Approach to Non-molecular Crystal Structures with Emphasis on the Arrangements of Cations,” *Struct. Bond.*, **61**, 79–144 (1985).

[17] A. Clark, “Introduction to the Mineral Kingdom”; p. 135 in *Illustrated Encyclopedia of Minerals*. Edited by A. Woolley. Hamlyn Publishing Group, London, U.K., 1990.

[18] N. D. Naeser, “Miocene Cooling in the Southwestern Powder River Basin, Wyoming—Preliminary Evidence from Apatite Fission-Track Analysis,” *U.S. Geol. Surv. Bull.*, O10–O11 (1992).

[19] M. H. El Gibaly, F. M. El Reweiny, M. Abdel-Nasser, and T. A. El Dahtory, “Studies of Phosphate Solubilizing Bacteria in Soil and Rhizosphere of Different Plants. Occurrence of Bacteria Acid Producers and Phosphate Dissolvers,” *Zentralbl. Bakteriол., Parasitenkd. Infektionskrankh. Hyg.*, **132**, 233 (1977).

[20] “WIN-RIETVELD—Crystal Structure Refinement and Determination, V2.51 (Windows NT),” Siemens AG, Analytical X-ray Systems AUT 37, D-76181, Karlsruhe, Germany.

[21] K. Sudarsanan, P. E. Mackie, and R. A. Young, “Comparison of Synthetic and Mineral Fluoroapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, in Crystallographic Detail,” *Mater. Res. Bull.*, **1**, 1331–38 (1972).

[22] L. Keller, J. Rask, and P. Buseck, “Lead Vanadium Oxide Chloride,” Powder Diffraction File, Card No. 43-1461. International Centre for Diffraction Data, Newton Square, PA, 1989.

[23] D. R. Clarke, “On the Detection of Thin Intergranular Films by Electron Microscopy,” *Ultramicroscopy*, **4**, 33–44 (1979).

[24] A. Bigi, A. Ripamonti, S. Bruckner, M. Gazzano, N. Roveri, and S. A. Thomas, “Structure Refinements of Lead-Substituted Calcium Hydroxyapatite by X-ray Powder Fitting,” *Acta Crystallogr., Sect. B: Struct. Sci.*, **B45**, 247–51 (1989).

[25] P. B. Moore, “Crystallochemical Aspects of the Phosphate Minerals”; p. 178 in *Phosphate Minerals*. Edited by J. O. Nriagu and P. B. Moore. Springer-Verlag Berlin, Germany, 1983.

[26] C. M. Jantzen, D. R. Clarke, P. E. D. Morgan, and A. B. Harker, "Leaching of Polyphase Nuclear Waste Ceramics: Microstructural and Phase Characterization," *J. Am. Ceram. Soc.*, **65** [6] 292–300 (1982).

[27] F. J. Ryerson, "Microstructure and Mineral Chemistry of Synroc-D," *J. Am. Ceram. Soc.*, **66** [9] 629–36 (1983).

[28] D. Singh, M. Tlustochowicz, and A. S. Wagh, "Development of Zirconium/Magnesium Phosphate Composites for Immobilization of Fission Products," *J. Am. Ceram. Soc.*, **82** [1] 43–49 (1999).

[29] D. R. Clarke, "Preferential Dissolution of Intergranular Amorphous Phase in a Nuclear Waste Ceramic," *J. Am. Ceram. Soc.*, **64** [6] C-89–C-90 (1981).

[30] "Background Document for Capacity Analysis for Land Disposal Restrictions— Phase IV (Second Supplement): Toxicity Characteristic Metal Wastes and Newly Identified Mineral Processing Wastes (Proposed Rule)," U.S. Environmental Protection Agency, Office of Solid Waste, Washington, DC, April 1997.

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Table II. Rietveld Parameters Derived from Single-Phase and Two-Phase Models for Material of Nominal Composition $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$

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- Fig. 1. Schematic illustration of the apatite structure viewed along [001]. From left to right BO_4 tetrahedra, $\text{A}(1)\text{O}_6$ trigonal bipyramids, and $\text{A}(2)\text{O}_8$ polyhedra are emphasized.
- Fig. 2. Backscattered electron micrographs of polished sintered pellets having bulk starting compositions of (a) $(\text{Ca}_3\text{Pb}_7)(\text{VO}_4)_6\text{F}_2$, (b) $(\text{Ca}_5\text{Pb}_5)(\text{VO}_4)_6\text{F}_2$, and (c) $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$.
- Fig. 3. Average unit cell constants versus composition. (Standard deviation error bars are smaller than the size of the symbols.)
- Fig. 4. Diffraction pattern from $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$. The upper data show the experimental data overlaying the calculated patterns derived from (a) single-phase apatite with $x = 3$ and (b) two-phase apatite with 65 wt% $x = 2.4$ and 35 wt% $x = 0.8$ to yield an average $x = 3.3$. The differences between the calculated and experimental patterns are shown in the lower charts. (The third reflection from the left is due to the internal silicon standard.)
- Fig. 5. HRTEM images taken from $[011] \equiv [1\bar{2}13]$ zone axis of (a) $(\text{Ca}_{10})(\text{VO}_4)_6\text{F}_2$ and (b) $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ apatites. The structure drawing (c) provides the correlation of the image with crystal structure in this orientation.
- Fig. 6. (a) STEM image of a cryptocrystalline region B, lying between well-ordered apatite A. Lattice images of (b) periodic region A and (c) aperiodic region B.
- Fig. 7. Through focal series of a grain boundary in $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ with (a) overfocus, (b) near focus, and (c) underfocus.
- Fig. 8. STEM/BSE images of $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ thin section (a) before (b) after leaching for 90 h in TCLP liquor showing etching of grain boundary phases and preferential dissolution along some crystallographic planes.

Fig. 9. TEM images and selected area diffraction pattern showing dissolution along $\{10\bar{1}0\}$.

Fig. 10. SE image of leached $(\text{Ca}_5\text{Pb}_5)(\text{VO}_4)_6\text{F}_2$ showing morphology of etch pits and channels and the relationship to crystal facets.

Fig. 11. BSE images of two-phases $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$ pellet surfaces (a) before and (b) after leaching for 360 h. The calcium-rich crystals (darker regions) are removed by this treatment, while the lead-rich crystals are preserved.

Fig. 12. TCLP leach data for two-phase $(\text{Ca}_7\text{Pb}_3)(\text{VO}_4)_6\text{F}_2$.

Element	Ideal composition (Ca ₇ Pb ₃)(VO ₄) ₆ F ₂		White phase lead-rich		Dark phase calcium-rich	
	at. %	Formula unit	at. %	Formula unit	at. %	Formula unit
Ca	16.7	7	15.2	6.4	17.6	7.4
Pb	7.1	3	8.6	3.6	6.2	2.6
V	14.3	6	13.4	5.6	14.0	5.9
F	4.8	2	6.8	2.9	7.2	3.0
O	57.1	24	ND	ND	ND	ND

Table I.

Parameter	Single-phase		Two-phase					
	Nominal composition (Ca ₇ Pb ₃)(VO ₄) ₆ F ₂ , $x = 3$		Refined composition					
			Pb-poor apatite (65 wt%) (Ca _{8.0} Pb _{2.0})(VO ₄) ₆ F ₂ , $x = 2.0$		Pb-rich apatite (35 wt%) (Ca _{5.1} Pb _{4.9})(VO ₄) ₆ F ₂ , $x = 4.9$		Overall composition (Ca ₇ Pb ₃)(VO ₄) ₆ F ₂ , $x = 3$	
			Occupancy [†]	Stoichiometry	Occupancy [†]	Stoichiometry	Occupancy [†]	Stoichiometry
Ca 1	0.23	2.8	0.282	3.4	0.181	2.2	0.25	3.04
Pb 1	0.10	1.2	0.051	0.6	0.152	1.8	0.09	0.96
Ca 2	0.35	4.2	0.380	4.6	0.242	2.9	0.33	3.96
Pb 2	0.15	1.8	0.120	1.4	0.258	3.1	0.17	2.04
	<u>Refined Cell</u>		<u>Refined</u>	<u>Algebraic[‡]</u>	<u>Δ%</u>	<u>Refined</u>	<u>Algebraic[‡]</u>	<u>Δ%</u>
a (Å)	9.8530		9.8532	9.8004	−0.54	9.8495	9.9361	+0.88
c (Å)	7.1077		7.1020	7.0748	−0.38	7.1095	7.1917	+1.16
V (Å ³)	597.6		597.2	588.5	−1.5	597.3	614.9	+2.9
R_B	14.3		15.6			12.0		
R_p	17.3				17.2			
R_{wp}	22.3				21.9			
R_{exp}	15.7				15.7			
S	1.42				1.39			
D	1.04				1.08			

[†]Fractional multiplicity for A(1)-site at position (4f) and A(2) site at position (6h). [‡]Derived from refined x and $\mathbf{a} = (0.0458x + 9.7068)$ and $\mathbf{c} = 0.0018x^2 + 0.0279x + 7.0118$.

Table II.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

Fig. 12.