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Model Apatite Systems for the Stabilization of Toxic Metals: II, Cation and Metalloid Substitutions in Chlorapatites

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Environmental chlorapatites, of the form $A_{10}(B_xC_{1-x}O_4)_6Cl_2$, where $A = Ca, Cd, \text{ or } Pb$; $B/C = P, V, \text{ or } Cr$ and $0 \leq x \leq 1$, were synthesized by solid-state reactions. Crystal structure variations, primarily lattice parameters, were examined through powder X-ray diffraction methods, while performance and long-term durability of these waste form apatites were assessed by a combination of the toxicity characteristic leaching procedure (TCLP) and the American Nuclear Society (ANS) method. As expected, an overall dilation of unit cell edges was observed with increasing ionic substitutions. However, a discontinuity in linearity was often observed, generally for $x \geq 0.5$. The correlation of microstructural changes and leach testing shows that lead chlorapatite is found to be more suitable for waste stabilization than calcium and cadmium analogues.

I. Introduction

Apatites, predominantly the phosphate-based analogues, have found application for the stabilization of contaminated soils¹ and hazardous industrial wastes.²⁻⁶ Their thermodynamic and chemical stability under a wide range of conditions, relative

insolubility in natural environments, and radiation resistance make them effective materials for remediation.⁷⁻¹⁰ Apatites are increasingly important for hazardous and nuclear waste disposal. Incinerator ash, produced from the combustion of industrial and nuclear wastes, contains significant quantities of toxic and radioactive metals, such as Cr, Cd, Pb, As, and Zn, and Cs, Sr, and Pu, respectively.¹¹⁻¹⁵ Typically, industrial wastes are heaped as tailings or deposited directly in controlled landfills, which is costly and, in some circumstances, leads to the gradual spread of toxic metals via the hydrosphere. It is, therefore, desirable to stabilize waste before disposal in forms that avoid excessive bulking.¹⁶ While many approaches are used to remediate contaminated sites,^{17,18} immobilization is often most suitable to reduce the mobility of non-biodegradable waste.¹⁹ *In situ* (e.g., for contaminated soils) and *ex situ* (e.g., for fly ash) techniques usually involve amendments for fixation of heavy metals, primarily through adsorption or transformation to other less-soluble compounds.²⁰ *In situ* immobilization is generally most cost-effective, as contaminants are treated in place with minimal disruption to the landscape, hydrology, and eco-systems, as opposed to *ex situ* immobilization, which requires excavation, treatment, and disposal methods.¹⁷

Assessment of the performance of ceramic waste forms relies largely on the determination of leach rates using standard test methods, especially the toxicity characteristic leach procedure (TCLP),^{21,22} although this is a poor simulation of landfill conditions. While TCLP is a useful screening method, the scientific limitations of the approach are well known,^{16,23,24} 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 (crystallo-chemical incorporation or adsorption), and the manner in which apatite-related phases may enhance or degrade performance.¹⁶ Because of its limitations, the American Nuclear Society (ANS) 16.1 Leach Test Procedure²⁵ is sometimes used to complement the TCLP method.

As part of a wider-ranging study of alternative stabilization materials, we report the preparation and characterization of a series of chlorapatites, $A_{10}(B_xC_{1-x}O_4)_6Cl_2$, where A = Ca, Cd, or Pb; B/C = P, V, or Cr and $0 \leq x \leq 1$. Cadmium, lead, vanadium, and chromium were chosen for substitution, as these are common contaminants. The aims of this work were to establish the structural and chemical continuity of these apatite series, investigate the relationship between chemistry and waste form durability, and seek a clearer understanding of the dissolution mechanism through leach testing.

II. Crystal Chemistry of Chlorapatites

Apatites have the generic formula $A_5(BO_4)_3X$, where A comprises larger mono-, di-, or trivalent cations, typically Ca, Sr, Ba, Cd, and Pb. B are metalloids, commonly P, As, V, Mn, and Cr, while X represents halides and anion radicals.^{26–29} The structural aristotype for the apatite family has $P6_3/mcm$ symmetry,^{29–33} and while $P6_3/m$ is the most common subgroup, it is by no means dominant.²⁹ For example, an accurate structure determination of calcium chlorapatite, $Ca_{10}(PO_4)_6Cl_2$, found it to be pseudohexagonal and best described as monoclinic, $P2_1/b$, with $a = 9.628(5) \text{ \AA}$, $b = 19.256(10) \text{ \AA}$, $c = 6.764(5) \text{ \AA}$, $\gamma = 120.0(0)^\circ$.³⁴

Crystallo-chemical features atypical of apatites produce a structure very tolerant to ionic substitutions.^{28,35–38} As shown in Fig. 1, the structure consists of regular BO_4 tetrahedra, as well as two crystallographically distinct A sites: A(1) and A(2). A(1) O_6 metaprisms and BO_4 tetrahedra share edges to form zeolite-like channels parallel to $[001]$.¹⁶ The channels contain interstices that accommodate the A(2) atoms, disposed such that they form two $[001]$ triangles rotated by 60° with respect to each other. The A(2)₃ triangles are partially filled with X anions or stereochemically active lone pair electrons, in the case of Pb apatites. A(2) atoms adopt irregular A(2) O_6X coordination spheres that readily distort to enhance the capacity of apatite to immobilize cations of different sizes.

Kriedler and Hummel³⁹ determined the ionic radii boundaries for substitution into chlorapatites to be $0.80 \text{ \AA} \leq R_A$ (coordination number, CN, VIII) $\leq 1.35 \text{ \AA}$ and $0.29 \text{ \AA} \leq R_B$ (CN IV) $\leq 0.60 \text{ \AA}$, for ions occupying the A and B positions, respectively. In principle,

substitution of Cd (R_{Cd} (CN VIII) = 0.95 Å), Pb (R_{Pb} (CN VIII) = 1.19 Å), V (R_{V} (CN IV) = 0.36 Å), and Cr (R_{Cr} (CN IV) = 0.35 Å) into prototype chlorapatite should be effective for waste stabilization.

III. Experimental Procedures

(1) *Synthesis*

Apatites of composition $\text{A}_{10}(\text{B}_x\text{C}_{1-x}\text{O}_4)_6\text{Cl}_2$, where A = Ca, Cd, or Pb, B/C = P, V, or Cr and $0 \leq x \leq 1$, were prepared by solid-state reaction. Starting materials were mixed in stoichiometric proportions and fired at different temperatures in alumina crucibles for 15 h (Table I). Sintering was conducted just below the melting point of the end-member apatites. These powders were subsequently manually ground with an agate mortar and reheated at the same temperatures for a further 15 h to drive the reactions toward completion. Chlorine loss was controlled by closing the system with platinum seals. For leach tests, powders were pressed into pellets ($\sim 10 \text{ mm} \times 2\text{--}4 \text{ mm}$) and sintered at the above temperatures for 15 h. Each pellet had a mass of $\sim 1\text{--}1.5 \text{ g}$.

(2) *Characterization*

(A) *Powder X-ray Diffraction (XRD)*: Powder XRD patterns were collected using a Siemens D5005 X-ray diffractometer (Bruker-AXS, Karlsruhe, Germany), running at 40 kV and 40 mA using unmonochromated $\text{CuK}\alpha$ X-ray radiation ($K_{\alpha 1} = 1.540596 \text{ Å}$, $K_{\alpha 2} = 1.544493 \text{ Å}$). Divergence and anti-scatter slits of 0.5 mm were inserted, while receiving and detector slits were 0.1 and 0.6 mm, respectively. Soller slits in the incident and diffracted paths were used to limit beam divergence to within 2.3° . A postspecimen monochromator was used to reduce background. Samples were mechanically ground to powder to minimize preferred orientation effects and mixed with approximately 25 wt% of standard silicon powder with $a_0 = 5.43088 \text{ Å}$ (NIST 640c, National Institute of Standards Technology, MD) to allow internal calibration of d -spacings. For characterization purposes, initial data were collected in 0.04° steps over the 2θ range of $5^\circ\text{--}65^\circ$, with a counting time of 1 s per step. Samples were rotated around the holder axis at 30 rpm.

Crystal structures were refined by Rietveld analysis^{40–42} using the fundamental parameter method.^{43,44} A hexagonal $P6_3/m$ model was used as a starting point. For each data set, a four coefficient background polynomial, zero error, and sample displacement were refined, followed by unit cell parameters, scale factor, peak shape, and positional parameters. As a preliminary model, lattice parameters and atomic coordinates were taken from literature values (Table II). For those compounds that did not have known crystallographic data, starting models were based on their apatite analogues. Isotropic displacement parameters were initially set to $1 \text{ \AA}^2$ for all atoms and refined. Occupancy of atoms at the B/C-site was fixed at the assumed composition and not refined.

(B) Scanning Electron Microscopy: Scanning electron microscopy (SEM) was conducted using a JEOL JSM-5310LV instrument (Jeol, MA), operated at 20 keV and with a low vacuum of $\sim 25\text{--}29$ Pa to minimize charging. Images of sintered pellets were collected before and after polishing with $10 \text{ }\mu\text{m}$ diamond paste. Additional microscopy was conducted after leach testing. Semi-quantitative energy-dispersive X-ray microanalysis of the apatites and their alteration products was undertaken using an Oxford Link Si(Li) X-ray detector and associated software (Link Analytical, Oxford, UK).

(3) Leach Tests

Two different leach tests were used to determine elemental losses of Ca, Cd, Pb, P, V, and Cr. The first method was a scaled-down modification of the TCLP method²¹ in which extractions were conducted on individual sintered pellets (~ 1.3 mm diameter, $\sim 1.0\text{--}1.5$ g) using acetic acid of pH 2.88, prepared by diluting 5.7 mL of glacial acid with deionized water to a volume of 1 L. A solid:extraction-fluid weight ratio of 1:20 was maintained. Pellets were immersed in $\sim 17\text{--}23$ mL of leach solution in an extraction bottle that was tightly closed and rotated at 30 rpm for leach periods of 18 h and 3 d. Extracted ion concentration was measured with a Bruker SRS3500 wavelength dispersive X-ray fluorescence spectrometer (XRF, Bruker-AXS, Karlsruhe, Germany). Quantification was completed using manufacturer software and calibrated against standard solutions.

The second method was an adaptation of the ANS procedure (ANS 16.1 Test Procedure) using distilled H₂O as the leachate. Sintered pellets were tested statically with a solid:extraction-fluid weight ratio of 1:20. Specimens were supported by clips to ensure that the entire external surface was exposed to the leach-ant. The leachate was sampled and completely replaced after cumulative leach times of 2, 7, and 24 h from initiation of the test. Subsequent leachate sampling and extractant replacements were made at 24 h intervals for the next 4 d. Long-term stability was assessed at intervals of 14, 28, and 43 d so the entire test was extended to 90 d. Unlike the TCLP method, leach data from the ANS leach test procedure were treated as leach rates to correlate trends in leachability. Concentrations of the ions in the leachates were measured under the same XRF conditions cited above.

IV. Results

(1) *Synthesis and Crystallographic Data*

Synthesis of 90 chlorapatites was attempted. Although a majority crystallized easily, the synthesis of chromium-substituted apatites proved more difficult. The product apatites displayed a wide array of colors, ranging from white, yellow, blue-purple, reddish-brown to light and dark green. Phase purity of each sample was ascertained by quantitative XRD and, from the structure field diagrams (Fig. 2), the average ionic radii of ions occupying the positions constructed. Boundaries of the structure fields were determined by observing which compositions produced single-phase apatites or where there was more than one phase present. The phase distribution diagrams for all nine series are shown in Fig. 3.

Refinements of all the chlorapatites fit the hexagonal model agreeably. Although monoclinic forms are well documented,³⁴ such occurrences were not observed in this study. The lattice parameters for the nine series are shown in Fig. 4. There was an overall increase in cell dimensions with larger ionic substitutions; however, discontinuities of cell parameters were often observed. For the (Ca, Cd, Pb)₁₀(V_xP_{1-x}O₄)₆Cl₂ series, in particular, discontinuity was more apparent for the *c* parameter than the *a* parameter, indicating a departure from Vegard's Law.

(2) *Microstructural Features*

Porosity varied as a function of composition, with lower melting point joints displaying greater grain growth and pore closure. For example, a set of representative microstructures for the $\text{Pb}_{10}(\text{V}_x\text{P}_{1-x}\text{O}_4)_6\text{Cl}_2$ series illustrate the correlation of crystal morphology with composition (Figs. 5(a)–(c)). In vanadium-poor apatites, pore sizes were smaller, but as vanadium content and melting point increased, porosity was more obvious.

A similar observation was made for selected cadmium series with different B-cation substitutions as shown in Figs. 5(d) and (e). In addition, secondary phases were evident as expected for the XRD data (Fig. 3). For $\text{Cd}_{10}(\text{P}_{0.6}\text{Cr}_{0.4}\text{O}_4)_6\text{Cl}_2$ and $\text{Cd}_{10}(\text{V}_{0.5}\text{Cr}_{0.5}\text{O}_4)_6\text{Cl}_2$, microanalysis showed that the lighter regions, with higher average atomic number, corresponded to the non-apatite phases, which were regularly distributed among apatite crystals. For $\text{Cd}_{10}(\text{V}_{0.6}\text{P}_{0.4}\text{O}_4)_6\text{Cl}_2$, which is biphasic and contained 10 wt% $\text{Cd}_2\text{V}_2\text{O}_8$, differentiation from the apatite was not possible by microscopy.

(3) *Dissolution Mechanism*

(A) *Toxicity Characteristic Leaching Procedure*: For the apatite end-members, comparison of experimental TCLP leach data with regulatory limits[†] (Table III) showed that, while lead and chromium levels were in compliance, cadmium losses exceeded regulatory limits. This is tentatively ascribed to greater porosity, which afforded greater accessibility to the leachant and a higher proportion of less durable cryptocrystalline regions. This proposition is supported by the observation that, after 3 d, metal extraction for cadmium remained constant. On the other hand, lead and chromium extraction decreased after the removal of near-surface soluble grain boundary materials.

(B) *ANS Procedure*: Leach rates derived from the ANS method showed a general decline with time, as comparisons of the data for the lead–calcium analogues demonstrate (Fig. 6). For cadmium compounds (and in contrast to TCLP testing), cadmium was below detection limits in the leachate. Lead, chromium, and vanadium levels are all within regulatory limits. The trend for all three lead series was similar, with the leach rate

declining rapidly in the first 24 h, after which there was a steady decrease until no detectable loss of Pb was observed. The calcium series showed a more erratic decline, and for $\text{Ca}_{10}(\text{CrO}_4)_6\text{Cl}_2$, the leachate immediately took on a green-yellow color.

(C) Alteration Accompanying TCLP and ANS Procedures: $\text{Ca}_{10}(\text{VO}_4)_6\text{Cl}_2$ and $\text{Ca}_{10}(\text{CrO}_4)_6\text{Cl}_2$ were the only apatites to display obvious changes to surface morphology after acetic acid and H_2O leach tests, together with erratic leach rates (Fig. 6). For $\text{Ca}_{10}(\text{VO}_4)_6\text{Cl}_2$, five distinct crystal morphologies were observed after ANS testing (Fig. 7(c)). Equant crystalline blocks containing calcium and carbon were prevalent and confirmed as calcite by XRD. Rosette and prismatic calcite morphologies were observed less commonly. In addition, crystals rich in calcium and vanadium were present; however, unequivocal identification of these minor phases was not possible. The chemical composition and morphology of the tabular crystals are consistent with the hydrated triclinic form, $\text{Ca}_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. For $\text{Ca}_{10}(\text{CrO}_4)_6\text{Cl}_2$, shown in Fig. 7(f), euhedral morphologies were also developed during the leaching period and determined to be CaCO_3 .

V. Discussion

Under the present synthesis conditions, the chlorapatite series, $\text{A}_{10}(\text{B}_x\text{C}_{1-x}\text{O}_4)_6\text{Cl}_2$, where $\text{A} = \text{Ca}, \text{Cd}, \text{or Pb}$ and $\text{B/C} = \text{P}, \text{V}, \text{or Cr}$ and $0 \leq x \leq 1$, often yielded minor non-apatite phases (Fig. 3). End-member and mixed V–P chlorapatites were more readily synthesized with higher apatite fractions than their Cr–P and V–Cr analogues. For the V–P series, CaV_2O_8 and CdV_2O_8 forms were present in relatively minor quantities. For the mixed Cr–P and V–Cr chlorapatites, however, it was common to see considerably larger percentages of secondary and tertiary non-apatite phases, mainly in the form of calcium/cadmium/lead chromium oxides, especially around $x = 0.5$. It is anticipated that longer-term annealing would bring the reactions to completion, while complete equilibration and stabilization of lattice parameters may require several weeks,⁴⁸ and are presently under investigation.

Monoclinic apatite forms are well-documented, in particular for $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$.³⁴ However, all chlorapatites in this study fitted the hexagonal model at the available

resolution of the XRD data. Lattice parameters for known end-member apatites were generally found to be in good agreement with previously published values (Table II). As expected, overall cell dimensions for the nine series dilated with larger ionic substitutions ($\text{Cd}^{2+} < \text{Ca}^{2+} < \text{Pb}^{2+}$, while $\text{P}^{5+} < \text{Cr}^{5+} < \text{V}^{5+}$). Vegard's Law of linearity was obeyed over limited compositional ranges; however, there were distinct discontinuities that arose for both the a and c parameters. Particularly for the P–V chlorapatites, c parameters displayed erratic behavior after $x = 0.5$, possibly reflecting the presence of X-ray amorphous material and changes in apatite composition. In fluorapatite waste forms, it has been shown that discontinuities are related to changes in A-cation partitioning between the A(I) and A(II) sites.⁴⁹ Moreover, such discontinuities vary as a function of equilibration. In separate investigations of synthetic $(\text{Ca}_{10}\text{Pb}_{10-x})(\text{VO}_4)_6\text{F}_2$ vanadinite⁴⁸ and gem-grade ellestadite,⁵⁰ the importance of miscibility gaps and nanoscale phase domains has recently been recognized. Slight variations between structures reflect rather significant distinctions in crystal chemical behavior, which are believed to be because of differences in the position and size of the halide ions of the Cl and F ions.^{51–53}

The TCLP data after 18 h and 3 d showed that with the exception of cadmium, toxic metal losses were to be within regulatory limits for these trial apatite systems. For cadmium, exposure to cryptocrystalline regions is believed to have led to poorer durability. The ANS method showed that, over 90 d, cadmium and lead dissolution rates were more stable than their calcium counterparts. The variability in leach rate for most calcium apatites arose from the uncontrolled precipitation of CaCO_3 .

Overall, lead phosphate, vanadate, and chromate chlorapatites are most durable. Lead levels were always within regulatory limits and were less soluble than their calcium and cadmium counterparts under the test conditions. This may have been anticipated, for while there is no published work on lead vanadium or lead chromium apatites to our knowledge, lead phosphate apatites are known to be less soluble than their calcium counterparts.⁵⁴ In addition, lead phosphate chlorapatites have been shown to be the most stable and least-soluble environmental form of lead under a wide variety of conditions.¹⁷ Although the cadmium chlorapatites were the most durable in the ANS method, cadmium levels exceeded TCLP limits.

The synthesis conditions used in this reconnaissance study produced undesirable secondary, and in some cases tertiary, phases and high open porosity, leading to less than optimal durability. Current work is directed toward the optimization of synthesis conditions (temperature and time) and the inclusion of sintering additives to enhance sinterability and yield denser, more homogeneous ceramics.

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Chloro-apatites ($0 \leq x \leq 1.0$)	Starting materials	Calcination temperature (°C)
$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$	CaO , CaCl_2 , and H_3PO_4	900
$\text{Ca}_{10}(\text{VO}_4)_6\text{Cl}_2$	CaO , CaCl_2 , and V_2O_5	900
$\text{Ca}_{10}(\text{CrO}_4)_6\text{Cl}_2$	CaO , CaCl_2 , and Cr_2O_3	900
$\text{Cd}_{10}(\text{PO}_4)_6\text{Cl}_2$	CdO , CaCl_2 , and H_3PO_4	600
$\text{Cd}_{10}(\text{VO}_4)_6\text{Cl}_2$	CdO , CaCl_2 , and V_2O_5	600
$\text{Cd}_{10}(\text{CrO}_4)_6\text{Cl}_2$	CdO , CaCl_2 , and Cr_2O_3	600
$\text{Pb}_{10}(\text{PO}_4)_6\text{Cl}_2$	PbO , CaCl_2 , and H_3PO_4	700
$\text{Pb}_{10}(\text{VO}_4)_6\text{Cl}_2$	PbO , CaCl_2 , and V_2O_5	700
$\text{Pb}_{10}(\text{CrO}_4)_6\text{Cl}_2$	PbO , CaCl_2 , and Cr_2O_3	700
$\text{Ca}_{10}(\text{V}_x\text{P}_{1-x}\text{O}_4)_6\text{Cl}_2$	CaO , CaCl_2 , and H_3PO_4 , and/or V_2O_5	800
$\text{Ca}_{10}(\text{Cr}_x\text{P}_{1-x}\text{O}_4)_6\text{Cl}_2$	CaO , CaCl_2 , and H_3PO_4 , and/or Cr_2O_3	800
$\text{Ca}_{10}(\text{V}_x\text{Cr}_{1-x}\text{O}_4)_6\text{Cl}_2$	CaO , CaCl_2 , and V_2O_5 , and/or Cr_2O_3	800
$\text{Cd}_{10}(\text{V}_x\text{P}_{1-x}\text{O}_4)_6\text{Cl}_2$	CdO , CaCl_2 , and H_3PO_4 , and/or V_2O_5	600
$\text{Cd}_{10}(\text{Cr}_x\text{P}_{1-x}\text{O}_4)_6\text{Cl}_2$	CdO , CaCl_2 , and H_3PO_4 , and/or Cr_2O_3	600
$\text{Cd}_{10}(\text{V}_x\text{Cr}_{1-x}\text{O}_4)_6\text{Cl}_2$	CdO , CaCl_2 , and V_2O_5 , and/or Cr_2O_3	600
$\text{Pb}_{10}(\text{V}_x\text{P}_{1-x}\text{O}_4)_6\text{Cl}_2$	PbO , PbCl_2 , and H_3PO_4 , and/or V_2O_5	600
$\text{Pb}_{10}(\text{Cr}_x\text{P}_{1-x}\text{O}_4)_6\text{Cl}_2$	PbO , PbCl_2 , and H_3PO_4 , and/or Cr_2O_3	600
$\text{Pb}_{10}(\text{V}_x\text{Cr}_{1-x}\text{O}_4)_6\text{Cl}_2$	PbO , PbCl_2 , and V_2O_5 , and/or Cr_2O_3	600

Table I

End-member apatites	Value (Å)	Current work (Å)
Ca ₁₀ (PO ₄) ₆ Cl ₂	$a = 9.598(2)$ $c = 6.776(4)^{45}$	$a = 9.5927(1)$ $c = 6.7668(1)$
Cd ₁₀ (PO ₄) ₆ Cl ₂	$a = 9.633(4)$ $c = 6.484(4)^{46}$	$a = 9.623(2)$ $c = 6.5177(1)$
Pb ₁₀ (PO ₄) ₆ Cl ₂	$a = 9.866(3)$ $c = 7.426(2)^{36}$	$a = 9.9925(3)$ $c = 7.3460(3)$
Ca ₁₀ (VO ₄) ₆ Cl ₂	Starting model: Pb ₁₀ (VO ₄) ₆ Cl ₂	$a = 9.9407(3)$ $c = 6.9169(3)$
Cd ₁₀ (VO ₄) ₆ Cl ₂	Starting model: Pb ₁₀ (VO ₄) ₆ Cl ₂	$a = 10.1117(2)$ $c = 6.5595(3)$
Pb ₁₀ (VO ₄) ₆ Cl ₂	$a = 10.331(1)$ $c = 7.343(1)^{47}$	$a = 10.3242(9)$ $c = 7.3556(6)$
Ca ₁₀ (CrO ₄) ₆ Cl ₂	Starting model: Ca ₁₀ (PO ₄) ₆ Cl ₂	$a = 9.9612(2)$ $c = 6.8820(2)$
Cd ₁₀ (CrO ₄) ₆ Cl ₂	Starting model: Cd ₁₀ (PO ₄) ₆ Cl ₂	$a = 10.1127(2)$ $c = 6.5598(1)$
Pb ₁₀ (CrO ₄) ₆ Cl ₂	Starting model: Pb ₁₀ (PO ₄) ₆ Cl ₂	$a = 10.3448(3)$ $c = 7.3903(2)$

Table II

		Metal content after 18 h and after 3 d (in brackets)							
Regulatory limit (ppm) [†]		Ca ₁₀ (VO ₄) ₆ Cl ₂	Ca ₁₀ (CrO ₄) ₆ Cl ₂	Cd ₁₀ (PO ₄) ₆ Cl ₂	Cd ₁₀ (VO ₄) ₆ Cl ₂	Cd ₁₀ (CrO ₄) ₆ Cl ₂	Pb ₁₀ (PO ₄) ₆ Cl ₂	Pb ₁₀ (VO ₄) ₆ Cl ₂	Pb ₁₀ (CrO ₄) ₆ Cl ₂
Cd	1.0			2.2 (2.1)	4.2 (4.1)	4.1 (4.2)			
Cr	5.0		1.0 (1.8)			0.3 (0.05)			0.8 (0.2)
V	24.0	2.9 (3.3)			1.2 (0.4)			1.1 (0.6)	
Pb	5.0						3.0 (0.3)	3.8 (1.0)	3.2 (1.6)

[†]U.S.A. (EPA). Singapore (NEA). TCLP, toxicity characteristic leaching procedure.

Table III

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7