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## Nanolayered Tin Phosphate: A Remarkably Selective Cs Ion Sieve for Acidic Waste Solutions

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Here, we report a unique tin phosphate that is remarkably selective to  $^{137}\text{Cs}^+$  from extremely acidic solutions because of its special layered structure with an unusually large interlayer space. This acidic exchanger is superior to other existing materials in terms of its selectivity and capacity for  $^{137}\text{Cs}^+$  from acidic solutions.

to the current cesium exchangers specifically from such solutions.

Nuclear accidents at Three Mile Island, Chernobyl and Fukushima led to the release of hazardous radioactive species such as Cs, Sr, I etc. into the environment<sup>1-4</sup> but contamination by  $^{137}\text{Cs}$  occurred over a larger area of Fukushima because of its higher volatility than  $^{90}\text{Sr}$  at the time of accident and hence Cs was proposed to be extracted with acid from contaminated soils of Fukushima for remediation<sup>5</sup>. Reprocessing of spent nuclear fuel also generates extremely acidic solutions containing  $^{137}\text{Cs}^+$ . Selective  $\text{Cs}^+$  exchangers such as  $\gamma$ -Zr phosphate<sup>1</sup>, Na-phlogopite mica<sup>2</sup>, zeolites<sup>1,2</sup>, Na silicotitanate (Na-ST)<sup>6-8</sup>, gallium antimony sulfide<sup>9</sup>, manganese tin sulfide<sup>10</sup>, Na titanate<sup>11</sup>, and a vanadosilicate<sup>12</sup> have been developed for the separation of  $^{137}\text{Cs}$  from nuclear waste solutions. Na-CST is excellent for  $\text{Cs}^+$  uptake from defense wastes of very high pH and large Na concentration<sup>13</sup>. Vanadosilicate<sup>12</sup> and Na-CST<sup>13-15</sup> selectively remove  $\text{Cs}^+$  from slightly acidic wastes of pH 1 (0.1M HCl). However,  $\text{Cs}^+$  selective ion exchangers are still needed for extremely high acidic conditions (1 to 3 M HCl), encountered in reprocessed wastes from spent nuclear fuel<sup>16-18</sup> or acid extracts to remove radioactive  $^{137}\text{Cs}^+$  from contaminated soils at Fukushima<sup>5</sup>. Here, we report a nanolayered tin phosphate material which is superspecific for  $^{137}\text{Cs}^+$  from extremely acidic solutions and remarkably superior

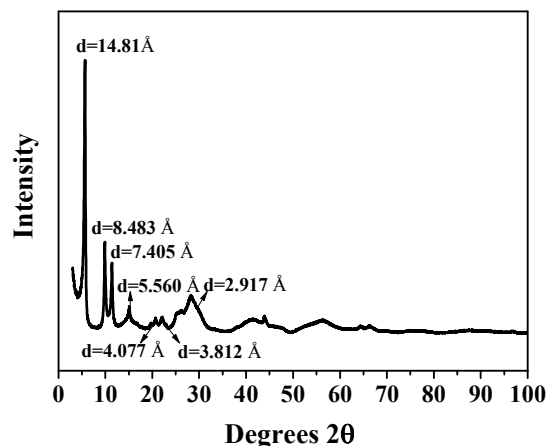


Figure 1 Synchrotron powder XRD pattern of the 15Å SnP-H<sup>+</sup> phase synthesized at pH=0.85 by conventional-hydrothermal process at 210°C/8 days.

We synthesized a nanolayered 15Å tin phosphate, SnP-H<sup>+</sup> phase as determined by powder X-ray diffraction (XRD) under microwave-hydrothermal (M-H)<sup>19</sup> conditions (Figure S1) as well as conventional-hydrothermal (C-H) conditions in a facile one-step process with earth abundant elements (Figure 1). The main peak of this tin phosphate is at about 15Å ± 0.5Å (Figure 1 and Figure S1) and therefore, it is referred to here as a 15Å SnP-H<sup>+</sup> phase. Synchrotron powder XRD showed only limited number of crystal planes in the pattern (Figure 1) and hence the exact crystal structure could not be determined but suggests a layered phase based on the reflections at 14.8Å (001) and 7.4Å (002). The 15Å SnP-H<sup>+</sup> phase is considered to be a nanolayered phase similar to SnP-NH<sub>4</sub> phase<sup>20</sup> or  $\gamma$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O( $\gamma$ -ZrP)<sup>21</sup> based on its swelling behavior with

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octadecylamine. The SnP-NH<sub>4</sub> phase has three layers of water molecules in the interlayers<sup>20</sup>. However,  $\gamma$ -ZrP has only two layers of water molecules<sup>21</sup> while the 15Å SnP-H<sup>+</sup> phase contained three layers of water molecules based on its analyzed chemical composition of 1Sn to 2P molar ratio and thermal gravimetric (TGA) analysis (Figure S2), which showed a 14.4% weight loss amounting to three layers of water molecules in this SnP-H<sup>+</sup> phase. Infrared (IR) spectroscopy (Figure S3) clearly showed a larger interlayer water band as indicated by the deformation vibration at 1633 cm<sup>-1</sup> for the 15Å SnP-H<sup>+</sup> phase compared to that at 1624 cm<sup>-1</sup> for the 7.6Å  $\alpha$ -Sn(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O ( $\alpha$ -SnP) phase with only one layer of water molecules in the interlayers confirming the presence of more interlayer water in the former.

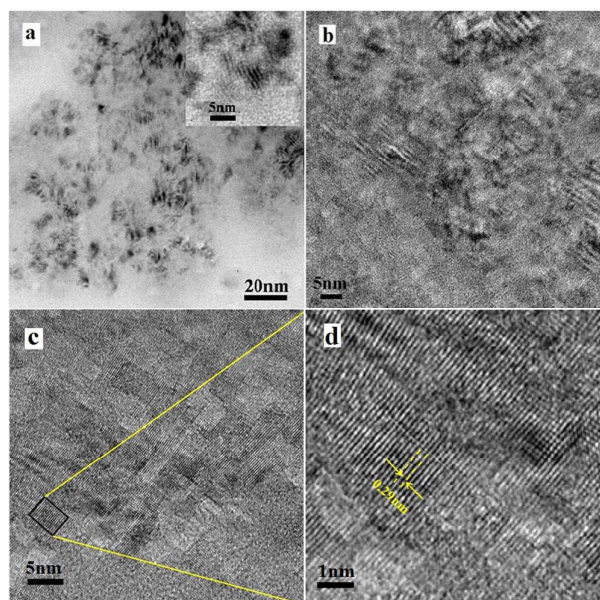


Figure 2. High-resolution transmission electron micrographs of the nanolayered 15Å-H<sup>+</sup> SnP phase: (a) layer structure of 15Å SnP-H<sup>+</sup> phase and inset is at higher magnification, which clearly shows layers of about 15Å or 1.5nm, (b) layer structure of 15Å SnP-H<sup>+</sup> phase at much higher magnification revealing layers and much smaller 0.29 nm crystal planes (c and d) of the 15Å SnP-H<sup>+</sup> phase. The 0.29 nm crystal planes are possibly the 5<sup>th</sup> order of the 1.5 nm or 15Å layers.

Further characterization by scanning electron microscopy revealed a highly agglomerated phase of nanoparticles as can be seen at higher magnification (Figure S4). Transmission electron microscopy confirmed nanoparticles with a plate-like morphology (Figure S5), which is a well-known morphology for layered materials<sup>22</sup>. High resolution transmission electron microscopy revealed the nanolayered nature of the 15Å SnP-H<sup>+</sup> phase at two different magnifications (Figure 2a and 2b). The inset in Figure 2a clearly shows the thickness of each layer to be about 15 Å confirming the XRD data presented in Figure 1 and Figure S1. A still higher magnification shows lattice fringes with a spacing of 0.29 nm or 2.9 Å (Figure 2c and 2d). This 0.29 nm d-spacing could also be seen in the XRD patterns (Figure 1 and Figure S1). The 0.29 nm d-spacing is apparently the 5<sup>th</sup> order of the 1.5nm or 15Å main peak. Based on the

characterization of the 15Å SnP-H<sup>+</sup> phase by TEM, Synchrotron and conventional XRD, TGA and IR techniques, we suggest a schematic of the probable crystal structure for this phase (Figure 3) based on the analogous crystal structure of  $\gamma$ -ZrP<sup>23, 24</sup>. This schematic polyhedral model<sup>23, 24</sup> (Figure 3) and the schematic ball and stick model<sup>21</sup> (Figure S6) are useful to understand the selective Cs<sup>+</sup> uptake mechanism by the 15Å SnP-H<sup>+</sup> phase (vide infra). Because this nanolayered 15Å SnP-H<sup>+</sup> phase could be synthesized under extremely low pH conditions (pH=0) (Table S1), we hypothesized that this material could be very stable and useful to remove Cs<sup>+</sup> from highly acidic waste solutions such as the reprocessed waste solutions from nuclear spent fuel<sup>16-18</sup> or acid extracts generated for removing radioactive <sup>137</sup>Cs<sup>+</sup> from contaminated soils at Fukushima<sup>5</sup>. Therefore, we proceeded to determine the Cs<sup>+</sup> selectivity of this nanolayered phase using very highly acidic solutions and compared it with several currently available acid stable exchange media.

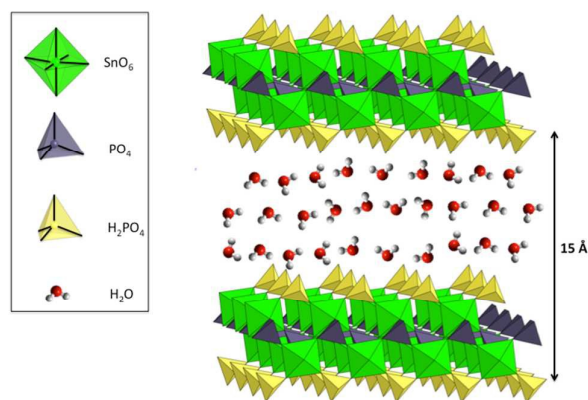
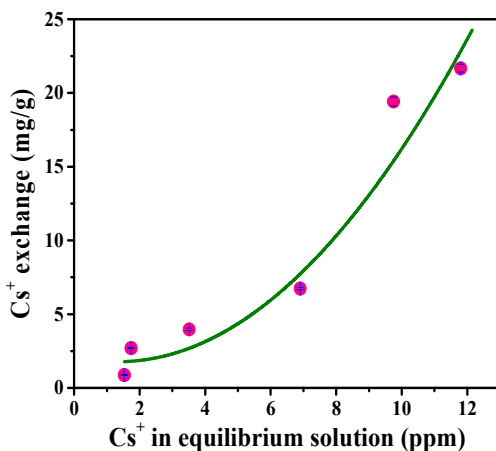


Figure 3. Schematic polyhedral crystal structure of the 15Å SnP-H<sup>+</sup> phase as a layered phase based on the analogous crystal structure of  $\gamma$ -ZrP, Zr(HPO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O<sup>23, 24</sup>.

All the Cs exchange studies were conducted using the SnP-H<sup>+</sup> material synthesized at pH=0 under M-H treatment at 195° C/2hrs. Experiments were conducted for H<sup>+</sup> ↔ Cs<sup>+</sup> exchange using different concentrations of Cs<sup>+</sup> from 1M HCl and an exchange isotherm was determined (Figure 4). Different CsCl solutions of 0.0125, 0.025, 0.05, 0.1, 0.15 and 0.2 mM in 1M HCl containing H<sup>+</sup>: Cs<sup>+</sup> milliequivalent ratios of 80000, 40000, 20000, 10000, 6667 and 5000, respectively were used for determining the isotherm (Figure 4). The isotherm suggests that Cs<sup>+</sup> was very selectively taken up from different solutions of Cs<sup>+</sup> even though the competing protons were several orders of magnitude higher than the Cs<sup>+</sup> ions. In addition, the isotherm is very steep suggesting that no saturation of the total capacity of the novel 15Å SnP-H<sup>+</sup> phase occurred unlike in the case of  $\gamma$ -ZrP reported by us earlier<sup>1</sup>. This result suggests that the new 15Å SnP-H<sup>+</sup> phase has a much higher capacity for further exchanging Cs<sup>+</sup>. A plot of the current Cs exchange data did not fit well with Langmuir adsorption isotherm as it showed a very poor correlation coefficient of 0.192 and hence a q-max could not be calculated. However, a maximum capacity of 160-200 mg/g was achieved on a similar material<sup>20</sup> by selective exchange from

synthetic groundwater. The observed very high selective uptake of  $\text{Cs}^+$  over  $\text{H}^+$  could be attributed to the special interlayer structure of the new phase with three layers of water molecules (Figure 3 and Figure S6). The higher interlayer space as a result of three layers of water molecules apparently facilitates easier dislodging of the larger hydrated protons of  $\sim 6.6\text{\AA}$  in diameter<sup>25</sup> and their easier diffusion out of the large interlayers by selective exchange of  $\text{Cs}^+$  on to the exchange sites forming inner sphere complexes<sup>2</sup> (Figure 3 and Figure S6).



**Figure 4.** Cesium exchange/uptake isotherm of the  $15\text{\AA}\text{SnP-H}^+$  phase using different  $\text{CsCl}$  solutions of 0.0125, 0.025, 0.05, 0.1, 0.15 and 0.2mM in 1M HCl.

After establishing above that the new phase is extremely selective for  $\text{Cs}^+$  from highly acidic solutions, we compared the uptake of cesium by the  $15\text{\AA}\text{SnP-H}^+$  phase with well-known cation exchangers such as Na-ST ( $\text{Na}_2\text{Ti}_2\text{SiO}_7 \cdot 2\text{H}_2\text{O}$ ),  $\alpha\text{-SnP}$ ,  $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  ( $\alpha\text{-ZrP}$ ) and  $\gamma\text{-ZrP}$ . The synthetic  $\text{Na}_2\text{Ti}_2\text{SiO}_7$  was procured from UOP Company [See Supplementary Information (SI)] while the  $\alpha\text{-SnP}$ ,  $\alpha\text{-ZrP}$  and  $\gamma\text{-ZrP}$  layered phases were synthesized by us as described in SI and all their powder XRD patterns matched with standard patterns. The  $\alpha\text{-SnP}$  exchanger was previously synthesized<sup>26, 27</sup> by refluxing amorphous tin phosphate gel with phosphoric acid but here we used a rapid microwave-hydrothermal method (See SI).  $\text{Cs}$  exchange capacity of  $\alpha\text{-SnP}$  was determined by titration with hydroxide but no selective exchange of  $\text{Cs}$  was carried out previously<sup>26</sup>. Comparative uptake of cesium by  $15\text{\AA}\text{SnP-H}^+$  phase with the above well-known cation exchangers was determined using 0.2 mM  $\text{CsCl}$  in 1M HCl solution. The  $\text{Cs}^+$  removal expressed as  $K_d$  by the various cation exchangers under strong acidic condition are shown in Figure 5 and Table S2. These results clearly show that the nanolayered  $15\text{\AA}\text{SnP-H}^+$  phase is the best among all 5 of the cation exchangers tested here for the removal of  $\text{Cs}^+$  from highly acidic 1M HCl solution. There was little or no uptake of  $\text{Cs}^+$  by all the previously developed layered acidic exchangers of  $\alpha\text{-SnP}$ ,  $\alpha\text{-ZrP}$  and  $\gamma\text{-ZrP}$  (Figure 5 and Table S2). The lack of selectivity for  $\text{Cs}^+$  by the layered phases of  $\alpha\text{-SnP}$ ,  $\alpha\text{-ZrP}$  and  $\gamma\text{-ZrP}$  could be explained by their narrower interlayer spaces compared to that of the  $\text{SnP-H}^+$  phase which has much larger interlayer space because of 3 layers of water molecules in the interlayers (Figure 3 and

Figure S6) as follows: Protons are surrounded by water molecules and these  $\text{H}_3\text{O}^+$  ions of larger hydrated diameter ( $\sim 6.6\text{\AA}$ )<sup>25</sup> do not diffuse out easily from the narrow interlayer spaces of  $\alpha\text{-SnP}$ ,  $\alpha\text{-ZrP}$  and  $\gamma\text{-ZrP}$  but can easily diffuse out from the larger interlayer space of  $15\text{\AA}\text{SnP-H}^+$  phase after exchange with  $\text{Cs}^+$  ions of lower hydrated diameter ( $\sim 4.4\text{\AA}$ )<sup>25</sup>. Hence little or no  $\text{Cs}^+$  uptake occurred in these well-known layered phases of  $\alpha\text{-SnP}$ ,  $\alpha\text{-ZrP}$  and  $\gamma\text{-ZrP}$  (Figure 5) because of their narrower interlayer space. However, the larger interlayer space of the  $\text{SnP-H}^+$  phase allows easier displacement of the larger  $\text{H}_3\text{O}^+$  ions by the  $\text{Cs}^+$  ions of a smaller hydrated diameter of  $\sim 4.4\text{\AA}$ <sup>25</sup>. In addition, the less hydrated  $\text{Cs}$  ions are preferred by the exchanger as they form inner sphere complexes<sup>2</sup> with the exchanger, i.e., the  $\text{Cs}$  ions come in close contact with the negative sites as these ions can easily shed their hydration shell<sup>2</sup>.  $\text{Cs}$  or any other ion selectivity is governed by the interplay among many different factors such as the steric, charge density, charge location etc. factors of the exchanger and hydrated size, charge, hydration energy etc., of the cations<sup>28</sup>. The larger interlayer space (steric factor) of the present  $\text{SnP-H}^+$  layered phase and lower hydration energy of the  $\text{Cs}$  ions seem to be the main factors for  $\text{Cs}^+$  ion selectivity over highly hydrated and larger  $\text{H}_3\text{O}^+$  ions. The  $\text{SnP-H}^+$  phase also showed better  $\text{Cs}$  selectivity than the  $\text{Na}_2\text{Ti}_2\text{SiO}_7$  phase (Figure 5). The selective  $\text{Cs}^+$  removal was found to have no correlation to the total cation exchange capacity (CEC) of the phases (Table S3) but it is related to the ease or difficulty of accessing the exchange sites either through the interlayers in the layered phases or through the pores in the three dimensional network structure of  $\text{Na}_2\text{Ti}_2\text{SiO}_7$ .

We further compared the selective  $\text{Cs}^+$  exchange by the  $15\text{\AA}\text{SnP-H}^+$  phase with  $\text{Na}_2\text{Ti}_2\text{SiO}_7$  phase using different HCl concentrations containing  $\text{Cs}^+$ . The  $15\text{\AA}\text{SnP-H}^+$  phase was found to be even much better for  $\text{Cs}^+$  removal from higher concentrations of 2M and 3M HCl than the  $\text{Na}_2\text{Ti}_2\text{SiO}_7$  phase (Figure 6). The larger  $\text{Cs}$  uptake in the presence of higher concentration of acid suggests that this anomalous behavior may be related to the increasing stability of  $15\text{\AA}\text{SnP-H}^+$  phase with increasing acidity (Table S1). However, further detailed studies are needed to confirm this hypothesis. Retention of  $\text{Cs}^+$  taken up was also determined by leaching these two phases with 1M HCl for 24 hours. The  $\text{Na}_2\text{Ti}_2\text{SiO}_7$  phase released  $11 \pm 0.5\%$  of its  $\text{Cs}^+$  while the  $15\text{\AA}\text{SnP-H}^+$  phase released only  $6.6 \pm 0.1\%$  of its  $\text{Cs}^+$  i.e., better retention of  $\text{Cs}^+$  by the  $15\text{\AA}\text{SnP-H}^+$  phase. After  $\text{Cs}^+$  is selectively separated from acidic solutions, it can be immobilized in the interlayers of the  $\text{SnP}$  phase by heating before final disposal in an analogous manner to other layered phases<sup>1,2,29</sup>.

Our results clearly show that the nanolayered  $\text{SnP-H}^+$  material designed and synthesized here is eminently suited for the superselective removal of radioactive  $^{137}\text{Cs}^+$  ions from highly acidic solutions which are encountered by reprocessing of spent nuclear fuel<sup>16-18</sup> or by acid extraction of contaminated



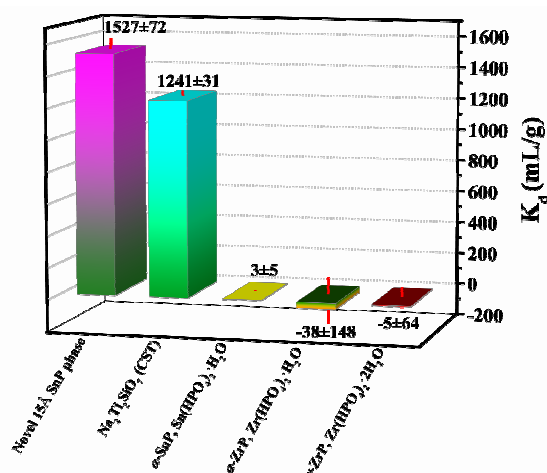


Figure 5. Comparative uptake of cesium by 15Å SnP-H<sup>+</sup> phase with well-known cation exchangers from 1M HCl (initially 0.2 mM Cs in 25 mL of 1 M HCl, using 0.025 g sample).  $K_d$  is defined as the ratio of the amount of Cs<sup>+</sup> exchanged per g of exchanger to the amount of remaining (unexchanged) Cs<sup>+</sup> per milliliter of solution.<sup>1,2</sup>

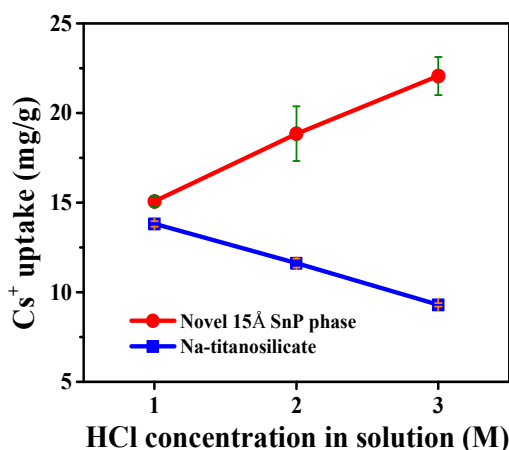


Figure 6. Comparative uptake of cesium by 15Å SnP-H<sup>+</sup> phase with Na<sub>2</sub>Ti<sub>2</sub>SiO<sub>7</sub> cation exchanger from 1M, 2M or 3M HCl (initially 0.2mM Cs in 25 mL of 1 M, 2M or 3M HCl, 0.025 g sample).

soils at Fukushima<sup>5</sup> and is remarkably superior to the existing cation exchangers for these acidic solutions. However, if contaminated soils were to be completely digested to extract Cs, acidic solutions with many other ions would result and selective Cs uptake from such solutions would have to be a future study. The key to the unparalleled performance of this new phase is in the design and synthesis of the SnP-H<sup>+</sup> layered phase with larger interlayer space, which facilitates better diffusion of large hydrated protons out of the interlayers after exchanging with Cs ions unlike all the existing layered phases as they have smaller interlayer space.

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