Treatment of metal chloride wastes from spent fuel treatment

Part II: Synthesis of apatite with Ca(OH)₂ and H₃PO₄

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Abstract

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) was synthesized by the precipitation reaction with Ca(OH)₂ and H₃PO₄ in order to compare the structural changes and thermal treatment conditions of precipitates after the precipitation reaction with or without metal chlorides. The product of the precipitation reaction without metal chloride was monetite(CaHPO₄) and brushite(CaHPO₄·2H₂O) and developed into apatite structure by the thermal treatment, via C4, C3, C2 and amorphous apatite. As the Ca/P molar ratio of input materials was increased, the crystal phase after thermal treatment at 900°C for 10hr was changed from Ca₂P₂O₇ and Ca₅(PO₄)₂ to Ca₁₀(PO₄)₆(OH)₂. Hydroxyapatite was obtained at Ca(OH)₂/H₃PO₄=2.32 molar ratio of input materials.

1. Introduction

Apatites form a large family of compounds with the general chemical formula M(I)M(II)₁₀(YO₄)₆X₂, where M= monovalent, divalent or trivalent metal, Y=P, Si, V or Os and X=F, Cl, I, OH, or O. A well-known representative member of apatitic family is calcium phosphate fluoroapatite Ca₁₀(PO₄)₆F₂. Calcium phosphates have many potential application as biomaterials, catalytic materials, fluorescent lamp phosphor, etc [1-2]. Also, apatite-type rare earth metal silicate can exhibit quite high oxide-ion conductivity and good characteristics on laser host [3]. In the environmental aspects, apatite as inorganic sorbents has a role in wastewater treatment process [4]. Apatite or britholite is a prospective waste form in the immobilization of radioactive element, which, however, have not been extensively studied on the application to waste form [5].

Single phase ceramic waste forms, except NZP(sodium zirconium phosphate), could be very useful on the application to the specific waste nature due to the unique crystal lattice structure. In the previous study we noted that the precursor of apatite can take a constant content of Cs, though in the existence of relatively high content of LiCl [6]. However, it was not revealed the formulations of starting materials into the final structure, apatite. In this study, it was investigated on Ca/P molar ratio and thermal condition to form the apatite structure without metal chlorides wastes. It is very meaningful to compare the experiments without or with metal chlorides wastes in order to look for the proper formulations of starting materials, to determine on whether the major phase of waste form is a hydroxy-apatite, britholite or chloroapatite, which are related with waste loading and volume reduction.

2. Experimental

The starting materials selected for the preparation of the apatite ceramic were Ca(OH)₂
and H₃PO₄ with reagent grade. The reaction was performed by mixing two solutions. A solution contains Ca(OH)₂ in 50ml H₂O and B solution contains H₃PO₄ in 50ml H₂O. B solution was added into A solution with vigorous stirring for 1hr at the atmospheric condition. With constant H₃PO₄ mole, 0.1mole, the mole of Ca(OH)₂ was varied from 0.1 to 0.232mole with the step change of 0.032~0.035. The final pH was checked and the precipitates was filtered, dried at 105°C in an electric oven for 24hr and was weighed. Each dried sample was identified by X-ray diffraction (Rigaku, monochrometer, CuKα) before and after thermal treatment at 300, 500, 900°C for 10hr. Also, the TG/DTA analysis was performed in an air atmosphere at a heating rate of 10°C/min.

3. Result and Discussion

Known compounds in the CaO–P₂O₅–H₂O system include Ca(H₂PO₄) · xH₂O, CaHPO₄ · yH₂O, Ca₃(PO₄)₂, Ca₁₀(PO₄)₆(OH)₂, Ca₂PO₄(OH) · 2H₂O, Ca₃H₂(PO₄)₆ · 5H₂O and Ca₄P₂O₇. A large excess of water ultimately results in the formation of stable hydroxyapatite. In aqueous solution, the general reaction route to hydroxyapatite is as follows[7]

\[
Ca(H₂PO₄)₂ + nH₂O → CaHPO₄ + H₃PO₄ + nH₂O
\]

\[
10CaHPO₄ + mH₂O → Ca₁₀(PO₄)₆(OH)₂ + 4H₃PO₄ + (m - 2)H₂O
\]

All the calcium orthophosphates described above can be also changed to the crystal of one kind from those of another. However, all these compound are all insoluble in water and the reaction may take considerable time to go completion. Hydroxyapatites reported to have non-stoichiometric compositions include Ca-deficient varieties, tricalcium phosphate hydrate and various precipitated products with Ca/P ratios between about 1.3 and 2.0. The table 1 shows the batch composition and the identified crystal phases of thermally treated precipitates with respect to Ca/P ratio of input materials.

The major phases of precipitates dried at 105°C were monetite (CaHPO₄) and brushite (CaHPO₄ · 2H₂O). The peak intensity of monetite was decreased with the increase of Ca/P molar ratio and the peak of the unreacted portlandite begin to appear for Ca/P ratio of 1.67. However, amorphous apatite was detected over Ca/P ratio of input materials, 1.32. As the Ca/P was increased, the precipitates contain more amorphous apatite. This trend was similar to the effect of the concentration of metal chloride in previous study. Figure 1 shows TG curves which have three distinct step, 160~200, 360~490, and 570~895°C. The water evolving during thermal treatment is of three different origin: adsorbed water, structurally incorporated water and water evolving as a result of interaction of the calcium phosphates compounds.

The adsorbed water is desorbed at 100~160°C for all samples. The weight loss at 160~200°C may be caused by the evolution of lattice water. The weight loss at 200~600°C is occured by the following reaction.

\[
2HPO₄²⁻ → P₂O₇⁴⁻ + H₂O↑
\]

In case of Ca/P>1.67, the unreacted portlandite also is decomposed into CaO and H₂O. When the Ca/P was higher than 1.67, weight loss was appeared at 600~900°C. This could be caused by the phase transition from calcium oxide phosphate and amorphous apatite to crystalline apatite. As seen from XRD pattern in figure 2, the phase was changed from monetite or brushite to calcium oxide phosphate at the thermal treatment temperature, below.
600°C. It must be noted that the DTA curves over 600°C was altered from exothermic heat to endothermic heat as the Ca/P molar ratio is increased. When the polyphase containing C4, C3, C2 and amorphous apatite change to C2 or C3, exothermic phase transition was occurred. When the polyphase was altered to apatite structure, heat was required. All the thermally treated compound, except Ca/P=1, contain C4, C3, C2 and amorphous apatite. Depending on Ca content, the phases were formed as Ca$_2$P$_2$O$_7$, Ca$_3$(PO$_4$)$_2$ and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ after the thermal treatment at 900°C for 10hr. When the Ca/P ratio of starting materials was increased, the major phases are changed from Ca$_2$P$_2$O$_7$ and Ca$_3$(PO$_4$)$_2$, to Ca$_{10}$(PO$_4$)$_6$(OH)$_2$. From the DTA curves, it could be concluded that the polyphase is not favorable in developing apatite structure because more heat is required to obtain apatite structure. However, the peak indicated in figure 4(d) was very sharp, which means the increase of crystallinity. When Ca/P ratio of input materials was 2.32, the only apatite structure was detected after thermal treatment at 900°C for 10 hours.

4. Conclusion

In the precipitation reaction with Ca(OH)$_2$ and H$_3$PO$_4$, hydroxyapatite was obtained at Ca/P=2.32 of input materials after thermal treatment at 900°C. All the precipitates contain monetite(CaHPO$_4$) and brushite(CaHPO$_4$·2H$_2$O) regardless of initial Ca/P molar ratio and Ca$_2$P$_2$O$_7$, Ca$_3$(PO$_4$)$_2$, and apatite, via C4, C3, C2 and amorphous apatite as intermediate form, were obtained at the thermal treatment temperature of 900°C, depending on the Ca/P ratio.

Table 1. Batch composition, phase formed after thermal treatment and pH in residual solution.

<table>
<thead>
<tr>
<th>Starting materials(mol)</th>
<th>Phase after thermal treatment for 10hr</th>
<th>Residual solution</th>
</tr>
</thead>
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<tr>
<td>Ca(OH)$_2$: H$_3$PO$_4$: Ca/P</td>
<td>105°C(24hr) 300°C 500°C 900°C</td>
<td>pH</td>
</tr>
<tr>
<td>0.098 0.101 0.98</td>
<td>M, B C2, B, O C2, B C2</td>
<td>2.52</td>
</tr>
<tr>
<td>0.132 0.101 1.31</td>
<td>M, B, A, C4, C3, C2, A C4, C2, O, A C3</td>
<td>7.35</td>
</tr>
<tr>
<td>0.168 0.100 1.68</td>
<td>M, B, A, P C4, C2, A C4, C2, C3, A C3, A</td>
<td>13.54</td>
</tr>
<tr>
<td>0.201 0.101 2.00</td>
<td>M, P, B, A C4, A, P C4, A, P A, C3</td>
<td>13.67</td>
</tr>
<tr>
<td>0.232 0.100 2.32</td>
<td>C4, P, M, B C4, C3, C2, P A, C4, P A</td>
<td>13.76</td>
</tr>
</tbody>
</table>

Symbol: M=CaHPO$_4$, B=CaHPO$_4$·2H$_2$O, O=Ca(OH)(PO$_4$)$_2$, C2=Ca$_2$P$_2$O$_7$, C3=Ca$_3$(PO$_4$)$_2$, C4=Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, A=Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, P=Ca(OH)$_2$.  

Figure 1. TG/ DTA curves with respect with Ca/P molar ratios
Figure 2. XRD pattern of the precipitates with various input Ca/P and thermal treatment temperature.

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Reference