Enhanced Cesium Removal through Heterogeneous Chemical Precipitation on Modified Magnesium Silicate Mineral

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Abstract

Serious concern over the environmental threat remains with the medium-life fission products such as $^{90}\text{Sr}$ and $^{137}\text{Cs}$, the main heat sources of radioactive waste during long-term storage. It is more difficult to remove Cs(I) ions than Sr(II) ions from radioactive wastewater for its higher physicochemical mobility. We proposed a new approach to precipitate Cs ions as MgCsPO$_4$·6H$_2$O (struvite group) by using the mecha-chemically modified serpentine (Mg silicate) as Mg source after comparing different Mg compounds. It was found that at room temperature and low Cs concentration, no obvious struvite precipitation happened with a homogeneous phase when soluble Mg salts of nitrate, chloride etc. were used with Cs$^+$ and PO$_4^{3-}$ ions in a pure solution. It was interesting to note that the modified insoluble serpentine simply precipitated Cs$^+$ up to 90 % at the same conditions, with capacity as high as 173 mg/g, the best reported data. Compared with the mineral itself, the easier dissolution of Mg ions from the modified serpentine, not as high as the soluble Mg salts, facilitated Cs$^+$ precipitation reaction on the solid surface as heterogeneous phase and the remaining solid silicate part inside would work as supporting matrix for easier growth of struvite crystals.

Keywords: Cesium Removal; Heterogeneous Chemical Precipitation; Struvite; Serpentine; Ball-milling.

1. Introduction

Much attention had been paid to disposal medium-life fission products from the serious concern over the environmental threat, such as soluble $^{137}\text{Cs}$ (cesium) and $^{90}\text{Sr}$ (strontium), which are the main heat sources of radioactive waste during long-term storage. Especially, $^{137}\text{Cs}$ is chemically similar to potassium, and it can quickly spread to the surrounding environment and remains for hundreds of years, meanwhile emitting high-energy $\gamma$-rays.$^{1,3}$ It is more difficult to remove Cs(I) ions than Sr(II) ions from radioactive wastewater for its higher physicochemical mobility. $^{137}\text{Cs}$ can be removed from wastewater by chemical precipitation, adsorption, ion exchange, evaporation, extraction, biological methods, membrane separation, electrodialysis, etc.$^{4,13}$ To chemical precipitation, few choices were available due to the high solubility of almost all the cesium compounds, except for cesium-tributyl phosphate, (Ksp=1.1*10$^{-10}$, easily decomposed by irradiation and difficult to be disposed), Cs$_2$[Co(NO$_3$)$_6$] (Ksp=5.7*10$^{-16}$, very expensive), Cs$_2$[Fe(CN)$_6$] (Ksp=1.3*10$^{-16}$, no industrial production of many original materials except Fe$_2$[Fe(CN)$_6$], which are still difficult to be applied in engineering practice for large amounts of wastewater treatment.

Cs and Ta (thallium) can replace the ions on Fe$_2$[Fe(CN)$_6$], (Prussian blue, a mass-produced dye) to form insoluble substances, so that it can be excreted with feces, which has a certain effect on the emergency treatment of poisoning. As a remover of Cs, Prussian blue had been used in Goiania's smashing damage, Chernobyl nuclear accident and emergency medical care for the best performance and non-toxicity. Various ferrous cyanides were successfully synthesized by co-precipitation method in laboratory for ion-exchange of Cs-containing radioactive wastewater including K$_2$NiFe(CN)$_6$, Ni$_2$Fe(CN)$_6$, Zn$_2$Fe(CN)$_6$, K$_2$ZnFe(CN)$_6$, et c., and their composite adsorbents based on non-woven fabrics, sodium alginate, magnetic hydrogel bead, chitosan, resin, et c.$^{17,19}$ In practical application of these compounds, there exist a lot of problems including difficult solid
liquid separation of fine muddy sediment, high cost and complex processes of further treatment for secondary pollutants containing potential toxic metals.

Cs(AlSi₂O₆)·H₂O (pollucite) is a subspecies mineral of the zeolite group, which is currently known as the richest Cs-containing mineral. Many researchers had used natural zeolite and artificially synthesized zeolite²⁰⁻²¹ to remove Cs, F and other pollutants from aqueous solutions including drinking water, radioactive wastewater, mine wastewater, pharmaceutical wastewater. Zeolite is the preferred adsorption material for Cs removal in the Fukushima nuclear accident for good adsorption and ion exchange performance. In previous publications, chabazite had a stronger adsorption capacity and partition coefficient (Kd) than natural clinoptilolite, natural mordenite and synthetic mordenite²². Adsorption of Cs on the synthesized zeolite A was a spontaneously endothermic process and the removal effect was affected by the water flow, the height of adsorption column layer and the initial concentration, and the adsorption rate constant (Ksp) increased with the raised flow²³. Zeolite is suitable in general for the treatment of high concentration Cs-containing wastewater.

It is necessary to find a better way to achieve the stabilization of low concentration Cs in wastewater for economic and technical feasibility. Struvite (Mg(NH₄)PO₄·6H₂O) crystallization technology is usually used for recovery of NH₄⁺ and phosphorus from sludge liquor. There exists the possibility of Cs⁺ to replace NH₄⁺ in the structure of struvite so that MgCsPO₄·6H₂O could be formed in theoretical mole ratio in chemical precipitation reaction as shown in Eqs. 1, 2 below.

\[
\begin{align*}
\text{Mg}^{2+} + \text{Cs}^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} & \rightarrow \text{MgCsPO}_4 \cdot 6\text{H}_2\text{O} (\text{S}) \\
K_{sp} &= [\text{Mg}^{2+}][\text{Cs}^+][\text{PO}_4^{3-}] = 2.5 \times 10^{-11}
\end{align*}
\]

In this paper, the treatment effect of Cs⁺ and reaction mechanism were analyzed firstly by comparative study of activating magnesium silicate mineral and carbonate minerals modified with the coexistence of phosphoric acid. Then soluble magnesium salts and other insoluble magnesium were widely considered as Mg sources. We noticed that activating magnesium silicate mineral by means of ball-milling had the potential capacity to be applied to remove Cs from radioactive wastewater.

2. Materials and Methods

2.1 Materials

MgSO₄, MgCl₂, Mg(NO₃)₂·6H₂O, CsNO₃ and H₂PO₄ from Aladdin Industrial Corporation, Sinopharm Chemical Reagent Co., Ltd. in analytical grade were used as purchased without further purification. Minerals of magnesite (MgCO₃) from Haicheng, Liaoning province and serpentine (Mg₆Si₅O₁₆(OH)₈) from Jinchuan Mines, Gansu province, China were obtained. The chemical compositions of mineral magnesite and serpentine are shown in Table 1.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>MgO</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>SO₃</th>
<th>CaO</th>
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</thead>
<tbody>
<tr>
<td>magnesite</td>
<td>47.01</td>
<td>0.73</td>
<td>0.22</td>
<td>0.27</td>
<td>0.01</td>
<td>0.50</td>
</tr>
<tr>
<td>serpentine</td>
<td>39.77</td>
<td>46.23</td>
<td>1.03</td>
<td>0.10</td>
<td>0.01</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 1. Main Chemical Compositions of magnesium minerals (Wt %)

2.2. Methods

Surface modification of magnesium samples: the experiments were carried out under air condition in a planetary ball mill (Fritsch, Pulversitset-7, Germany), equipped with two stainless-steel pots (45 cm³ inner volume). Firstly, two grams of the sample or mixture with SiO₂ were added into the milling pot with 7 stainless-steel balls (15 mm in diameter, 14 g). The mass ratio of ball to the sample or mixture was 49:1. Rotational speed of the mill was changed from 0 to 600 rpm with grinding time changed up to 180 min.

Solution chemical properties of the modified magnesium samples and Cs removal test: 0.1 g of the milled samples was agitated in 100 mL ultra-pure water to prepare samples for the measurement of pH value. Different masses of the milled samples and H₃PO₄ solution (pH=3) to prepare samples for the dissolved concentrations of Mg²⁺ in acid solution. Different masses of the milled samples and H₃PO₄ were added to 100 ml of 1 mmol/L CsNO₃ solution (equivalent to 133 mg/L) to conduct experiment of Cs precipitation. The mixed solutions were vigorously shaken at a frequency of 250 rpm at room temperature (25 ± 2 °C) with a fixed shaking time of 180 min. The suspensions were filtered and the solid residues were dried in 105 °C for more than 300 min.

2.3. Characterization

The pH values of all solutions were measured by a pH meter (METTLER TOLEDO FE 210 – Five Easy...
TM, Switzerland) at room temperature (25 ± 2 °C), according to《Water Quality-Determination of pH Value-Glass Electrode Method》(GB/T 6920-86). In accordance with 《Water Quality-Determination of Calcium and magnesium-Atomic absorption spectrophotometric method》(DZT 0064.36-1993), the concentrations of Cs and Mg ions in supernatants were measured with atomic adsorption spectroscopy (Shimadzu AA-6880, Kyoto, Japan). X-ray diffraction analysis (XRD: RU-200 B/D/ MAX-RB, Tokyo, Japan) was performed to identify the crystalline phases of minerals. The scanning electron microscopic analysis (SEM, HITACHI-SU 8010 with EDS accessory, COXEM, EM-30 AX PLUS) was conducted to observe the surface morphology of the samples.

The removal efficiency of Cs (I) was calculated by the following equation:
\[ \eta = \frac{(C_0 - C_e)}{C_0} \times 100\% \] (3)

Where, \( C_0 \) represents the initial concentration and \( C_e \) the concentration after treatment. The unit of \( C_0 \) and \( C_e \) is mg/L.

3. Results and Discussion

3.1. Mechano-chemical changes of magnesium minerals after modification

Preliminary experiments were conducted to activate magnesium minerals by ball-milling with different milling speed (0-600 rpm) for 60 min. Crystal structures of magnesite and serpentine and the modified samples after milling at 600 rpm for 60 min were analyzed by XRD, and results are shown in Figure 1.

As shown in Figure 1, the peaks of the original serpentine fit well with the data of PDF 07-0417 (antigorite--\( \text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8 \), a type of serpentine). After modification, the characteristic peaks disappeared, indicating that the crystal structure of \( \text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8 \) had been destroyed completely into an amorphous state. Similar change was observed with the patterns of modified magnesite, of which significant decrease in peak intensity was obtained after modification, while the peaks of the original sample fit well with the data of PDF 08-0479 (magnesite). Several characteristic peaks (104), (113) and (116) remained observable after ball-milling, suggesting that magnesite was relatively more stable than serpentine against the mechanical action of knock, shear and impact from ball moving. Difference in Mohs’ scale of hardness: 4.0~4.5 for magnesite and 3.0~3.5 for serpentine, respectively may be one reason for such difference in structure destruction resulting from the modification.

To understand the reason for what had changed with the modified magnesium mineral samples after the milling operation, changes in pH with different milling speed from the dispersion of modified magnesium minerals in ultra-pure water were monitored. The effect of milling speed was first examined with milling time fixed at 60 min and the results are shown in Figure 2.
With an increase in milling speed, similar changes were observed with two magnesium minerals. Increase in pH was obtained at the beginning of milling operation up to 200 rpm and levelled off without large change with milling speed up to 600 rpm. 500 rpm of milling speed was used for next experiments to examine other parameters. With the original sample without milling operation, the pH of magnesite in water was higher than that of serpentine. The modified serpentine sample gave higher pH in water than the milled magnesite, indicating that much stronger change occurred in the structure of serpentine by milling operation than that of magnesite, resulting in easier dissolution of the modified serpentine. The milled sample containing Mg hydroxide gave higher pH than Mg carbonate, which may be related with their different hydrolysis mechanism (as shown in Eqs. 4-8 below).

$$Mg_6Si_4O_{10}(OH)_8 = O-Si-Mg-OH$$ (4)

$$Mg(OH)_2 = Mg(OH)^+ + OH^-$$ (5)

$$Mg(OH) = Mg^2 + CO_3^2^-$$ (6)

$$MgCO_3 \rightleftharpoons Mg^{2+} + CO_3^{2-}$$ (7)

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$ (8)

During the mechano-chemical modification, mechanical force would rupture the Mg-O octahedrons in serpentine and magnesite. OH around Mg tended to dissolve into water to give increase in solution pH value. In case of magnesite, dissolution of MgCO_3 and further hydrolysis of CO_3^{2-} were to be understood the main reason for the increase in pH value. The pH changes implied different dissolution properties of the modified magnesium minerals.

As confirmation of the Mg dissolution from the equation 4-8, the dissolved Mg ions concentrations from the sample at the optimal parameters (500 rpm, 60 min) in phosphoric acid solution (pH=3.0, mole ratio of Mg/H_3PO_4 fixed at 5:1.2) were measured and the results are shown in Figure 3.

Mg ions concentrations in the phosphoric acid solution were different among the modified magnesium minerals in fixed mole ratio of Mg/H_3PO_4 (5/1.2). In case of the modified magnesite, the dissolved Mg ions concentration achieved at 95.7 mg/L (4 mmol/L), while the modified serpentine dissolved 23.55 mg/L (nearly 1 mmol/L). They could provide more than 10 times of Mg ions for 0.1mmol/L Cs ions to form struvite in phosphoric acid solution (Eqs. 1). Mg ions concentrations was not the restrictive impact factor for precipitation of Cs ions. It was interesting to notice that the modified magnesite dissolved more Mg ions than the modified serpentine in phosphoric acid solution, which implied that there will obtain different Cs removal efficiency by two modified samples.
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Figure 3. The dissolved Mg ion concentrations of modified samples in phosphoric acid solution.

3.2. Enhanced Cs(I) removal by the modified serpentine

The removal capacity of Cs(I) by the modified magnesium minerals were evaluated through the decrease in Cs ions of its phosphoric acid solution with the addition of the magnesium minerals. The changes in Cs removal efficiency of two modified samples with different milling speed are shown in Figure 4 with a fixed mole ratio of Mg/Cs/H₃PO₄ (5/1/1.2) and milling time of 60 min.

Figure 4. Changes in Cs removal efficiency of two modified samples with different milling speed

Different performances for Cs removal between two modified minerals were observed. Removal efficiency by using the modified magnesite was within 9%, a very slow increase in the speed range from 0 to 600 rpm. However, very large increase in Cs removal efficiency was obtained by using serpentine, giving a much higher value of 74.60% at 400 rpm from 7.56% at 200 rpm. Further increase in milling speed up to 500 and 600 rpm gave Cs removal efficiency at 88.78% and 93.52%, respectively. Modified serpentine demonstrated much better performance than magnesite, although Mg dissolution from magnesite was much higher than that of from serpentine shown in Figure 3.

The amounts of the magnesium minerals required for the efficient Cs removal were examined, and Figure 5 shows the changes in Cs removal efficiency of the modified samples with different dosage, when the mole ratio of H₃PO₄/Cs was fixed at 1.2, and milling condition was set at 500 rpm, 60 min.
Different patterns for Cs removal efficiency of the modified samples were obviously obtained. In case of the modified magnesite, the removal efficiency of Cs ions remained at low value less than 10 % with increased dosage up to 0.85 g/L. And the calculated adsorption capacity was in a low value around 17 mg/g. In case of the modified serpentine, the removal efficiency of Cs ion was gradually increased from 73.16 % to 88.78 % with the used dosage of 0.36 g/L to 0.55 g/L. Although adsorption capacity showed gradual decrease with the increase in dosage, the data around 173 mg/g of the adsorption capacity was still the highest when compared with other adsorbents, as summarized in Table 2.

Table 2. Cs adsorption performances of as-reported adsorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption rate (min)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium iron (III) hexacyanoferrate (II)</td>
<td>1440</td>
<td>17.30</td>
<td>24</td>
</tr>
<tr>
<td>KTiFC-TiO₂-SiO₂-Ca-Alg</td>
<td>1440</td>
<td>23.55</td>
<td>25</td>
</tr>
<tr>
<td>Ion-imprinted polymer</td>
<td>120</td>
<td>32.90</td>
<td>26</td>
</tr>
<tr>
<td>SiO₂-AMP-Ca-Alg</td>
<td>30</td>
<td>37.57</td>
<td>27</td>
</tr>
<tr>
<td>Montmorillonite-iron oxide composite (MIOC)</td>
<td>60</td>
<td>52.60</td>
<td>28</td>
</tr>
<tr>
<td>Ammonium molybodophosphate-calcium alginate composite</td>
<td>300</td>
<td>58.97</td>
<td>29</td>
</tr>
<tr>
<td>Ammonium Molybodophosphate/Al-MCM-41 Composite</td>
<td>480</td>
<td>73.90</td>
<td>30</td>
</tr>
<tr>
<td>Ammonium molybodophosphate</td>
<td>120</td>
<td>75.15</td>
<td>31</td>
</tr>
<tr>
<td>Ammonium molybodophosphate-polyacrylonitrile</td>
<td>1440</td>
<td>81.30</td>
<td>32</td>
</tr>
<tr>
<td>Dibenzo-30-crown-10-ether (DB30C10) immobilized</td>
<td>30</td>
<td>107.16</td>
<td>33</td>
</tr>
<tr>
<td>Mesoporous adsorbent</td>
<td>180</td>
<td>173</td>
<td>Thi</td>
</tr>
<tr>
<td>The modified serpentine</td>
<td>180</td>
<td>173</td>
<td>7</td>
</tr>
</tbody>
</table>

3.3. Mechanism discussion

Phase composition of the solid sediment from the precipitation reaction with Cs nitrate by using modified serpentine at 500 rpm, 60 min were analyzed by XRD and the result is shown in Figure 6. The pattern matched well with the standard card PDF 25-0650 (Magnesium Cesium Phosphate Hydrate, CsMgPO₄·6H₂O), where the main characteristic peaks could be attributed to it: including lattice plane (110), (200), (211), (004), (220), (400), (320), (330), (511) et c. No information of serpentine was observable due to the amorphous state by modification. Not shown here, the serpentine mineral without modification demonstrated little reaction with Cs⁺ and PO₄³⁻ compositions, as shown in Figure 4, and remained as the main phase after the agitation in the solution. The formation of MgCsPO₄·6H₂O after the reaction among the modified Mg₆Si₄O₁₀(OH)₈ with Cs⁺ and PO₄³⁻ in solution indicated that a precipitation reaction occurred, rather than a general adsorption of Cs on the serpentine surface. The modified serpentine in this research was different from other adsorbents. In case of magnesite, no enough amount of sediment was recovered for XRD analysis.
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Figure 6. XRD patterns of the solid residues after water bath oscillating.

In order to observe the microstructure with the existence and distribution of Cs in the sediment after the reaction of the modified serpentine with Cs nitrate and phosphoric acid, SEM-EDS analyses and the elemental mappings of Cs, Mg, Si, P and O of the sediment sample were carried out and the results are shown in Figure 7.

Figure 7. SEM image (a) of the modified serpentine; SEM image (b), EDS analysis (c) and elemental mapping of the solid residues.

Original serpentine has a regular platy structure and it changed into aggregated particles after ball-milling.
It is well known that agglomeration phenomenon occurs easily with the intense milling operation. The morphology of the modified serpentine had changed largely with many nanoparticles deposited on the surface (Figure 7-b), when dispersed in the solution for Cs removal, suggesting that the compositions in the sediment were different from the starting sample, supporting the result from XRD analysis. EDS analysis (Figure 7-c) and elemental mappings clearly showed that the Cs, Mg, P and O elements were evenly distributed on the surface of the sediment, proving the uniform dispersion of MgCsPO$_4$·6H$_2$O on the modified serpentines nanoparticles. Almost the same mapping patterns of the four elements indicated their existences in the same compound. The chemical composition with mole ratio of Mg/Cs/P was 2.24/1/1.67 in the composites, near to that of struvite product by XRD (Figure 6). It is interesting to note that element Si only gave a different mapping pattern from other four elements because Si did not take part in the precipitation reaction of struvite and was left as silica composition with Mg dissolution out to form the product.

![Figure 8](image_url)

**Figure 8.** Cs removal efficiency with various magnesium compounds.

To understand the reason for the excellent performance of the modified serpentine, various magnesium soluble salts and minerals were compared for Cs removal with a fixed mole ratio of Mg/Cs/P (5/1/1.2). As shown in Figure 8, three kinds of soluble Mg salts and two modified Mg carbonates gave values less than 10%, much lower than that of the modified serpentine. Although three soluble compositions of Mg, Cs and P together have the tendency to form insoluble Mg and Cs phosphate, conditions as low concentrations around 100 ppm and room temperature would not enable the formation of solid phosphate particles stable enough to prevent Cs dissolution at a satisfactorily low level. The easy Mg dissolution of the modified magnesite shown in Figure 3 gave a similar behavior to soluble chloride, nitrate and sulfate, indicating that soluble Mg source was not favorable for Cs precipitation. Existing state of Mg inside the modified serpentine was different from both soluble Mg salt and the original serpentine, not so soluble as the chloride, nitrate or sulfate and not so stable as the raw mineral. This kind of metastable state of Mg in serpentine after ball-milling was understood as the key factor for the effective incorporation of Cs into the phosphate. When Mg was too active as the case of modified magnesite, it tended to dissolve into solution to lose the power to stabilize Cs from the solution.

Such understanding was summarized in Figure 9 with two possible reaction pathways corresponding to both soluble Mg source and metastable Mg source of the modified serpentine. In case of homogeneous phase with soluble Mg source, tiny struvite sols might be formed when the compositions were agitated together. On the other hand, such tiny sols might dissolve to give the compositions free as ions into solution, finally to give a very low Cs removal efficiency. In case of the modified serpentine, Mg inside the structure of serpentine became active to show tendency to dissolve into solution. However, it was still bound with silica part inside the solid particles, different from the soluble Mg salts easily dissolved in the solution. When the solid particles were agitated in the solution, Mg would move gradually to particle surface to contact with Cs and P compositions to form struvite phase and the Mg amounts inside the solid particles were high enough to form struvite particle size large enough to avoid relative dissociation to leave Cs back into solution again.
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**Figure 9.** Schematic pathways of precipitating Cs by magnesium compounds.

**4. Application of Serpentine with Impurities**

Although serpentine resources are rich in reserves and many mines of high quality are available in China and the world, it is needed to examine the possibility of using some tailings with serpentine and other gangue minerals inside. Quartz (SiO$_2$) and many other silicate minerals are widely distributed in nature, and appear in almost all natural mines. These silicate minerals are quite hard materials against milling operation and are usually chosen as grinding aids in mineral processing for its high Mohs’ hardness. To explore the effect of silicate impurities in serpentine on the Cs removal efficiency, experiments were carried out with different amounts of quartz added and Cs removal efficiency were monitored under the same fixed mole ratio of Mg/Cs/H$_3$PO$_4$ (5/1/1.2).

**Figure 10.** Cs removal efficiency by the modified serpentine with different added amount of SiO$_2$.

Figure 10 shows the changes in Cs removal efficiency with the adding percentage of SiO$_2$. The addition of SiO$_2$ gave a very positive effect with higher removal efficiency of Cs ions. The removal efficiency of Cs ions increased from 90.73 % to 94.64 % following the added SiO$_2$ to serpentine from 5 % to 35 %, indicating that the mixture of serpentine and SiO$_2$ had better performance than the pure serpentine sample. Better removal effect by ball-milling of serpentine with impurities could be used for the treatment of $^{137}$Cs in radioactive wastewater instead of purified serpentine. This provided a new idea for the resource utilization of the serpentine tailings.

**5. Conclusions**

In general, mechano-chemical modification of magnesium silicate serpentine allowed easier dissolution of Mg ions. Different from soluble Mg salts and original mineral, such metastable Mg demonstrated excellent capacity to form struvite precipitate in the solution with both Cs and P compositions together, achieving efficient removal of Cs ions from the radioactive wastewater. The remaining silica of serpentine served as nucleus seed to promote the precipitation of struvite crystal in the solid-liquid heterogeneous reaction system. This process had
provided an effective method to stabilize radioactive waste with cesium ions. The widely available cheap serpentine mineral particularly with some silicate impurities may serve as an excellent environment-friendly precipitant for resource application of serpentine tailings.

References