Hydrothermal conversion of analcime-pollucite solid solution from soil for immobilization of Cs in situ and its characterization

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Abstract
Pollucite, considered as an ideal host material for immobilization of Cs, rarely exists in pure form but analcime-pollucite solid solution in nature due to the coexistence of Cs and Na in fact. Thus, a novel hydrothermal method has been proposed to directly synthesis analcime-pollucite solid solution instead of pure pollucite so as to in-site immobilize Cs in its structure. The result showed that Cs/Na ratio of starting material, hydrothermal time and hydrothermal temperature were the main factors in the hydrothermal synthesis of the solid solution. Different Cs/Na ratio could result in different solid solution formations, and however, even with little polluted Cs in soil (small Cs/Na), the composition of the synthesized solid solution seemed to be closer to that of pollucite than analcime. This suggests that the hydrothermal synthesis of the analcime-pollucite solid solution can be used to immobilize the polluted Cs in soil. The solid solution could be formed readily even at a low curing temperature (150 °C) or for a short curing time (2 h), while a higher temperature and longer time could promote the solid solution formation. The extended X-ray absorption spectrum fine structure (EXAFS) and near-infrared spectrum (NIR) analyses proved that Cs⁺ entered into the structure of the formed solid solutions via replacement of water molecules, and it also led to a distortion of the framework of the solid solution with the change of the Cs–O bond length. This revealed that the Cs was indeed immobilized into the structure like that of pure pollucite. Because of the steady immobilization of Cs in structure, the concentration of Cs leached from the solid solutions was very low (4.3 × 10⁻⁶ g/(m²-d)), even lower than that of the pure pollucite (1.88 × 10⁻⁵ g/(m²-d)) and pollucite-based ceramic (2.67 × 10⁻⁵ g/(m²-d)). Therefore, the hydrothermal synthesis of the analcime-pollucite solid solution from soil (metakaolin) is available for effective treatment of huge amounts of Cs-polluted soil.

1. Introduction
Exploring and searching for ideal host materials and technologies for solidifying radioactive waste is very urgent and important for the development of nuclear energy. At present, lots of approaches have been developed for treating nuclear wastes [1, 2]. Generally, low- and medium-level radioactive wastes are treated by cement solidification [3–5], asphalt solidification [6] and plastic solidification [7], while high-level radioactive wastes are treated by glass solidification [8–10] and artificial rock solidification [10, 11].

After Fukushima nuclear accident in Japan, a huge amount of nuclear-polluted soil has been produced, and up to today it remains a formidable problem how to treat the nuclear-polluted soil effectively. Among the radioactive elements existing in the polluted soil, Cs-137 arises significant concern due to its long half-life period and high hazardous impacts. For the aforementioned massive Cs-polluted soil, the conventional methods, such
as cement solidification and glass solidification, are not available because several times of solidification basis materials (e.g. cement or glass) are also needed for those solidifications. For the artificial rock solidification, the radioactive elements can be immobilized in its crystal structure, which is considered as an optimal strategy for immobilization of radioactive waste with lower leaching rate and better radiation resistance.

Pollucite (CsAlSi$_2$O$_6$) contains high concentration of Cs (more than 40%wt) in its structure. Furthermore, Cs with relatively larger size is limited by the smaller size of the structural channels of pollucite, and therefore the Cs cannot leak out unless the frame structure is completely destroyed. Such high capacity ratio, excellent thermal stability and good chemical stability makes pollucite be an optimal host material for immobilizing Cs-137. In recent years, scholars at home and abroad have synthesized pollucite to immobilize Cs (radioactive waste) in various methods such as sintering method [12], hot pressing method [13], but the synthesis temperature of pollucite is very high or the equipment is very complex. Our previous work showed that for the huge amounts of the Cs-polluted soil [14, 15] and/or Cs-polluted incineration ash [16–18], they could be synthesized into pollucite for in-situ immobilizing the polluted Cs with a hydrothermal technology. The hydrothermal technology has been used to synthesize inorganic materials widely [19–21], and recently it has also been applied to organic material conversion [22–24].

Although pollucite has been considered as an ideal host material for immobilization of Cs, in fact, the pure pollucite rarely exists in nature. From its geological evolution, pollucite converts into clay minerals and finally weathers to soil via analcimization in adaptable situations [25, 26]. Research has also shown that pollucite is always accompanied by analcime formation, and forms a series of continuous solid solution covering all ratios with the isomorphic mineral analcime [27, 28] because of the inevitable coexistence of sodium and cesium in soil. Generally, natural pollucite is usually expressed by the chemical formula (Cs,Na)AlSi$_2$O$_6$·nH$_2$O, and divided into pollucite (Pol$_{95}$–Pol$_{100}$), sodian pollucite (Pol$_{50}$–Pol$_{95}$), cesian analcime (Pol$_{50}$–Pol$_{95}$) and analcime according to its Cs/Na ratios [29]. The research on synthesizing pure pollucite to immobilize radioactive Cs has drawn focus recently [15, 16, 30]. When it comes to in situ immobilization of Cs in the Cs-polluted soil, however, the hydrothermal synthesis process of analcime-pollucite solid solutions from polluted-soil and its behavior of immobilization of Cs remain to be studied because the soil contains diverse alkali metals and thus solid solutions are formed readily and inevitably. Although analcime-pollucite solid solutions [31, 32] have been synthesized hydrothermally for immobilization of Cs, these researches mainly focused on the synthesis of the solid solutions with coal fly ash and chemicals and the influence of Cs/Na ratio on the morphology of the formed solid solutions.

In order to synthesize the analcime-pollucite solid solution from soil and then in-situ immobilize Cs within the Cs-polluted soil, firstly the hydrothermal synthesis of the analcime-pollucite solid solution from soil or clay minerals should be studied, followed by the investigation of micro-immobilizing behavior, i.e. Cs$^+$ coordination environment in the structure, solid solution structure micro-characteristics and Cs leaching properties.

Based on the above analysis, the analcime-pollucite solid solution was synthesized from soil (metakaolin) to immobilize the polluted Cs of the soil. Our study is aimed at: (1) exploring the influence of Cs/Na ratio, hydrothermal temperature and hydrothermal time on the synthetic solid solutions; (2) analyzing the evolution of the morphology and microstructure of the solid solution; (3) researching the coordination environment of Cs$^+$ entered in the structure of the solid solution; (4) verifying the immobilization effect of Cs in the solid solution with the leaching test.

2. Materials and methods

2.1. Materials

The complex composition of soil varies largely from the regions. In order to ensure universal adaptability in the research, the metakaolin (Al$_2$Si$_2$O$_5$), which is calcined from kaolinite and is a main clay mineral of soils, was chosen as a model raw material to replace soil for synthesis of analcime-pollucite solid solution in this study. Furthermore, the calcined kaolinite can remove some impurities, especially organic impurities, which is good for the precise microstructural analyses.

Determined by X-ray fluorescence (XRF, Brux SR3400, German), the composition of metakaolin is shown in table 1. Compared with the soil composition from Lanzhou city (China) in our previous work [14], the main

| Table 1. Chemical composition of metakaolin (mass%) |
|-----------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
|                 | SiO$_2$      | Al$_2$O$_3$  | A$_2$O        | CaO          | MgO          | TiO$_2$      | Fe$_2$O$_3$  | P$_2$O$_5$   | LOI          |
| Metakaolin      | 42.9         | 33.8         | 0.21          | 0.46         | —            | 0.64         | 0.51         | 0.29         | 21.16        |

'A' indicates Na or K.
components of metakaolin are very similar to soil with both main compositions being SiO$_2$ and Al$_2$O$_3$. More importantly, the metakaolin contains a small amount of alkali metal elements (A$_2$O), which is also beneficial to the research. Metakaolin (powders, industrial grade) was purchased from Shanghai Zhenjiang Chemical Ltd. Non-radioactive Cs-133 was used as a simulant radioactive element instead of Cs-137. Cesium hydroxide and cesium chloride (particles, chemically pure) were from China Lithium Industrial Ltd. Other additives such as sodium hydroxide (flaky, analytically pure), silica (powder, analytically pure), calcium hydroxide (powder, analytical grade) were all from Sinopharm Reagent Co. Ltd.

2.2. Hydrothermal synthesis
The metakaolin (soil) mixed with appropriate silica or alumina at certain Si/Al molar ratio was used as the starting materials, and then cesium hydroxide or sodium hydroxide solution were added to form pollucite, analcime and their solid solutions. The mixtures were added in a 40 mm $\times$ 15 mm $\times$ 5 mm stainless steel mold, and then shaped under the pressure of 30 MPa using isostatic press machine (FY-15, Tianjin Sichuang Jingshi Technology Co. Ltd.). The green samples were hydrothermally reacted in Teflon-lined stainless steel autoclave [33] for different periods (0–30 h) at different temperatures (150 °C–200 °C), then dried in an oven at 80 °C for 24 h before characterizing.

2.3. Characterization
The crystalline phases of the samples were analyzed by X-ray diffractometer (XRD, Shimadzu XRD-6100, Cu K$\alpha$, 30 kV, 30 mA), and the data was collected at the scanning speed of 6° min$^{-1}$ between 2θ range of 5–55°; the microscopic morphology was observed by scanning electron microscope (SEM, Quanta 200 FEG, FEI); the absorption in a region of 800–2600 nm was measured by using near infrared spectrophotometer (IR, U-4100, Hitachi); the structured water was studied by thermos-gravimetric analyzer (TG, STA449C, Netzsch) in an air atmosphere with the heating rate at 5 °C min$^{-1}$. The extended X-ray absorption spectrum fine structure (EXAFS) in the Beijing Institute of High Energy Physic was used to analyze the microscopic behavior of the neighboring atoms around the absorbing atom. The device is equipped with 2.8 GeV electron energy storage ring, the planar bi-crystalline Si (111) monochromator and the corresponding solid detector. The EXAFS spectra of the Cs-L$_{III}$ absorption edge (5012 eV) were tested in

![Figure 1. XRD patterns of samples with different ratio of Cs/Na in 200 °C hydrothermal treatment for 10 h](image-url)
the transmission mode, further analyzed by ATHENA module, the radial structure functions were obtained by Fourier transform. And the EXAFS spectra of the corresponding layer in K-space, which contains the coordination information of Cs-O and Cs-T (Si/Al), could be obtained by inverse Fourier transform.

The leaching test was also performed in deionized water based on the leaching testing protocol of ASTM 1285-02 (American Society for Testing Materials, 2008) to examine the stability of the immobilization of Cs. The samples were first ground into powder of a size ranging from 100–200 mesh, then the powder was mixed with deionized water at a liquid-to-solid ratio of 10:1, and finally the mixed solid-liquid mixture was kept in an oven at 90 ± 2°C for different days (7–56 days). After different days of leaching, the supernatant was cooled, and then diluted 1000 times to determine the concentration of Cs by using inductively coupled plasma mass spectrometer (ICP-MS). The standard normalized leaching rate NRi can be expressed by equation (1):

$$NRi = \frac{C_i{_{\text{sample}}}}{(f_i)(SA/V)(t)}$$  

(1)

Where $C_i{_{\text{sample}}}$ is the concentration of Cs in the leaching solution (g/L), $f_i$ is the mass percentage of Cs in the sample, $SA$ is the surface area of the sample (m², measured by specific surface area analyzer with BET method), $V$ is the volume of the leaching solution (L), and $t$ is the test time (day).

3. Results and discussion

3.1. Synthesis of analcime-pollucite solid solution

3.1.1. Effects of Cs/Na on analcime-pollucite solid solution formation

The analcime-pollucite solid solutions were synthesized by adjusting the addition content of CsOH and NaOH to a ratio of (Cs+Na): Al:Si = 0.75:1:1.5 at 200°C for 10 h. XRD patterns of these solid solutions, pollucite and analcime are shown in figure 1. The location of diffraction peaks for both pure pollucite and pure analcime are similar, but the intensities of peaks are different. For the sample with Cs:Na = 1:9, the location and intensity of the peaks are very similar to that of analcime, while the peak intensity corresponding to (321) appears stronger than that of analcime, reflecting that the composition of the new phases is very close to analcime but has some traces of pollucite. However, at Cs:Na = 2:8, the location and intensity of the peaks becomes closer to that of pollucite, which reflects that the composition of the solid solution phases synthesized becomes more similar to pollucite, and also suggests that the solid solution immobilizes Cs more easily than Na. With more Cs addition, at Cs:Na = 5:5, the solid solution phase appears to transform to the pure pollucite which is same as that at Cs:Na = 10:0. The results above indicates that the coexistence of Cs and Na in soil can effectively promote the formation of analcime-pollucite solid solution, while the composition of the formed solid solution seems to be closer to that of pollucite.

Figure 2. SEM images of samples of different ratios of Cs/Na after 200°C hydrothermal treatment for 10 h. (a) Cs/Na = 0:10; (b) Cs/Na = 2:8; (c) Cs/Na = 10:0; (d) enlarge of the image in (c).
Figure 2 shows the SEM images of the samples with different Cs/Na ratios. Figure 2(a) reveals the trioctahedron analcime with size of above 2 μm at Cs:Na ratio of 0:10. When Cs/Na ratio is 2:8 (figure 2(b)), a lot of particles with different sizes are formed, and according to XRD results shown in figure 1, the formed phases should be the analcime-pollucite solid solutions. As the Cs/Na ratio increases to 10:0 (figures 2(c) and (d)), lots of fine and spherical pollucite particles with a size of about 50 nm are formed. From the morphology evolution of the solid solution formed with different Cs/Na ratios, the morphology of the solid solution particles become smaller and rounder from analcime to pollucite, because lower electronegativity of Cs⁺ endows stronger condensation polymerization on Si(Al)-O tetrahedral framework, and thus it is favored to form spherical grains, which is consistent with the morphology reported in literature [31].

3.1.2. Effects of curing temperature and time on analcime-pollucite solid solution formation
Effects of the curing temperature and time on the solid solution synthesized with the molar ratio of (Cs + Na): Al:Si = 0.75:1:1.5 (Cs:Na = 2:8) were also studied. The XRD patterns of the samples obtained at curing temperatures of 150 °C and 200 °C for 10 h are shown in figure 3(a). Without hydrothermal curing, the main phases are the quartz, while after curing at temperature of 150 °C, new phases of the analcime-pollucite solid solution are formed besides sodalite. The XRD results also reveal that no obvious change in the intensity of peaks of the solid solution is observed for a higher curing temperature (200 °C), suggesting that the analcime-pollucite solid solution forms readily even at a low curing temperature.

The influence of curing time on the phases evolution of solid solution formed with (Cs + Na):Al:Si = 0.75:1:1.5 (Cs:Na = 2:8) at 200°C is also shown in figure 3(b). Compared with the sample without hydrothermal curing (0 h), the new phases of analcime-pollucite solid solution are formed after only 2 h, and more of the solid solution are formed after longer hydrothermal time. The above research reveals that although higher temperature and longer time are favored to form the solid solution, the solid solution is found to form readily.
Figure 5. Thermal-gravimetric analysis of samples of different Cs/Na ratio in 200 °C hydrothermal treatment for 10 h.

Table 2. Analysis of general chemical formula $\text{Cs}_x\text{Na}_y\text{AlSi}_2\text{O}_6 \cdot z\text{H}_2\text{O}$ of the solid solution

| Cs/Na | Relative molecular mass | Water contents/mass% | Elemental molar ratio of $\text{Cs}_x\text{Na}_y\text{AlSi}_2\text{O}_6 \cdot z\text{H}_2\text{O}$ |
|-------|-------------------------|----------------------|--------------------------------------------------------------------------------------------------|
| 0:10  | 220.16                  | 8.18                 | $x \quad y \quad z$ 0 1 1.000                                                                 |
| 1:9   | 227.67                  | 6.38                 | $0.1 \quad 0.9 \quad 0.807$                                                                       |
| 2:8   | 237.66                  | 5.73                 | $0.2 \quad 0.8 \quad 0.751$                                                                       |
| 5:5   | 264.84                  | 2.95                 | $0.5 \quad 0.5 \quad 0.430$                                                                       |
| 10:0  | 316.98                  | 1.55                 | $1 \quad 0 \quad 0.273$                                                                          |

Figure 6. Relationship between the content of structure water and addition of Cs.
3.2. Structure analysis of analcime-pollucite solid solution

Figure 4(a) shows the nano-spherical particles of the sample of Cs:Na = 2:8, and the EDS scanning images of rectangle area are also shown in figure 4(b). Cs and Na are distributed homogeneously in all grains, indicating that the added Na and Cs have entered Al(Si)-O frame structure and no obvious phase separation or aggregation seemed to occur. Therefore, the approximate composition of solid solutions therefore can be expressed by the chemical formula CsxNayAlSi2O6·zH2O.

TG analysis of the samples with different Cs/Na ratio can be seen in figure 5, the structural water content weighs the most which reaches up to 8.18% for the pure analcime, and it gradually decreases as the Cs content increases. The content of structure water and calculated elemental molar ratio parameters x, y and z in the formula CsxNayAlSi2O6·zH2O are listed in table 2. The Cs/(Cs+Na) and structural water weight fraction show good linear negative correlation (figure 6). This suggests that cesium ions must have replaced the partial positions of water molecules in analcime according to certain stoichiometric relationship, and it is consistent with the measured results of Hovis [34].

The near-infrared spectrum (NIR) reveals that, according to the hydroxyl vibration of water molecules, the absorption intensity of the first-order double frequency of 1924 nm (5197 cm⁻¹) and the second-order double frequency of 1416 nm (7062 cm⁻¹) weaken observably with the increase of Cs content, reflecting that the content of the structure water decreases (figure 7). At the same time, the peak at 2252 nm (4440 cm⁻¹) related to the combination of SiO₂ absorption frequency and hydroxyl stretching vibration frequency becomes stronger and stronger due to their vibration coupling. This stronger coupling effect might be attributed to the structure distortion caused by the extruded water molecules from the center of the six-membered ring along the [111] axis after Cs partially occupies the center of cavities.

Figure 7. Near infrared spectrum of samples of different Cs/Na ratio in 200 °C hydrothermal treatment for 10 h.

Figure 8. Cs-LIII edge EXAFS spectra of different ratio of Cs/Na in 200 °C hydrothermal treatment for 10 h
The EXAFS was also used to investigate the microscopic behavior of Cs in the structure of the synthesized solid solutions. As shown in figure 8(a), there is no any peak for analcime (Cs:Na = 0:10). With increasing Cs/Na ratio for the analcime-pollucite solid solutions, some peaks near the absorption limit of 5012 eV appear, and the peak intensity becomes stronger with more Cs addition (increasing Cs/Na), suggesting that more Cs has entered into the structure of the solid solution with increasing Cs/Na. At Cs/Na of 10:0, the strongest peaks show that the synthesized pollucite has embedded most Cs in its structure. Figure 8(b) shows the K-space oscillation curves of the sample with different Cs/Na, compared with pollucite (Cs:Na = 10:0) similar shapes can be observed, showing that the coordination environment of Cs in the structure of the solid solution is very similar to that in the pure pollucite. This also suggests that Cs was immobilized into the structure of the formed solid solutions rather than physically adsorbed in the pores. The R-space radial structure function (figure 8(c)) shows that smaller Cs–O bond lengths appear for the lower Cs/Na (solid solutions) than that of the pure pollucite, which might be ascribed to the fact that the coordinated O atoms shift to the side near to Cs ions caused by the structure distortion of Si(Al)-O tetrahedrons when the replacement of Cs by H2O happens, in agreement with previous work of the Fan et al.[14].

According to the above analysis, the model of analcime-pollucite solid solution could be described as one shown in figure 9(c). Na⁺ in the solid solution should occupy the same position as Na⁺ in the analcime (figure 9(a)), i.e. the 24c equivalent point (1/4, 1/8, 0); similarly Cs⁺ in the solid solution should replace the position of partial water molecules, which has the same position as Cs⁺ in the pollucite (figure 9(b)), i.e. 16b equivalent point (1/8, 1/8, 1/8); while the remaining water molecules, originally located in the center of the cavity in analcime, are squeezed into the center of the Si(Al)-O tetrahedral six-membered rings. This can explain the aforementioned changes of Cs–O bond.

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**Figure 9.** Structure models of analcime(a), pollucite(b) and analcime-pollucite solution(c)

**Figure 10.** XRD analysis of the specimens with different CsCl additions
As such, the analcime-pollucite solid solutions have the same Si(Al)-O tetrahedral multi-ring frame structure as the analcime and pollucite, fitting with the structural characteristics of natural analcime-pollucite solid solutions reported by geologists [35], while for the immobilization of Cs, the solid solution has a capability of immobilizing Cs in its structure like pollucite.

3.3. Synthesis of analcime-pollucite solid solution with CsCl and its leaching properties

The cesium hydroxide can promote the formation of solid solution in the hydrothermal process with its strong alkalinity. Therefore, hydrothermal synthesis of the analcime-pollucite solid solution with CsCl was also carried out, and the XRD patterns of the samples with (Cs + Na):Al:Si = 0.75:1:1.5, (Cs:Na = 2:8) at 200 °C for 10 h are shown in figure 10. The analcime-pollucite solid solution can be formed with CsCl addition, and some other new phase of sodalite (Na4Cl(Al3Si3O12)) exist. Similar with the CsOH addition shown in figure 1, the peak intensity corresponding to (211) and (220) decreases with more CsCl addition, suggesting that the composition of the formed solid solution phases tends to be similar to pollucite. From SEM images of figure 11, the morphology and grain size are shown clearly. When the content of CsCl is 1.1% (figure 11(a)), the solid solution exhibits some large spherical grains, and the sodalite exists around these solid solution grains. The size of the spherical grain for the formed solid solution also decreases with more CsCl addition reflecting that the formed solid solution becomes similar to pollucite (figures 11(a)–(d)). EDS scanning images (figure 11(a)) of rectangle area shown in figure 11(e) are aimed to inspect the element distribution of the solid solution. Figure 11(e) shows that Cs is mainly distributed in solid solution while Cl exists mainly outside the solid solution (in sodalite), which

![Figure 11: SEM images of the samples with different addition of CsCl of 1.1%(a), 2.1%(b), 4.1%(c), 7.9%(d) and EDS scanning images (e) of the rectangle area in (a)]

Table 3. Long term standard leaching rate of the samples with different content of CsCl

| The leaching content of Cs | 1.1% | 2.1% | 4.1% | 7.9% |
|---------------------------|------|------|------|------|
| 7-day leaching rate/(10⁻⁶ g m⁻²·day⁻¹) | 0.76 | 4.54 | 9.59 | 5.24 |
| 14-day leaching rate/(10⁻⁶ g m⁻²·day⁻¹) | 0.74 | 0.18 | 0.25 | 2.36 |
| 21-day leaching rate/(10⁻⁶ g m⁻²·day⁻¹) | 0.12 | 0.07 | 0.32 | 1.39 |
| 28-day leaching rate/(10⁻⁶ g m⁻²·day⁻¹) | 0.06 | 0.06 | 0.24 | 1.02 |
| 56-day leaching rate/(10⁻⁶ g m⁻²·day⁻¹) | 0.01 | 0.02 | 0.12 | 0.38 |

Table 4. Comparison of Cs leaching rates for various solidified samples

| Specimen                  | Cs content/% | Leaching period/d | Leaching temperature/°C | Leaching rate/(g/(m²·d)) | References |
|---------------------------|--------------|-------------------|-------------------------|--------------------------|------------|
| Tungstate-based glass-ceramic | 6.5          | 7                 | 90                      | 1.65 × 10⁻⁴               | [36]       |
| Pollucite-based ceramic    | 7.6          | 7                 | 90                      | 2.67 × 10⁻³               | [37]       |
| Synthesized pollucite      | 31.7         | 7                 | 90                      | 1.88 × 10⁻⁵               | [18]       |
| Analcime-pollucite solid solution | 6.2          | 7                 | 90                      | 4.3 × 10⁻⁶                | This work  |
demonstrates that the formed solid solution is rich in Cs even though only 1.1% CsCl is added and also reveals that the solid solution are formed readily even with CsCl addition.

The leaching characteristics of the samples with different CsCl additions are also shown in table 3, their 7-day standardized leaching rates are rather low and distributed between $0.76 \times 10^{-6} \text{ gm}^{-2} \text{ day}^{-1}$, and the sample with Cs content of 1.1% has the lowest leaching rate. The longer leaching time results in smaller leaching rate, and the 21-day leaching is an important turning point in the leaching process, at which the leaching rate will saturate.

The 7-day standard leaching rate of the synthesized analcime-pollucite solid solution was also compared with that of other materials (table 4), and the results showed that the concentration of Cs leached from solid solution is much lower than that from those materials. Even when compared with pure pollucite, its leaching performance is also quite impressive. This proves that the hydrothermal synthesis of the analcime-pollucite solid solution from soil can be used to immobilize Cs in the polluted soil.

4. Conclusions

In order to treat the Cs-polluted soil, the analcime-pollucite solid solutions were synthesized from soil (metakaolin), and the in-situ immobilizing behavior of Cs was also studied. The Cs/Na ratio of the starting material, hydrothermal time and hydrothermal temperature show intensive influence upon the solid solution formation and microstructure. The analcime-pollucite solid solutions were formed readily with the coexistence of Cs and Na in soil, and the Cs/Na ratio of soil could result in different solid solution formations.

Even with little Cs in soil (e.g. at Cs/Na of 2/8), the composition of phase synthesized was closer to that of pollucite than analcime, suggesting that the solid solution could immobilize Cs like that of pollucite. The solid solution was formed readily even at a low curing temperature of 150 °C or for a short curing time of 2 h, while higher temperature and longer time promoted formation of the solid solution.

The EXAFS and NIR results showed that the Cs was actually immobilized into the structure of the formed solid solutions instead of physically adsorbed in the pores, and during in-situ immobilization process the Cs$^+$ gradually replaced water molecules in the structure, which leads to the distortion of the solid solution framework due to the change of the Cs-O–bond length.

The leaching rates of Cs from the solid solutions was very low ($4.3 \times 10^{-6} \text{ g/(m}^2\cdot\text{d})$), which is even lower than that of the pure pollucite and pollucite-based ceramic.

Above all, the hydrothermal synthesis of the analcime-pollucite solid solution from soil (metakaolin) can be applied to treatment of huge amounts of Cs-polluted soil.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

Authors declare no Conflicts of interest.

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