Hydrothermal conversion of model polluted soil into zeolite P to in-situ immobilize heavy metals via zeolitization and its microstructure behavior

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Abstract

To develop a new technology to remediate pollution sites stably and effectively, hydrothermal conversion of polluted soil (model soil) into zeolite P for in situ immobilization of Heavy Metals (HM) was carried out. Zeolite P could be synthesized from soil hydrothermally with a large range of Al/Si ratio (0.33–1.0) in 48 h at 200 °C. With immobilizing heavy metals (Cr, Zn and Cd), the crystallization of Zeolite P (Cr-ZP, Zn-ZP and Cd-ZP) was delayed with the order of Cr > Zn > Cd because the stronger the ligand effect of heavy metals have, the more heavily the nucleation and growth were influenced. During immobilization via zeolitization, a self-adaptive structuring behavior was confirmed by EDAX, BET and Rietveld refinement analyses: zeolite P structured more [AlO4]− to immobilize HM because the flexible 8-member-Ring channels (8 mRs) with higher Al/Si ratio could complex with more HM readily. The encapsulated HM occupied the original Na positions (Na1 and Na2) of zeolite P competitively because of their different cation size, e.g., the smallest Cr3+ could substitute all Na1 because Na1 is closer to the Framework Oxygen (FO); the largest Cd2+ however, substituted Na1 (9%) and Na2 (14%) evenly. The shrunken 8 mRs due to heavy metal immobilization also caused different chemical environments for different heavy metals immobilized because the smaller heavy metal cation could get closer to the framework, and also coordinated with more FO.

1. Introduction

Human activities, for instance, industrial processes, mining and disposal of wastes, etc, have created a legacy of numerous heavy metal contaminated sites worldwide. The contaminants not only threaten living species and human beings [1], but also resulted in the sites derelict. To mitigate the risk and further reutilize the sites, three remedial ways, i.e. physical, chemical and biological methods, were developed. The physical and chemical remedial methods, such as excavation, thermal treatment and chemical soil washing etc, could change the soil property, cause secondary pollution readily, and required complex equipment [2, 3]. Although biological remediation could maintain the original soil property [4, 5], it was rarely applied to the sites because of its long treating period.

Recently a new method to use mineralogical materials for pollution treatment has been exploited [6–8] in which the mineralogical material was mixed into soil to adsorb contaminants in the soil, and it even acted as the fourth category of pollution treatment methods following the physical, chemical and biological methods [9]. Among mineralogical materials, natural and synthesized zeolites have been also considered as superior soil amendments due to their high cation exchange capacity [10, 11]. Because synthesized zeolite performs better...
remediation efficiency [12], there has been a growing interest in the use of synthesized zeolites. For instance, Zheng et al [13] found that synthesized cancrinite performs excellent remediation effect on Pb-polluted soil, in which the accumulated Pb in vegetable decreased obviously compare to that before mixing cancrinite. In addition, synthesized analcime was able to exchange the Cu$^{2+}$ from Cu-polluted soil, and the plant pot experiment confirmed its good remediation performance [14].

Moreover, its similar chemical composition (aluminosilicate) to soil will not change the soil property. However, the sorption stability and/or cation exchange capability of zeolite would be influenced greatly by the soil composition and environment, including competing cations, organic matters and pH value [15, 16]. In addition, the added minerals was not fully effective due to the fact that the complexation of heavy metal cations on inner surface of mineral blocks the cation diffusion and accessibility of the cationic sites during adsorption [17].

To enhance the stability, a high temperature ($\geq$1000 $^\circ$C) synthesis of mineral (spinel) to in situ immobilize heavy metals in soil was even carried out, and the heavy metals were incorporated into the crystal structure and hardly released [18, 19]. However, the high treating temperature could inevitably damage the properties of soil, and also increase the cost of disposal. Accordingly, it is necessary to explore an efficient remediation technology for the heavy metal contaminated sites which could both steadily immobilize the heavy metals and preserve the original soil property.

It is well known that soil is a weathering product of minerals and abounds with aluminosilicates [20], and therefore it can be probably re-converted into minerals. With simulating the diagenetic process underground, hydrothermal technology could dissolve the Al and Si of soil readily, and in situ restructure them into the needed minerals, like zeolites [21, 22]. As an environmental and energy-saving processing, hydrothermal technology has been also applied to reduction of organic materials or CO$_2$ into value-added chemicals [23–25]. Furthermore, because of the moderate treating temperature ($\leq$200 $^\circ$C), the inherent properties and performance of soil could be reserved [26]. Chen et al demonstrated that Cs-polluted soil could be synthesized into a zeolite containing cesium (pollutant, Cs$_2$Al$_2$Si$_2$O$_7$·H$_2$O) hydrothermally, and EXAFS result suggested that almost all the polluted Cs was encapsulated into the 6-member-ring structure of, and reach the very low leaching rate after hydrothermal conversion [27].

Zeolite P has been widely applied to uptake/water treatment due to its excellent cation exchange [28–31]. Studies also indicated that zeolite P could be hydrothermally synthesized from coal fly ash to immobilize the heavy metals in the coal fly ash [32–34]. In addition, zeolite P was found to form during geopolymerization of polluted soil at 60 $^\circ$C by incubation [35]. The above studies indicate that multi-member-ring structure of zeolite would potentially in situ encapsulate pollutant during its forming, and provide a more efficient and stable remediation for heavy metal polluted soil rather than absorbing or cation exchanging.

Zeolite P structures two flexible 8-membered ring channels (8 mRs) [36] in its unit cell. The cations (Na$^+$) are accommodated in the 8 mRs, and coordinated with the framework oxygen and structural H$_2$O. Since the size and charge of heavy metal cations are very different (Cr$^{3+}$ (62 pm), Zn$^{2+}$ (74 pm), Cd$^{2+}$ (95 pm) in this study) [37], the immobilized cations should influence the flexible 8 mRs at different level during zeolitization, and coordinate with different oxygen (framework oxygen and structural H$_2$O). Therefore, the microstructure behavior of zeolite P for in situ immobilizing different heavy metals, and the chemical environment evolution of the cations before/after in situ immobilization should be studied in-detail.

However, not only the complex constitutions of soil, such as the organic matters and oxides, have non-negligible effect on immobilizing heavy metals [38], but also the elements (Ca, K and Fe) dissolved from soil, can be also captured by the new formed zeolites during zeolitization [39]. For this reason, a simplified model soil was used to substitute real soil for investigating the microstructure behavior of zeolite P during in situ immobilization. To the best of our knowledge, such a study has not been reported in the literature so far.

The objective of this work was to (1) synthesize pure zeolite P from model of soil, and discuss the synthesis conditions and mechanism; (2) immobilize heavy metals by zeolite P via zeolitization, and evaluate its immobilization mechanism; and (3) evaluate the microstructure behavior and chemical environments evolution of zeolite P during in situ immobilization of the different heavy metals. The results are expected to provide theoretical information on in situ immobilizing heavy metal of polluted soil via zeolitization, and explore a new in situ zeolitization technology for soil remediation.

2. Materials and methods

2.1. Hydrothermal synthesis of zeolite P

Zeolite P, an aluminum silicate containing sodium, has three different types, such as Zeolite P1 (Na$_6$Al$_6$Si$_{10}$O$_{32}$·12H$_2$O), Zeolite P2 (Na$_8$Al$_8$Si$_{17}$O$_{32}$·14H$_2$O) and Zeolite P (Na$_{3.5}$Al$_{3.5}$Si$_{12.5}$O$_{32}$·14H$_2$O) [40]. For investigating the heavy metal in situ immobilization behavior by zeolite P (P1 and P2) via hydrothermal
zeolitization, the study mixed NaAlO₂ into pure silica as a simplified model soil, due to the fact that Si(SiO₂) and Al(Al₂O₃) are the second-most and third-most abundant elements in soil [41–43], so as to eliminate the influence of impurities of soil.

For the starting materials with different Al/Si molar ratios (0.0, 0.33, 0.67, 1.0 and 1.33) prepared, NaAlO₂ was first dissolved in 30 ml distilled water, and then certain amounts of SiO₂ was added to achieve a certain Al/Si of the starting material. After stirring for 5 min, the mixture was sealed in a Teflon (PTFE) lined stainless steel autoclave (50 ml) and treated at 200 °C for 48 h. After reaction, the solid part was centrifugally separated and dried at 80 °C for 24 h.

2.2. Synthesis of zeolite P for heavy metals immobilization

For studying the mechanism of in situ immobilization of heavy metals via zeolitization, Cr, Zn and Cd were chosen for immobilization in this study due to not only their higher concentrations in the polluted soil but also their different sizes and charges (62 pm of Cr³⁺, 74 pm of Zn²⁺ and 95 pm of Cd²⁺). Certain amounts of Cr³⁺, Zn²⁺ and Cd²⁺ solutions were added into SiO₂ to form the mixtures of Cr-SiO₂, Zn-SiO₂ and Cd-SiO₂ with different heavy metal/SiO₂ (R/Si) molar ratio of 0.05/3, 0.10/3, 0.15/3 and 0.20/3, and dried in an oven (45 °C for 7 days) at normal pressure. NaAlO₂ solution was then mixed with the polluted silica till Al/Si ratio of 0.67 to obtain a final 30 ml mixture. After stirring for 5 min, the mixtures were moved to the Teflon reactors and treated hydrothermally at 200 °C for different times. The solid parts of the synthesized zeolite P (ZP) with immobilized Cr, Zn and Cd (Cr-ZP, Zn-ZP and Cd-ZP) were centrifugally separated and dried at 80 °C for 24 h.

Both NaAlO₂ and SiO₂ (hydrophilic fumed silica) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China. Analytical pure Zn(NO₃)₂·6H₂O, Cd(NO₃)₂·4H₂O, and Cr(NO₃)₃·9H₂O (heavy metals) were obtained from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China.

2.3. Characterizations

All the dried solid specimens were manually ground into fine powders first. The mineralogical phases were measured using a XRD of Rigaku Ultima IV diffractometer operating at 40 kV and 40 mA with Cu Kα radiation with a continuous scan covering angles of 5° to 55° (2θ) at a scanning rate of 5° min⁻¹. After conductive coating (gold), the morphology of the solids was observed with the Scanning Electron Microscopy-Energy Dispersive X-ray Analysis (SEM-EDAX, Quanta 200, FEI). The BET specific surface area information was measured by nitrogen gas sorption analysis (Quantachrome, Autosorb-NOVA 2200e), during which ZP, Cr-ZP, Zn-ZP and Cd-ZP specimens were firstly outgassing at 105 °C for 3 h under highly reduced pressure, and then measured at 77.15 K. To identify the microstructure behavior of zeolite P before/after immobilizing heavy metals, Rietveld Refinements were also carried out. The sample powders were further milled and passed 1800-mesh sieve, and then the XRD patterns were collected using a Rigaku D-MAX 2550VB3+ /PC diffractometer operating at 40 kV and 100 mA with Cu Kα radiation and a bent graphite monochromator. The step scan covered the angular range of 5°–55° (2θ) with 0.02° of step size, 2 s per step. The patterns were refined, and structure information was obtained using the Rietveld technique as implemented in the computer program package EXPGUI [44] according to the ICSD XRD patterns. To further investigate the chemical environment variation before/after in situ immobilization of the heavy metals by zeolite P, XPS spectra of the dried fine powders (Cr-SiO₂, Zn-SiO₂, Cd-SiO₂, Cr-ZP, Zn-ZP and Cd-ZP) was conducted by X-ray Photoelectron Spectroscopy (XPS, XPSESCALAB 250Xi, Thermo Fisher Scientific) with an energy resolution of 0.44 eV (Ag 3d5/2).

3. Results and discussion

3.1. Hydrothermal synthesis of zeolite P

The Al/Si ratio was found to be a key factor for zeolite P formation [45], and then the Al/Si effect on zeolite P formation was studied (figure 1). Without Al addition (Al/Si = 0), no obvious driffusion peak with a typical background feature appeared. With increasing Al/Si, a new phase formed and its peak intensity became stronger till Al/Si of 1.00. Meanwhile, sodalite (JCPDS #89-9098) formed from Al/Si of 1.00, and its peak intensity increased for the higher Al/Si of 1.33. XRD analysis shows that the main new phase is zeolite P (JCPDS #71-0962), which suggests that zeolite P could be synthesized in a large range of Al/Si due probably to the flexibility of the Al-Si linkage in the framework of zeolite P [46].

To further study the mechanism of hydrothermal synthesis of zeolite P, XRD analyses of the specimens with Al/Si of 0.67 at different times and temperatures were carried out (figures 2(a) and 2(b)). Although the product was still amorphous at 8 h, the bulge shifted from 22° (Al/Si = 0 of figure 1) to 28°, reflecting that an early precursor of zeolite P tended to form under hydrothermal condition. Zeolite P appeared at 16 h clearly, and the intensity of zeolite P peaks kept growing and reached strongest at 48 h. However, the peaks of zeolite P became very weak, meanwhile analcime (JCPDS #70–1575) formed at 72 h, reflecting a transformation from zeolite P to
analcime. Similarly, figure 2(b) shows that the shift occurred at 160 °C, and then zeolite P formed stably from 180 °C to 200 °C. At 220 °C, almost all of the zeolite P transformed into analcime.

The SEM image (figure 3(a)) shows typical spherical granular clusters of the formed zeolite P [29], on which a lot of tetragonal columns and some combined fine particles are formed (figure 3(b)). Furthermore, the EDAX result for the column confirms that the molar ratio of Na/Al/Si = 4/5.2/10 is in the range of the ideal compositions of zeolite P, i.e., Na/Al/Si = 6/6/10 of zeolite P1 and Na/Al/Si = 4/4/12 of zeolite P2. The
above results revealed that a good crystalline zeolite P could be hydrothermally synthesized readily from the soil (model soil).

Accordingly, the hydrothermal synthesis of zeolite P might be described as follows: the model soil is dissolved hydrothermally first, and then the dissociative tetrahedra of $[\text{SiO}_4]^{-}$ and $[\text{AlO}_4]^{-}$ connect and thus forms the amorphous precursor. After that, the precursor gradually restructures and crystallizes into the spherical granular clusters of zeolite P at certain Al/Si, which is composed of a few combined fine particles and the tetragonal columns. Further for a longer time or higher temperature, zeolite P can convert into a more stable zeolite of analcime.

3.2. Behavior of immobilization of heavy metals by zeolite P via zeolitization

For a better comprehension of in situ heavy metal immobilization behavior via zeolitization, three different heavy metals (Cr$^{3+}$ (62 pm), Zn$^{2+}$ (74 pm) and Cd$^{2+}$ (95 pm)) were introduced, and their mixtures were used as the heavy metal-contaminated model soils (Cr-SiO$_2$, Zn-SiO$_2$ and Cd-SiO$_2$). The three zeolite Ps (ZP) synthesized from Cr-SiO$_2$, Zn-SiO$_2$ and Cd-SiO$_2$ were marked as Cr-ZP, Zn-ZP, and Cd-ZP respectively. The XRD analyses of the evolution of Cr-ZP with curing time, Zn-ZP with different Zn/Si ratio, and the comparison of ZP, Cr-ZP, Zn-ZP and Cd-ZP are shown in figure 4.

As shown in figure 4(a), with introducing Cr$^{3+}$ zeolite P tended to form at 48 h, and the peak intensities of zeolite P enhanced continuously with increasing time. Compared with that without Cr$^{3+}$ introduction (figure 2(a)), the introduced Cr$^{3+}$ seemed to exert a strong retardation influence on the zeolitization, and the formed zeolite P could also sustain a longer time. The result shows that the introduced heavy metal (Cr$^{3+}$) has influenced the crystallinity of the formed zeolite P greatly.

The influence should be attributed to the metal ligand effect of heavy metals (Cr$^{3+}$, Zn$^{2+}$ and Cd$^{2+}$) [47], i.e., the metal ligand could weaken the crystallinity of zeolite P by either retarding the dissolution of SiO$_2$ or hindering nucleation and growth of zeolite P crystals. Figure 4(b), S.1 and S.2 (Supporting materials) show that the crystallinity of R-ZP (R = Cr, Zn and Cd) was influenced a little when R/Si = 0.05. With higher R/Si ratio, the peak intensity of zeolite P decreased by degrees due to the enhanced metal ligand effect. In other words, the higher the concentration of heavy metal ions was, the stronger the metal ligand effect would be and the more heavily the crystallinity of zeolite P was influenced.
particles, and for this reason the charge among the three heavy metals introduced, Cr\(^{3+}\) has the peak intensity to ZP suggesting that the introduced Cr exerts the most obvious effect while Cd has a small influence on the crystallinity of Cr-ZP and Cd-ZP respectively. Because of the smallest ionic radius and most charge among the three heavy metals introduced, Cr\(^{3+}\) should have the highest charge density, which results in the most obvious metal ligand effect on the crystallinity of zeolite P [48]. On the contrary, the largest size of the Cd\(^{2+}\) seemed to exert a weakest metal ligand effect on the crystallinity. The metal ligand effect on crystallinity decreases in the following order: Cr-ZP > Zn-ZP > Cd-ZP (figure 4(b)), which agrees with the stabilities of metal ligands (Cr\(^{3+}\) > Zn\(^{2+}\) > Cd\(^{3+}\)) reported by Abollino et al [17].

For the immobilization of heavy metal by zeolite P (Cr-ZP), SEM images (figure 5) show many combined fine particles around columns. The EDAX analyses show that both the fine particles and column crystals belong to zeolite P. The structural immobilization contents of Cr by zeolite P, however, were very different, e.g., Cr/Na/Al/Si = 0.52/4.23/6.07/10 in the fine particle (figure 5(a)) and Cr/Na/Al/Si = 0.05/3.65/5.55/10 in the column of Cr-ZP (figure 5(b)), revealing that the fine particles of zeolite P has a much greater capability of in situ immobilizing Cr during zeolitization. Furthermore, both Na content and Si/Al of Cr-ZP (fine particle and column) were lower than that of ZP (Na/Al/Si = 4/5.2/10), reflecting that more Cr\(^{3+}\) (fewer Na\(^{+}\) left) and more [AlO\(_4\)]\(^{-}\) had been structured to balance charge in 8 mRs of zeolite P. This also suggests that Cr has entered into the structure of zeolite P by substituting Na.

For immobilization of heavy metal (Cr) by zeolite P via zeolitization, the tetrahedrons of [AlO\(_4\)]\(^{-}\) and [SiO\(_4\)]\(^{-}\) form precursor first and then the precursor grows into fine particles and further crystallized into columns of zeolite P. Because of smaller size of Cr, more Cr should enter into the structure readily, for which the precursor had to structure more [AlO\(_4\)]\(^{-}\) to balance the extra positive charge introduced from Cr\(^{3+}\). As discussed above Cr\(^{3+}\) has the strongest metal ligand effect on the crystallinity, and thus the precursor could prefer to form fine particles, and for this reason the fine particle of Cr-ZP had immobilized more Cr (figure 5(a)) than that of the column (figure 5(b)).

The SEM image of Zn-ZP is shown in figure 6, and relatively more Zn seemed to be in situ immobilized by the columns of Zn-ZP, e.g., the EDAX result for the fine particle is Zn/Na/Al/Si = 0.26/3.34/5.52/10 (figure 6(a)) and for the column is Zn/Na/Al/Si = 0.35/2.32/5.44/10 (figure 6(b)). It should be noted that the Al/Si of both the fine particle and column for Cr-ZP (figure 5) was higher than that for Zn-ZP but similar to that of ZP (figure 3), suggesting that the precursor of Zn-ZP structured fewer [AlO\(_4\)]\(^{-}\) into the framework to balance the fewer positive charge from Zn\(^{2+}\) during immobilizing Zn. With the smaller change and larger size (smaller
EDAX result of Cd columns readily to be immobilized due to its easy crystallization. Therefore, more column of Zn-ZP forms which also resulted in that more Zn entered in the framework of the ZP. Compared with ZP of Na, the more structured and Cd, a better crystal morphology of Cd-ZP is shown in figure 7. The largest size of Cd\(^{2+}\) (95 pm) seemed to act a similar part like Cr\(^{3+}\) (62 pm) during crystallization of Cd-ZP, i.e. the fine particles immobilized more Cd. Compared with ZP of Na/Al/Si = 4/5.2/10 (figure 3), a much higher Al/Si was found for both the fine particle and the column for Cd-ZP, suggesting that more [AlO\(_4\)]\(^-\) tetrahedrons had been structured into the framework of Cd-ZP. With the more structured [AlO\(_4\)]\(^-\), the flexible 8 mRs should not only distort to accommodate the largest Cd\(^{2+}\) but also balance the extra positive charge from introduced Cd\(^{2+}\), which resulted in a more difficult crystallization. So that the fine particle should form more readily than the column, which leads to the result that the more Cd was immobilized preferentially in the framework of the fine particles.

For a specific porous investigating, nitrogen gas sorption analysis was also carried out. As shown in figure 8, the specific surface area of ZP (R/Si = 0.00) was the minimum (3.5 m\(^2\)/g). When heavy metals were introduced (R/Si > 0.05/3), the porous of zeolite P increased at different level. With higher R/Si ratio, the specific surface area of the three products further increased. Cr-ZP with Cr/Si ratio of 0.20/3 reached the highest specific surface area of 30.4 m\(^2\) g\(^{-1}\) among the three products, and the porous of R-ZP increased in the following order: Cr-ZP > Zn-ZP > Cd-ZP.

Accordingly, the porous increase should be attributed to the metal ligand effect on the crystallinity of zeolite P. Without heavy metal introduction, the synthesized zeolite P was good crystalline, and the particle size was ~20 μm (figure 3). In other words, the granular cluster of zeolite P (ZP, R/Si = 0.00) was compact, which resulted in the lowest specific surface area. Due to the different metal ligand effect of introduced heavy metals, the crystallinity of R-ZP decreased (figure 4). So that the synthesized zeolite P transformed to larger granular cluster with more fine particles, e.g., the particle size reached ~60 μm for Cr-ZP (figure 5), ~40 μm for Zn-ZP (figure 6) and ~20 μm (figure 7) respectively. Thus, the granular clusters of R-ZP changed to be much looser than ZP, and their specific surface area increased.

With introducing heavy metals, zeolite P seemed to exhibit a self-adaptive structuring behavior, in which more [AlO\(_4\)]\(^-\) was structured into the framework of both fine particles and columns. As a result, not only the Al/Si ratio of columns after immobilization of heavy metals further closed to that of zeolite P1 (Al/Si = 6/10), but also the granular cluster of R-ZP transformed to much looser ones. The results indicated that the self-adaptive
3.3. Microscopic behavior of immobilization of heavy metals by zeolite P via zeolitization

High resolution XRD (HRXRD) were used to study the microstructure behavior of the immobilization of different heavy metals by zeolite P in detail, and more microstructure information could be also obtained by using the computer program package EXPGUI. The overall diffraction profiles of ZP, Cr-ZP, Zn-ZP and Cd-ZP were calculated as the sum of the identified ICSD patterns, including two types of zeolite P (Zeolite P1 (Na₆Al₆Si₁₀O₃₂·12H₂O, ICSD #9550) and Zeolite P2 (Na₄Al₄Si₁₂O₃₂·14H₂O, ICSD #68504)), Analcime (NaAlSi₂O₆·H₂O, ICSD #2930), Nitratine (NaNO₃, ICSD #16709), and Otavite (CdCO₃, ICSD #20181).

After calibrating the scale factor and zero point, the residual factors (Rwp, Rp and χ²) of the four diffraction profile calculations reduced. The better residual factors between the collected and the calculated profiles were
achieved by using TYPE 1 Background Function with 10 coefficients, Pseudo-Voigt/FCJ Asym peak profile Function, and Cylindrical Spherical Harmonic Preferential Orientation Function to model the four diffraction profiles.

Zeolite P is the main phase for in situ immobilizing heavy metals (figure 4), and therefore the best residual factors were achieved till refining the unit cell parameters, atomic positions and occupation numbers of zeolite P (Zeolite P1 and Zeolite P2). According to EDAX results, two isotropic atom substitutes should be constrained for the refining of zeolite P of Cr-ZP, Zn-ZP and Cd-ZP, i.e. substitution of tetrahedra Al for Si, and substitution of R (Cr, Zn and Cd) for extraframework Na. The residual factors were not convergent until heavy metal cations (Cr$^{3+}$, Zn$^{2+}$ and Cd$^{2+}$) substituted for extraframework Na$^{+}$. For zeolite P1, a convergent result could be obtained which suggested that zeolite P1 played a dominating role in the in situ immobilization of heavy metals via zeolitization. Additionally, the lightweight atom (O) and thermal displacement parameters were not refined due to the poor sensitivity at low diffraction angle of X-ray powder diffraction.

As shown in figure 9, the final refinements of the collected profiles of ZP, Cr-ZP, Zn-ZP and Cd-ZP can be further refined into the compositions of zeolite P1, zeolite P2, analcime, nitratine, and otavite. ZP (figure 9(a)) could be refined into zeolite P1, zeolite P2 and analcime, and for Cr-ZP (figure 9(b)) and Zn-ZP (figure 9(c)), besides zeolite P1, P2 and analcime, nitratine also appeared which should be a reaction product of the replaced Na$^{+}$ and free NO$_3^-$ in the solution. While for Cd-ZP (figure 9(d)), nitratine might be too little to be detected, and the trace otavite should be a product of the added Cd$^{2+}$ with dissolved CO$_2$ during the experiment.

The relative content of the above compositions and the refined microstructure information for zeolite P1 in ZP, Cr-ZP, Zn-ZP and Cd-ZP were showed in table 1, which could provide the information on the in situ immobilization of heavy metals via zeolitization. From table 1, with the heavy metals introducing the proportion of zeolite P1 in Cr-ZP, Zn-ZP and Cd-ZP changed greatly compared with that of ZP, and their changes were also greater than that of zeolite P2 respectively. The larger variation suggests that the heavy metals immobilized in the framework exerts a larger influence on zeolite P1 formation than that of zeolite P2, and the influences on Cr-ZP and Cd-ZP seem to be larger than Zn-ZP. From figure 9, the peak intensities of Cr-ZP, Zn-ZP and Cd-ZP became weaker than that of ZP especially for Cr-ZP and Zn-ZP, suggesting that the heavy metals immobilized in

Figure 9. Observed (cross), calculated (line) and their difference (bottom line) of X-ray diffraction patterns of zeolite P without/with introduction of heavy metals. (a) ZP; (b) Cr-ZP; (c) Zn-ZP; (d) Cd-ZP.
tetrahedral structure of zeolite P1 increased from 40% to 60%, and the framework has made their crystallization with difficulty. In addition, the HRXRD analysis (figure 9) confirms a lot of amorphous phases for Cr-ZP and Zn-ZP (the bulge in the range from 20° to 35° in figures (b) and (c)), which might be due to the influence of metal ligand on the crystallinity. As discussed in 3.1, the metal ligand can influence the immobilization of heavy metals via crystallization for Cr-ZP and Zn-ZP.

Since the stronger sensibility for zeolite P1 formation during immobilization of heavy metals by ZP, table 1 also reveals the detail information on the self-adaptive structuring behavior with the substitution of original Na with the heavy metals introduced, and the substitution between [AlO4]− and [SiO4]2− in the framework of zeolite P1 [36] respectively. Before immobilization of heavy metals (ZP), there exist 32% Na1 in the structure of zeolite P1 available to be substituted with heavy metals, while after different heavy metals were introduced, the Na1 substitution rates by heavy metals have changed. For Cr-ZP, the all 32% Na1 was available to be substituted with Cr, while for Zn-ZP and Cd-ZP, only 17% and 9% Na1 could be substituted with Zn and Cd for Zn-ZP and Cd-ZP respectively. The different substitution rates might be caused by different difficulty of their substitution, and the smallest size of Cr3+ (62 pm) seemed to substitute Na1 (102 pm) most easily, while larger size of heavy metals, especially Cd2+ (95 pm), substituted Na1 with more difficulty. Although there also exist more Na2 (42%) in zeolite P1 available for substituting heavy metals than that of Na1, rarer Na2 could be substituted with Cr (0%) and Zn (3%). While 14% Na2 and 9% Na1 could be substituted with Cd suggesting that there exists a different substitution capability between Na1 and Na2.

According to the shortest distance between heavy metal and Framework Oxygen (R-FO) shown in table 1, for ZP the R1-FO (2.708 Å) is shorter than the R2-FO (2.736 Å), reflecting that the Framework O (8 mRs) possesses stronger attractive potential at Na1 than Na2 for immobilized heavy metals, which causes that the heavy metals prefer substituting Na1 to substituting Na2 for binding and balancing charge. Due to both the smaller size of heavy metal than Na and the stronger metal ligand effect, there tends to occur a competitive substitution between Na1 and Na2, e.g., the smallest heavy metal Cr substitutes Na1 much easier than Na2, leading to that the all Na1 have been substituted with Cr but nor of Na2. However, for the substitution of Na with larger heavy metals the competitive substitution seems to be inconspicuous, e.g., Cd seems to have similar performance of substituting Na1 and Na2 which might be due to the similar cation size of Cd2+ (95 pm) and Na+(102 pm).

On the other hand, table 1 shows that after immobilization of heavy metals the both Al1 and Al2 in the tetrahedral structure of zeolite P1 increased from 40% (ZP) to 48% (Cr-ZP), 45% (Zn-ZP), 48% (Cd-ZP) and from 29% (ZP) to 38% (Cr-ZP), 38% (Zn-ZP), 38% (Cd-ZP) respectively. This suggests that in the 8 mRs of zeolite P1 some [SiO4]2− has been substituted with [AlO4]−, which results in more negative charges carried for the framework of zeolite P1. The substituted heavy metal cations (Cr, Zn and Cd), therefore, could coordinate with more Framework O of zeolite P1 to balance their positive charges. The refined R/Si molar ratios of zeolite P1 show that the maximum content of immobilized heavy metals were 2.7/10 of Cr-ZP, 1.8/10 of Zn-ZP, and 1.9/10 of Cd-ZP in which the immobilization of Cr is more than that of Zn or Cd, in agreement with the above discussion.

| Phase composition (wt%) | Cr-ZP | Zn-ZP | Cd-ZP |
|-------------------------|-------|-------|-------|
| Zeolite P1 | 62.4 | 49.6 | 37.8 |
| Zeolite P2 | 34.5 | 29.0 | 57.9 |
| Alcalime | 3.1 | 21.8 | 12.6 |
| Nitratine | — | 8.8 | 8.8 |
| Otavite | — | — | 2.3 |

| Microstructure information of zeolite P1 | Cr-ZP | Zn-ZP | Cd-ZP |
|------------------|-------|-------|-------|
| Na1 | 0.32 | 0.15 | 0.23 |
| R1 | — | 0.32 | 0.17 |
| Na2 | 0.42 | 0.42 | 0.39 |
| R2 | — | 0.00 | 0.03 |
| Al1 | 0.40 | 0.48 | 0.45 |
| Si1 | 0.60 | 0.52 | 0.55 |
| Al2 | 0.29 | 0.38 | 0.38 |
| Si2 | 0.71 | 0.62 | 0.62 |

| Refined molar ratio | R/Na1/Al1/Si | 3.5/5.5/10 | 2.7/3.6/10 | 1.8/4.7/10 | 1.9/4.4/10 |
|---------------------|--------------|--------------|--------------|--------------|--------------|
| Shortest distance of R-FO (Å) | R1-FO | 2.708(30) | 2.297(3) | 2.4690(2) | 2.5632(2) |
| R2-FO | 2.736(22) | — | — | 2.404(2) | — |

| Cell parameters (Å) | R = b | 10.0172(3) | 10.0019(13) | 10.0033(9) | 10.0171(8) |
|---------------------|-------|--------------|--------------|--------------|--------------|
| R = c | 10.035(9) | 10.036(21) | 10.0395(13) | 10.0457(12) | — |
Based on the information obtained from Rietveld refinement, the microstructure of refined zeolite P1 without/with immobilizing heavy metals (Cr, Zn and Cd) could be further described visually. The microstructural visualization of the refined zeolite P1 of ZP (figures 10(a) and 10(c)) clearly shows the intersected 8 mRs structure and encapsulated Na⁺ inside. With immobilizing Cr (figures 10(b) and 10(d)), the Cr³⁺ could substitute for all the Na1 positions because the shorter Na1-FO distance (2.708 Å) has a stronger...
attraction potential. Meanwhile, the immobilized Cr\(^{3+}\) got much closer to the 8 mRs of zeolite P1 (Cr–FO of 2.2978 Å) due to the effect of binding and the flexible ellipsoid of 8 mRs. Thus, the unit cell parameters of zeolite P1 shrank as shown in table 1 and figure 10, i.e., a = b decreased from 10.0172 Å (ZP) to 10.0019 Å (Cr–ZP), and c decreased from 10.0579 Å (ZP) to 10.0369 Å (Cr–ZP). Similarly, the Zn\(^{2+}\) finally substituted a number of Na\(^{+}\) (most of Na1 position) in the 8 mRs of Zn–ZP, and while the Cd\(^{2+}\) managed to substitute almost same Na1 and Na2 in the 8 mRs of the Cd–ZP (figures 10(e)–(h)) respectively. The unit cell of zeolite P1, thus, tended to shrink according to the size of heavy metal cations immobilized, for instance, the c decreased to 10.0395 Å of Zn–ZP, 10.0457 Å of Cd–ZP respectively. Clearly, the smaller heavy metals can enter into the framework more readily, and the larger heavy metal immobilized can result in the larger distortion (shrink) of the framework. However, the ligand effect should be considered at the same time during the immobilization of heavy metals.

Although Cr–ZP, Zn–ZP and Cd–ZP were mainly crystallized into zeolite P1 and zeolite P2, the heavy metal seemed to prefer to be immobilized by zeolite P1. During the immobilization of heavy metals via crystallization, zeolite P1, possessing a higher Al/Si ratio (Al/Si = 6/10), could structure more AlO\(_4\)\(^–\), and thus led to the framework (8 mRs) distorting/shrinking more readily. On the other hand, the immobilized heavy metal cations substituted the original Na of zeolite P1 via a competitive substitution between Na1 and Na2. For instance, the smallest Cr\(^{3+}\) (62 pm) preferred to substitute all Na1 (32%) in framework in which Na1 is closer to the FO (Na1-FO = 2.708 Å and Na2-FO = 2.736 Å), while the larger size of Cd\(^{2+}\) (95 pm) leads to an even substitution of Na1 (9%) and Na2 (14%) with Cd.

3.4. Chemical environment variation of the introduced heavy metals during zeolitization

Rietveld refinement (table 1 and figure 10) reveals that the smaller heavy metal cations (Cr\(^{3+}\) and Zn\(^{2+}\)) were easier to substitute Na1 of zeolite P1 than the larger Cd\(^{2+}\). Therefore, the different heavy metals (different in both size and charge) would coordinate with different FO during immobilization, and the evolution of chemical environment of heavy metals before/after immobilization were studied by XPS (figure 11).

The XPS analysis (figure 11) shows definite shifts toward lower Binding Energy (BE) of each introduced heavy metal after zeolitization. In detail, for Cr 2p\(_{3/2}\) (figure 11(a)) the observed BE (circles) shifted from 577.18 eV (Cr–SiO\(_2\)) to 577.04 eV (Cr–ZP); for Zn 2p\(_{3/2}\) (figure 11(b)), the observed BE shifted from 1022.38 eV (Zn–SiO\(_2\)) to 1022.04 eV (Zn–ZP); for Cd 3d\(_{5/2}\) (figure 11(c)), the observed BE shifted from 406.28 eV (Cd–SiO\(_2\)) to 404.48 eV (Cd–ZP). The distortion in structure should account for the shifts due to the immobilization of heavy metals by ZP, i.e., the coordination of these heavy metals with FO of zeolite P has caused the chemical environment changes (shifts).
The deconvolution of the XPS spectra shows that each heavy metal can only exist one peak (dash line) before immobilizing by zeolitization, while the spectrum of the introduced heavy metal should split into a few peaks after zeolitization due to its chemical environment change. As shown in figure 11(a), the BE of Cr for Cr-SiO$_2$ (before zeolitization) was deconvoluted only into 577.25 eV, while for Cr-ZP (after zeolitization) the BE split into 577.4 eV and 576.8 eV, which belongs to Cr$^{3+}$-OH and Cr$^{3+}$-O respectively [49]. Similarly, the BE of Zn for Zn-ZP (figure 11(b)) split into 1022.7 eV (Zn$^{2+}$-OH) and 1021.9 eV (Zn$^{2+}$-O) and the BE of Cd for Cd-ZP (figure 11(c)) split into 404.8 eV (Cd$^{2+}$-OH) and 404.3 eV (Cd$^{2+}$-O) respectively. These results reveal that before zeolitization the introduced heavy metals in model soil existed electrostatically adsorbed/free, and while after the heavy metals were in situ immobilized by zeolite P1, the bond/coordination with both framework O (Cr-O, Zn-O and Cd-O) and structural H$_2$O (Cr-OH, Zn-OH and Cd-OH) resulted in the change for the chemical environment of heavy metals.

On the other hand, the dimensions of split for the peak of R-O and R-OH were also very different due to the different self-adapted results with the different sizes and charges of the heavy metals during immobilization of heavy metals by zeolite P. The difference is shown in table 2 as the R-O / R-OH area ratio. The much higher R-O / R-OH ratio for Cr$^{3+}$ and Zn$^{2+}$ than for Cd$^{2+}$, suggests that the smaller Cr$^{3+}$ and Zn$^{2+}$ have bonded/coordinated with more framework O than the larger Cd$^{2+}$. The smaller heavy metal cations, especially with more charges, should possess higher charge density, and thus have the capability of getting close to the 8 mRs with higher Al/Si ratio could complex with heavy metal readily; the immobilized heavy metals substituted the original Na (Na1 and Na2) competitively because of their different cation size, for instance, the smallest Cr$^{3+}$ could substitute all Na1 because Na1 is closer to the framework oxygen and possesses stronger attraction potential; for the largest Cd$^{2+}$, similar to Na$^+$ size, however, an even substitution of Na1 (9%) and Na2 (14%) with Cd was obtained.

As a result of self-adaption, the chemical environment of the encapsulated heavy metals were influenced with both framework Oxygen (R–O) and structure H$_2$O Oxygen (R-OH) at different levels. In other words, the smaller heavy metal cation could get closer to the framework, and thus coordinated with more FO.

| Table 2. Relative contents of R-O / R-OH in Cr-ZP, Zn-ZP and Cd-ZP conducted from deconvolution of XPS spectrums. |
|-------------|-------------|-------------|
| Cr-ZP       | Zn-ZP       | Cd-ZP       |
| R-O / R-OH  | 2.11        | 2.79        | 1.06        |

4. Conclusions

To develop a new hydrothermal soil remediation technology, model polluted soil was converted into zeolite P to in situ immobilize heavy metals in soil via hydrothermal zeolitization. The results can be summarized as follows:

Zeolite P could be synthesized from soil (model soil) hydrothermally with Al/Si ratio (0.33–1.0), which suggests that the zeolite could be synthesized in a large composition range. The longer curing time or higher curing temperature was favorable to zeolite P formation, while too long curing time (>48 h) or too high curing temperature (>200 °C) could make the formed zeolite P transform into analcime. With immobilizing heavy metals (Cr, Zn and Cd), zeolite P (Cr-ZP, Zn-ZP and Cd-ZP) formed more slowly because the heavy metal ligands exerted hinder effect on the nucleation and growth of zeolite P. The ligand effect due to the different heavy metals introduced could cause a delay in crystallization with the order of Cr > Zn > Cd, and resulted in a more porous granular cluster of zeolite P. Usually the larger the charge density of the heavy metals, the stronger the ligand effect.

With immobilizing heavy metals, zeolite P exhibited a self-adaptive structuring behavior: the framework of zeolite P structured more [AlO$_4$]$^{2-}$ to accommodate heavy metals because the flexible 8-member-Ring structure with higher Al/Si ratio could complex with heavy metal readily; the immobilized heavy metals substituted the original Na (Na1 and Na2) competitively because of their different cation size, for instance, the smallest Cr$^{3+}$ could substitute all Na1 because Na1 is closer to the framework oxygen and possesses stronger attraction potential; for the largest Cd$^{2+}$, similar to Na$^+$ size, however, an even substitution of Na1 (9%) and Na2 (14%) with Cd was obtained.

As a result of self-adaption, the chemical environment of the encapsulated heavy metals were influenced with both framework Oxygen (R–O) and structure H$_2$O Oxygen (R-OH) at different levels. In other words, the smaller heavy metal cation could get closer to the framework, and thus coordinated with more FO.

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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

The authors declare that they have no conflict of interest.

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