



Influence of soil washing with a chelator on subsequent chemical immobilization of heavy metals in a contaminated soil

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ABSTRACT

To assess the influence of soil washing with a chelator on the chemical immobilization of heavy metals, batch experiments were performed on the fine fraction of a contaminated soil under various operating conditions. Results show that pre-washing with EDTA facilitated the chemical immobilization of Cu and Cr, while an opposite effect for Pb and Zn was observed, in particular when Ca(OH)₂ was added as the immobilizing agent. Metal fraction analyses of the soils indicate that soil washing can reduce the metal mobility by removing the labile fractions, while it may also destabilize some strongly bound fractions, reversely increasing the mobility and thus compromising the subsequent immobilization performance to some extents. To secure an effective combination of soil washing and chemical immobilization for the remediation of heavy metal-contaminated sites, a comprehensive study on metal fraction distribution in the soil is needed.

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1. Introduction

The available remediation technologies for heavy metal-contaminated soils are mainly divided into two groups: namely immobilization, such as in situ chemical fixation, and separation/concentration, such as soil washing [1]. Soil washing is to transfer contaminants from the soil solid phase to the aqueous phase by dissolving or suspending them with some chelating agents or acid solutions, or to concentrate them into a small volume of soil via separating them from sand fractions [2]. However, a significant part of heavy metals usually remains in the washed soils, especially if the soil is rich in organic matter or clay minerals, which often have a strong affinity for the target heavy metals [3–5]. If these remaining heavy metals are present in stable mineral forms or bound to non-labile soil fractions, they are less mobile, less bioavailable, and thus less toxic. In fact, the heavy metal mobility and bioavailability are increasingly used to assess the success or failure of soil remediation instead of the remaining total metal content [6]. Although the majority of the originally labile metal fractions can be favorably removed by washing with chelating agents [7,8], some studies found that the remaining metals become more weakly associated with soil components or more readily mobile [9,10], likely due to the kinetic ligand-attacked metal detachment, soil dissolution, or the cation exchange between the chelator complexes and the soil particles.

The metal mobility in soils can be effectively reduced by the chemical immobilization via adsorption, complexation, precipitation/co-precipitation, or a combination thereof [11–16]. To sufficiently reduce the metal mobility and improve the soil quality on severely metal-contaminated sites, where most metals exist as labile forms [7,17], a large amount of immobilizing agents is often required. This may cause new problems like aggregate cementation or eutrophication of surface water [13,18,19].

Therefore, a combination of soil washing and chemical immobilization seems a feasible method to overcome the above-mentioned weaknesses. Soil washing can reduce the volume of the soil that requires further treatment by separating the sand fractions from the bulk soil, and may remove the most labile metal fractions to reduce the mobility. The subsequent chemical immobilization treatment can further immobilize the remaining mobile metals with a smaller amount of immobilizing agents. In fact, some studies tried this combination and added chemical agents to immobilize heavy metals such as Pb remaining in the soil after the soil washing [20,21]. In those studies, however, the influence of soil washing on the subsequent immobilization of heavy metals remained unclear.

Therefore, the objective of this study is to investigate the influence of soil washing on the subsequent chemical immobilization with a special interest in the feasibility of their sequential combination for the remediation of metal-contaminated fine soils. Ethylene diamine tetra-acetic acid and its salts (EDTA) have been extensively reported to appreciably increase the dissolution and mobility of heavy metals [7,22–25], having themselves a low aquatic toxicity and no bioaccumulation in organisms throughout the food chain [26]. Therefore, EDTA was selected as the representative chelator

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Nomenclature

| | |
|-------------|---|
| M_i | metal concentrations in the solid/solution extraction with $\text{HNO}_3/\text{H}_2\text{SO}_4$ solution (pH 3.2) [mg l^{-1}] |
| MI_i | M_i/R_i , metal mobility index, dimensionless number |
| N_{total} | the overall normality of S1 and S2 fractions in Cu, Cr, Ni, Pb, and Zn in the original soil [equiv. kg^{-1}], and herein was $195.7 \text{ equiv. kg}^{-1}$ |
| R_i | thresholds level of a metal-contaminated soil to be categorized as a hazardous solid [mg l^{-1}], and $R_{Cu} = 100 \text{ mg l}^{-1}$, $R_{Ni} = 5 \text{ mg l}^{-1}$, $R_{Zn} = 100 \text{ mg l}^{-1}$, $R_{Cr} = 15 \text{ mg l}^{-1}$, and $R_{Pb} = 5 \text{ mg l}^{-1}$, as prescribed by CMEP [46] |
| S1 | percentage of the exchangeable metal extracted in the first step of modified Tessier's sequential extractions [32], and was calculated based on the corresponding individual metal content in the original soil |
| S2 | percentage of the acid extractable metal extracted in the second step of the modified Tessier's sequential extractions [32], and was calculated based on the corresponding individual metal content in the original soil |
| S3 | percentage of the reducible metal extracted in the third step of the modified Tessier's sequential extractions [32], and was calculated based on the corresponding individual metal content in the original soil |
| S4 | percentage of the oxidizable metal extracted in the fourth step of the modified Tessier's sequential extractions [32], and was calculated based on the corresponding individual metal content in the original soil |
| S5 | percentage of the residual metal extracted in the final step of the modified Tessier's sequential extractions [32], and was calculated based on the corresponding individual metal content in the original soil |
| Sum | $\sum_{i=1}^5 MI_i$, sum of the mobility indices of Cu, Cr, Zn, Pb and Ni, dimensionless number |

for the soil washing in this study. The influence of soil washing with EDTA on the subsequent chemical immobilization is attained through comparing the results from a series of batch experiments, as illustrated in Fig. 1, and the details are described in Section 2.

2. Materials and methods

2.1. The studied soil

The studied soil was collected from a demolished electroplating plant in the north of Guangzhou city, China. Only the fine soil particles, after being sieved by a 60 mesh-laboratory test sieve, were employed herein, since the pilot soil washing test had demonstrated that the separated sand fractions were clean enough to be directly returned to the site after being washed by a 0.5 mmol l^{-1} EDTA solution, and only metals in the fine fractions needed further chemical immobilization. The characteristics of these fine soil particles are listed in Table 1. The soil was found to be slightly acidic, and contained five heavy metals at various concentrations: copper (Cu), nickel (Ni), chromium (Cr), lead (Pb), and zinc (Zn). Their speciation was further analyzed by

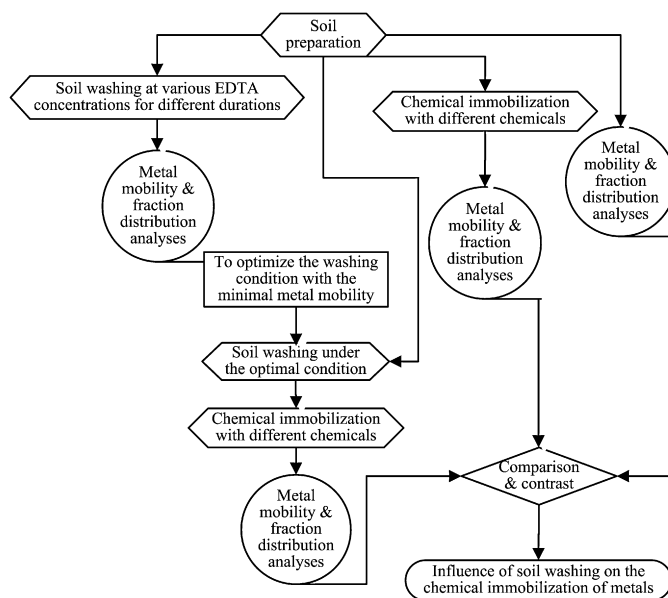


Fig. 1. The process of this study.

a D/Max-III A powder X-ray diffractometer (XRD, Rigaku Industrial Corp., Japan), operating with Cu $K\alpha$ radiation at 40 kV and 45 mA, scanning over the range $0\text{--}80^\circ$ in 2θ , step size 0.02° . The XRD spectra illustrate (Fig. 2) that the main metal species with a rather high concentration and crystallinity included zinc chromium carbonate hydroxide hydrate ($\text{Zn}_4\text{Cr}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$), chromium phosphate ($\text{Cr}_5(\text{P}_3\text{O}_{10})_3$), nickel sulfide (Ni_7S_6), lead chromium oxide (Pb_3CrO_6), nickel carbonate hydrate ($\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$), and lead oxide carbonate hydroxide ($\text{Pb}_{10}(\text{CO}_3)_6(\text{OH})_6\text{O}$).

2.2. Soil treatment

In this study, three treatments were evaluated in order to study the influence of the soil washing on the subsequent chemical immobilization: (1) the soil washing with EDTA was conducted on the original soil to minimize the metal mobility in the treated soils (Exps. 1.1–1.9 in Table 2), where each 1.00 g of the soil was mixed

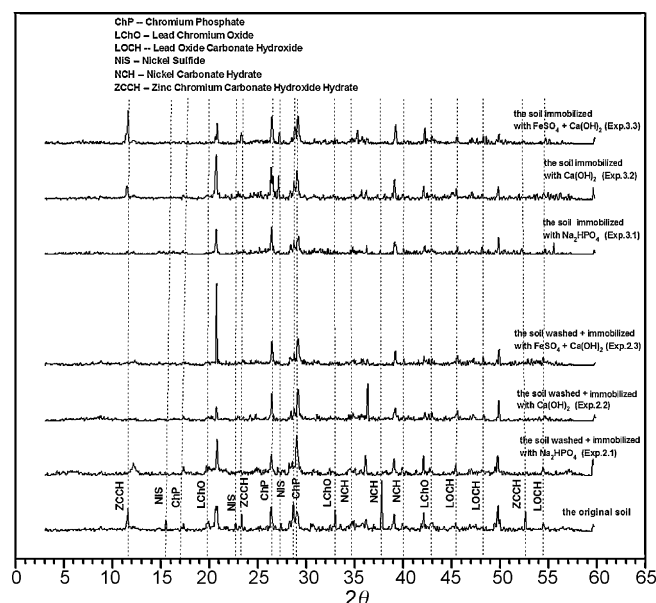


Fig. 2. XRD spectra of the original and treated soils.

Table 1
Characteristics of the soil.

| Soil properties | Value | Characterization method | Equipment |
|---|-------------|--|--|
| pH | 5.5 | Method 9045 in USEPA SW-846 [31] | 320 pH meter (Mettler Toledo, Switzerland) |
| Density (dry soil, g cm ⁻³) | 1.06 | | |
| Organic matter content (% by mass) | 5.89 | Heating the dried samples at 350 °C for 5 h | |
| Particle size distribution (by volume) | | | |
| Sand (≥50 μm) | 34.11% | Directly scanning on soil solution (1:10) | OMEC LS-POP(III) laser particle size analyzer (OMEC, China) |
| Silt (<50 μm, >2 μm) | 59.16% | | |
| Clay (≤2 μm) | 6.73% | | |
| Metal content (mg kg ⁻¹) | | | |
| Cu | 778 ± 25 | HCl–HF–HClO ₄ –HNO ₃ acid digestion, followed by Method 6010C of USEPA SW-846 [31] | Optima 3000XL inductively coupled plasma-atomic emission spectrometer (PerkinElmer, USA) |
| Cr | 3813 ± 186 | | |
| Zn | 13988 ± 552 | | |
| Pb | 995 ± 62 | | |
| Ni | 1965 ± 67 | | |

with 20.0 ml of EDTA solution of various concentrations at different washing durations using a 200 ± 10 rpm rotary shaker. Then, the mixture was centrifuged at 5000 rpm for 10 min to separate the washing solution from the soil. The supernatant was carefully discarded with a pipette, and the residue in the centrifuge vial was flushed with 10 ml of deionized water to completely remove the dissociated metals [27]. After separating the flushing water from the soil by centrifuging at 5000 rpm for 10 min, the metal mobility in the residual soil was analyzed. (2) The sequential combination of the soil washing and chemical immobilization was carried out (Exps. 2.1–2.3 in Table 2), where each 1.00 g of the original soil was firstly washed under the optimal conditions determined by Exps. 1.1–1.9. Then, the washed soil was intermittently shaken with 1.0 ml of solution containing different immobilizing agents for 7 days under room temperature, and the metal mobility and fraction distribution in the soil were again analyzed. (3) To serve as the control for the evaluation of the influence of soil washing on the subsequent chemical immobilization, the chemical immobilization with the same immobilizing agents was performed on the original soil without prior washing (Exps. 3.1–3.3 in Table 2), where each 1.00 g of the original soil was intermittently shaken with 1.0 ml of the different immobilizing solution for 7 days under room temperature.

The amounts of the added immobilizing chemicals were estimated based on the corresponding stoichiometric requirement

of the total metals, which need to be immobilized. The overall normality of all the ion exchangeable (S1) and acid extractable metals (S2) in the original soil was defined as N_{total} , and herein was 195.7 equiv. kg⁻¹. Although some previous research often used the molar ratio of 3/5 P/Pb as the basis of Pb₅(PO₄)₃Cl or Pb₅(PO₄)₃OH to lead-contaminated soils [12], the normality of Pb in S1 and S2 only accounted for 0.8% of N_{total} in this soil. Therefore, the phosphate amount was about 0.01 g g⁻¹ Na₂HPO₄ based on providing a 1/3 P/ N_{total} ratio for metal phosphate precipitates (Me₃(PO₄)₂, Me=Pb, Cu, Zn, Ni; or CrPO₄), as the previous study reported [28]. The added 0.01 g g⁻¹ lime here was 1.5 times of the stoichiometric amount to form metal-hydroxide precipitates, as used in some previous study [12]. Here both 0.01 g FeSO₄ and 0.01 g Ca(OH)₂ were added per one gram soil, because the precipitation of Fe oxides, followed by the Fe sulfate application, causes acid release, and the lime is usually used to avoid soil acidification. Due to the insufficient lime, the mobility of Cu, Zn and Pb in soil immobilized with Fe(II) sulfate and lime was ever observed to increase [29] and a ratio of lime/Fe oxide necessary for maintaining soil pH should be higher than 1:1 [19].

All experiments were quadruplicated, and the analyses on metal mobility and fraction distribution were duplicated. In addition, the soil sample was randomly collected in each experiment to minimize the potential distortion by soil heterogeneities. Both the averages and standard deviations are reported.

Table 2
Operating parameters of soil treatments.

| Purpose | Index | EDTA washing ^a | | Chemical immobilization ^b |
|--|----------|---------------------------|--|---|
| | | Washing time (h) | EDTA concentration (mmol l ⁻¹) | Chemicals added (based on a gram of the dry soil) |
| To identify the optimal conditions with the minimal resulting mobility of metals | Exp. 1.1 | 0.5 | 0.5 | None |
| | Exp. 1.2 | 0.5 | 1.0 | None |
| | Exp. 1.3 | 0.5 | 5.0 | None |
| | Exp. 1.4 | 1.0 | 0.5 | None |
| | Exp. 1.5 | 1.0 | 1.0 | None |
| | Exp. 1.6 | 1.0 | 5.0 | None |
| | Exp. 1.7 | 2.0 | 0.5 | None |
| | Exp. 1.8 | 2.0 | 1.0 | None |
| | Exp. 1.9 | 2.0 | 5.0 | None |
| To study the influence of soil washing on the sequential immobilization | Exp. 2.1 | 2.0 | 5.0 | 0.01 g Na ₂ HPO ₄ |
| | Exp. 2.2 | 2.0 | 5.0 | 0.01 g Ca(OH) ₂ |
| | Exp. 2.3 | 2.0 | 5.0 | 0.01 g FeSO ₄ , 0.01 g Ca(OH) ₂ |
| To serve as the control for Exps. 2.1–2.3 | Exp. 3.1 | None | None | 0.01 g Na ₂ HPO ₄ |
| | Exp. 3.2 | None | None | 0.01 g Ca(OH) ₂ |
| | Exp. 3.3 | None | None | 0.01 g FeSO ₄ , 0.01 g Ca(OH) ₂ |

^a 20 ml g⁻¹ of the washing solution/soil ratio.

^b 7-Day intermittently mixing under room temperature.

Table 3
Sequential extraction for metal fraction distribution [32].

| Extraction step | Metal fractionation | Extraction agents | Extraction conditions |
|-----------------|--|---|-----------------------|
| 1 | Exchangeable | 1 mol l ⁻¹ MgCl ₂ , pH 7 | 1 h, room temperature |
| 2 | Weakly complexed and bound to carbonates | 1 mol l ⁻¹ CH ₃ COONa, pH 5 | 5 h, room temperature |
| 3 | Bound to Fe/Mn oxides of low crystallinity | 0.04 mol l ⁻¹ NH ₂ OH-HCl in 25% (v/v) CH ₃ COOH | 6 h, 96 °C |
| 4 | Bound to organic matter and sulfides | 30% H ₂ O ₂ + HNO ₃ (pH 2), 3.2 M CH ₃ COONH ₄ in 20% (v/v) HNO ₃ | 5 h, 85 °C |
| 5 | Residual | Concentrated HCl, HF, HClO ₄ , HNO ₃ | 6 h, 190 °C |

2.3. Analyses of metals in the treated soil

2.3.1. Metal mobility

The metal mobility in soils was determined by the solid/solution extraction with HNO₃/H₂SO₄ solution, as prescribed by Chinese Ministry of Environment Protection (CMEP) with a minor modification [30]. This procedure involved shaking each 1.00 g of soil in 10 ml of the HNO₃/H₂SO₄ solution (which was diluted from a mixture of the concentrated HNO₃ and H₂SO₄ at the volume ratio of 2:1 to pH 3.20 ± 0.05 with deionized water) at 20 ± 2 °C for 18 ± 2 h on a rotary shaker at 200 ± 5 rpm, and the extract was subsequently separated from the soil by centrifuging at 5000 rpm for 10 min under room temperature. The supernatant was collected, and then acidified with 10% HNO₃ (by volume) to a pH less than 2 for heavy metal concentration analyses using an Optima 3000XL inductively coupled plasma-atomic emission spectrometer (ICP, PerkinElmer, USA), based on Method 6010C of USEPA SW-846 [31].

Similar to the previous study [32], the mobility index (MI) of different metals was defined with Eq. (1), with the aim to compare the potential hazardous effect caused by the mobility of different

toxic heavy metals:

$$MI_i = \frac{M_i}{R_i} \quad (1)$$

2.3.2. Metal fraction distribution

Although the sequential extraction procedure originally developed by Tessier et al. [27] is often criticized due to non-specificity of extractants and possible readsorption of metals during extraction, this scheme has been widely used to provide the qualitative information on the metal fraction distribution and their relative binding strength with the soil particles [33]. Therefore, the present metal fraction distribution was analyzed using this scheme, and the extractions were carried out progressively on 1 ± 0.005 g of the freeze-dried metal-contaminated soil. The detailed extraction conditions have been presented in our previous study [32] (Table 3). Following each extraction, the samples were centrifuged at 5,000 rpm for 10 min, and the supernatant was collected for the further metal concentration determination by ICP. Prior to the next extraction step, the residual was flushed with 10 ml of deionized water, and the solution was then removed after centrifugation.

Table 4
Metal mobility after washing in function of EDTA concentrations and durations.

| MI _i | Washed soils | | | Original soil | |
|-----------------|--------------------------------|----------------------------|----------------------------|----------------------------|---------------|
| | [EDTA] (mmol l ⁻¹) | Washing duration (h) | | | |
| | | 0.5 | 1.0 | | 2.0 |
| Sum | 0.5 | 3.381 ^a | 0.745 ^d | 0.603 ^g | 3.942 |
| | 1.0 | 0.808 ^b | 0.720 ^e | 0.619 ^h | |
| | 5.0 | 0.791 ^c | 0.696 ^f | 0.435 ⁱ | |
| Cu | 0.5 | 0.025 ± 0.000 ^a | 0.012 ± 0.001 ^d | 0.010 ± 0.00 ^g | 0.033 ± 0.001 |
| | 1.0 | 0.011 ± 0.000 ^b | 0.011 ± 0.002 ^e | 0.008 ± 0.000 ^h | |
| | 5.0 | 0.007 ± 0.001 ^c | 0.005 ± 0.001 ^f | 0.005 ± 0.000 ⁱ | |
| Cr | 0.5 | 0.637 ± 0.017 ^a | 0.639 ± 0.001 ^d | 0.514 ± 0.00 ^g | 3.676 ± 0.021 |
| | 1.0 | 0.717 ± 0.016 ^b | 0.625 ± 0.010 ^e | 0.535 ± 0.009 ^h | |
| | 5.0 | 0.677 ± 0.000 ^c | 0.604 ± 0.008 ^f | 0.359 ± 0.004 ⁱ | |
| Zn | 0.5 | 2.061 ± 0.005 ^a | 0.022 ± 0.000 ^d | 0.020 ± 0.00 ^g | 0.005 ± 0.000 |
| | 1.0 | 0.020 ± 0.000 ^b | 0.024 ± 0.005 ^e | 0.022 ± 0.000 ^h | |
| | 5.0 | 0.059 ± 0.000 ^c | 0.044 ± 0.000 ^f | 0.027 ± 0.000 ⁱ | |
| Pb | 0.5 | 0.086 ± 0.006 ^a | 0.011 ± 0.004 ^d | 0.009 ± 0.00 ^g | 0.006 ± 0.000 |
| | 1.0 | 0.008 ± 0.001 ^b | 0.010 ± 0.002 ^e | 0.009 ± 0.002 ^h | |
| | 5.0 | 0.012 ± 0.000 ^c | 0.010 ± 0.002 ^f | 0.007 ± 0.000 ⁱ | |
| Ni | 0.5 | 0.572 ± 0.007 ^a | 0.062 ± 0.001 ^d | 0.051 ± 0.00 ^g | 0.223 ± 0.006 |
| | 1.0 | 0.052 ± 0.002 ^b | 0.051 ± 0.004 ^e | 0.045 ± 0.001 ^h | |
| | 5.0 | 0.036 ± 0.000 ^c | 0.033 ± 0.004 ^f | 0.037 ± 0.000 ⁱ | |

^a Exp. 1.1.

^b Exp. 1.2.

^c Exp. 1.3.

^d Exp. 1.4.

^e Exp. 1.5.

^f Exp. 1.6.

^g Exp. 1.7.

^h Exp. 1.8.

ⁱ Exp. 1.9.

Comparison of the cumulative heavy metal contents from each extraction with their corresponding totals indicated 89%–107% of metal recovery efficiency, indicating an acceptable accuracy of this sequential extraction scheme.

3. Results and discussion

3.1. Mobility of metals in the soil washed by EDTA

Exps. 1.1–1.9 were performed to optimize the soil washing for attaining the minimum metal mobility. The relationship between the washing conditions and the MI values in the corresponding washed soils is presented in Table 4. Washing with an EDTA solution of a higher concentration and/or for a longer duration decreases the sum of MI values. Therefore, the soil washed in Exp. 1.9 obtained the lowest sum of MI values, and 2.0 h washing with 5.0 mmol l^{-1} EDTA was thus selected as the optimal operating condition for the later experiments.

As shown in Fig. 2, however, the mobility of some metals after washing increased under certain operating conditions. Especially, the Zn mobility from the soil washed in Exp. 1.1 was unexpectedly high, and a similar increase in the Pb and Ni mobility was also observed. In general, the added EDTA favors the complexation with the labile fractions of the target metals, and thus decreases metal mobility. However, previous studies showed that EDTA-promoted dissolution also plays a substantial role, especially concerning metal remaining in aged contaminated sites [34,35]. EDTA-promoted dissolution generally occurs in two steps: a fast destabilization where the free and/or complexed EDTA is bound to the metals via surface complexation, and a following rate-limiting mobilization [7,8,32]. The increase of these metal mobility in the washed soils are probably because the added EDTA solution has destabilized some metals which have a relatively strong bond with the soil, but has not completely mobilized them in time due in part to the insufficient EDTA dosage and washing duration.

A higher Zn mobility was observed in the soil washed with a more concentrated EDTA solution for a longer washing (Exps. 1.4–1.6 and Exps. 1.7–1.9). It is inferred that 2 h and/or 5.0 mmol l^{-1} EDTA may not be adequate to completely mobilize all the destabilized Zn by soil washing. However, the application of the higher EDTA concentration led to a decrease in the Cr, Cu and Ni mobility in the washed soils, hinting that the Zn mobilization may be slower than that of Cr, Cu and Ni, as reported in the previous study [36]. In addition, the higher Zn level in an absolute sense may also contribute to the increased EDTA demand to complete the mobilization of destabilized Zn.

To further confirm the potential mobilization of the metals destabilized by the added EDTA solution in the initial phase of the soil washing, the metal mobility in the soil washed in Exp. 1.9 was determined after 7-day ageing under room temperature, and the results are presented in Table 5, which also tabulates the mobility of soil componential elements, such as Fe, Mn, Ca, Mg and Al. Of interest, besides metals of concern, a great amount of Ca was released after washing. The pH of the EDTA washing solution initially was 4.9, and slightly increased to 5.3 at the end of the washing, so Ca release should be ascribed to the acid dissolution, as explained in our previous study [32]. As listed in Table 3, a higher mobility of Ca and Mg as well as Pb, Ni, and Zn after 7-day ageing, corroborates that the acid dissolution can also play a role for the Pb, Ni and Zn release besides EDTA destabilization. This is also indirectly supported by the thermodynamic estimation, which shows the hydroxide precipitates of Pb, Ni and Zn have a higher solubility than that of Cu and Cr at pH 4.9–5.3. Both the mobilization of the destabilized metals and acid dissolution are rate-limiting process [8,32], so they result in the metal mobilization during the ageing processes. These

released metals should consume some immobilizing agents, presumably compromising the performance of a subsequent chemical immobilization. With the aims to verify this hypothesis, the metal mobility and fraction distribution in the soil, immobilized by the added chemical agents with or without soil washing, were subsequently studied.

3.2. Heavy metal mobility and fraction distribution affected by EDTA soil washing in the immobilized soils

Table 6 shows the relationship between chemical immobilizations (in Exps. 2.1–2.3 with soil washing and Exps. 3.1–3.3 without soil washing) and the MI values in the treated soils. The corresponding metal fraction distribution is also presented in Table 7. As shown in Table 6, the washing in advance decreased the Sum of MI values in the soils immobilized with $\text{Ca}(\text{OH})_2$ or Na_2HPO_4 . That decrement can be mainly ascribed to a decrease in Cr mobility by the soil washing (from 2.537 in Exp. 3.1 to 0.372 in Exp. 2.1; from 2.950 in Exp. 3.2 to 0.664 in Exp. 2.2), since the total metal mobility in the original soil was dominated by Cr (93.2%), and 90.2% of MI_{Cr} was removed by soil washing. As above discussed, the soil washing with 5.0 mmol l^{-1} EDTA for 2.0 h was found to increase the mobility of Zn and Pb, and thus may increase their final mobility in the immobilized soils. In fact, Table 6 also shows that the washing increased the Sum of MI values from 0.067 to 0.091 in the soil immobilized with a mixture of FeSO_4 and $\text{Ca}(\text{OH})_2$, where the majority of Cr was successfully immobilized in the original soil (MI_{Cr} decreased from 3.676 to 0.037). That phenomenon indicates that the influence of soil washing on the metal final mobility in the immobilized soils depends on not only the washing operation itself but also the immobilization performance of the added chemical agents.

Besides, the different properties of heavy metals in contaminated soils often make the chemical immobilization more complicated. The immobilizing agents may effectively immobilize one or more metals, but impact an opposite effect on the mobility of other metals. As evidenced in Table 6, $\text{Ca}(\text{OH})_2$ was found to increase the Zn and Pb mobility, but to reduce the mobility of Cu, Cr and Ni in the original soil (Exp. 3.2). However, $\text{Ca}(\text{OH})_2$ increased the MI_{Cr} from 0.359 to 0.664 (Exp. 2.2) and resulted in a higher MI_{Pb} (from 0.009 in Exp. 1.9 to 0.025 in Exp. 2.2) in the washed soil. In addition, Na_2HPO_4 (Exp. 2.1) seemed incapable of decreasing the mobility of Ni and Cr in the washed soils, although it was found to immobilize some of them in the original soil (Exp. 3.1). These phenomena suggest that the EDTA soil washing can have a negative effect on the subsequent immobilization. The washing process may compromise the immobilization effectiveness of the added chemicals, if they are effective, or it can enlarge the increment of the metal mobility caused by the added chemicals if they do, due to the incomplete mobilization of the destabilized metals during the soil washing.

The comparison of the metal mobility in the soils treated by Exp. 3.2 and Exp. 2.2 demonstrates that the washing decreased the Cr and Cu mobility but increased the Pb and Zn mobility in the immobilized soils. The different level in the labile S1 fraction of Cr and Cu may explain the influence of the soil washing. Table 7 shows that the original soil had the measurable levels of Cr and Cu in the S1 fraction but negligible levels for Pb and Zn. The majority of these Cr and Cu fractions can be readily removed by the soil washing, and it may overcome the above-mentioned negative effect, leading to a decrease in their corresponding final mobility in the soils chemically immobilized. However, the negligible S1 levels of Pb and Zn resulted in a trivial removal by the soil washing, and highlighted the above-mentioned negative effect to increase their mobility. As an exception, the soil washing seemed not to significantly influence the Cr and Cu immobilization with a mixture of FeSO_4 and $\text{Ca}(\text{OH})_2$ in Exp. 2.3, as well as the Cu and Pb immobilization with Na_2HPO_4 .

Table 5
Metals leached by solid/solution extraction with HNO₃/H₂SO₄ solution.

| Heavy metal or soil componential element | Concentration of metal leached from the soil washed by Exp. 1.9 (mg l ⁻¹) | |
|--|---|--------------------|
| | Without ageing | After 7-day ageing |
| Cu | 0.54 ± 0.01 | 0.27 ± 0.03 |
| Cr | 7.34 ± 0.06 | 7.13 ± 0.19 |
| Zn | 2.69 ± 0.03 | 3.62 ± 0.36 |
| Pb | 0.045 ± 0.002 | 0.056 ± 0.008 |
| Ni | 0.184 ± 0.001 | 0.244 ± 0.024 |
| Mg | 0.72 ± 0.04 | 1.05 ± 0.03 |
| Ca | 37.65 ± 0.20 | 40.43 ± 0.57 |
| Al | 0.30 ± 0.06 | 0.36 ± 0.01 |
| Fe | 0.43 ± 0.19 | 0.35 ± 0.01 |

It is likely because the metal mobility reduction caused by these added chemicals greatly outweighed that resulting from the soil washing. Therefore, the metal fraction distribution, especially the level of the labile fraction, also dominates the influence of soil washing on the subsequent chemical immobilization, except that the added chemicals are so highly efficient to completely overwhelm the impact of the soil washing.

Table 7 also demonstrates that the soil washing often decreased the residual metal fraction (S5), which may be redistributed to the less refractory fractions, i.e., that bound to amorphous Fe/Mn oxides (S3) or to soil organic matter and sulfides (S4). During the ageing, some destabilized but not completely mobilized metal species will continue the mobilization process, inducing an increase in the metal mobility and consuming more immobilizing agents. As a result, the effectiveness of the subsequent chemical immobilization was compromised to a certain extent. Besides, the soil componential elements destabilized in the soil washing, especially Ca²⁺ by the acid dissolution, can nullify some Na₂HPO₄ by forming CaHPO₄ or Ca₂(PO₄)₃ precipitates, thus decrease the increment of the S2 fraction during the chemical immobilization. This can be indirectly corroborated by the lowest S2 levels of all five metals in the washed soil sequentially immobilized by Na₂HPO₄ (Exp. 2.1) among these three chemical agents as listed in Table 7. Moreover, the remaining EDTA can partly prevent the precipitation of target metals with the added agents in the subsequent immobilization. To further investigate the influences of the soil washing, the mobility and fraction distribution of the individual metal in the chemically immobilized soils are therefore discussed in details as follows.

3.2.1. Cu

As listed in Table 6, the soil washing with EDTA facilitated the decrease in the Cu mobility in the chemically immobilized soils with Ca(OH)₂, while its influence in the soils immobilized with Na₂HPO₄ or a mixture of FeSO₄ and Ca(OH)₂ was ignorable. This can be ascribed to their different effectiveness for Cu immobilization in the original soil, where the Ca(OH)₂ did not significantly reduce the Cu mobility as the other two immobilizers did, likely due to the complex between Cu²⁺ and the increasingly dissolved soil organic matter in such an alkaline environment [37] (pH 9.9).

This is also supported by the decrease in the S4 level of Cu as listed in Table 7. However, the soil washing significantly decreased the Cu mobility by removing the majority of its measurable S1 fraction (2.52%, as listed in Table 7), so it can in turn promote the immobilization effectiveness of Ca(OH)₂, thereby diminishing the variance of the resulting Cu mobility among these three immobilization treatments.

Both Na₂HPO₄ and a mixture of FeSO₄ and Ca(OH)₂ were found to successfully minimize the Cu mobility in the original soil (Exps. 3.1 and 3.3). The added Na₂HPO₄ can provide a slightly alkaline soil environment (pH 8.7), which was reported to favor the Cu immobilization. The ferric oxy-hydroxides, formed by the reaction of FeSO₄ and Ca(OH)₂ when exposed to air, was ever reported to effectively immobilize Cu by surface complex under such an alkaline environment (pH 9.4) [38]. Therefore, although the soil washing significantly lessened Cu mobility by removing the liable Cu fraction, it did not demonstrate a further enhancement for chemical immobilization.

The Cu fraction distribution as listed in Table 7 demonstrates that the chemical immobilization on the original soil decreased S1 and S4 fractions of Cu, but increased its S2 and S3 fractions. The added immobilizing agents often prefer to first react with the labile S1 fraction to form oxy-hydroxide or carbonate precipitates, which are often extracted during the second step of Tessier's sequential extraction to increase the S2 fraction in the original soil. Besides, a more alkaline environment maintained by the added chemicals also facilitates the dissolution of soil organic matter [37,39]. As a result, the Cu species bound to the dissolved organic matter are mobilized along and the S4 fraction consequently decreases. The precipitation reaction between the mobilized Cu and the added immobilizing agents as well as the inner-sphere complexing with the Fe/Mn oxides under such an alkaline condition may also break the bonds between Cu and soil organic matter, leading to a further increase in the S2 or S3 fractions of Cu. However, the soil washing was found to redistribute the Cu species: S1, S3 and S5 decreased, but S2 and S4 increased to different extents [29]. Therefore, the increase in S2 and the decrease in S4 caused by the added immobilizing agents were counterbalanced by the soil washing.

Table 6
Metal mobility in function of immobilizers with or without EDTA washing.

| M _i | Soil without immobilization | | Soil immobilized by Na ₂ HPO ₄ | | Soil immobilized by Ca(OH) ₂ | | Soil immobilized by FeSO ₄ + Ca(OH) ₂ | |
|----------------|-----------------------------|-------------------------|--|-------------------------|---|-------------------------|---|-------------------------|
| | Original soil | With washing (Exp. 1.9) | Without washing (Exp. 3.1) | With washing (Exp. 2.1) | Without washing (Exp. 3.2) | With washing (Exp. 2.2) | Without washing (Exp. 3.3) | With washing (Exp. 2.3) |
| Sum | 3.942 | 0.435 | 2.566 | 0.436 | 3.091 | 0.756 | 0.067 | 0.091 |
| Cu | 0.033 ± 0.001 | 0.005 ± 0.000 | 0.004 ± 0.000 | 0.002 ± 0.000 | 0.019 ± 0.001 | 0.003 ± 0.000 | 0.001 ± 0.000 | 0.003 ± 0.000 |
| Cr | 3.676 ± 0.021 | 0.359 ± 0.004 | 2.537 ± 0.06 | 0.372 ± 0.014 | 2.950 ± 0.104 | 0.664 ± 0.044 | 0.037 ± 0.005 | 0.035 ± 0.013 |
| Zn | 0.005 ± 0.000 | 0.027 ± 0.000 | 0.001 ± 0.000 | 0.022 ± 0.001 | 0.013 ± 0.004 | 0.019 ± 0.001 | 0.007 ± 0.001 | 0.017 ± 0.002 |
| Pb | 0.006 ± 0.000 | 0.007 ± 0.000 | 0.002 ± 0.000 | 0.004 ± 0.001 | 0.011 ± 0.000 | 0.025 ± 0.004 | 0.002 ± 0.001 | 0.002 ± 0.001 |
| Ni | 0.223 ± 0.006 | 0.037 ± 0.000 | 0.025 ± 0.002 | 0.037 ± 0.002 | 0.098 ± 0.032 | 0.044 ± 0.000 | 0.020 ± 0.000 | 0.036 ± 0.003 |

Table 7
Metal fraction distribution in the treated soils.

| Fraction of heavy metals ^a (%) | | Soil without immobilization | | Soil immobilized by Na ₂ HPO ₄ | | Soil immobilized by Ca(OH) ₂ | | Soil immobilized by FeSO ₄ + Ca(OH) ₂ | |
|---|----|-----------------------------|-------------------------|--|-------------------------|---|-------------------------|---|-------------------------|
| | | Original soil | With washing (Exp. 1.9) | Without washing (Exp. 3.1) | With washing (Exp. 2.1) | Without washing (Exp. 3.2) | With washing (Exp. 2.2) | Without washing (Exp. 3.3) | With washing (Exp. 2.3) |
| Cu | S1 | 2.53 ± 0.06 | 0.73 ± 0.20 | 0.79 ± 0.01 | 0.41 ± 0.02 | 1.49 ± 0.06 | 0.31 ± 0.00 | 0.34 ± 0.00 | 0.61 ± 0.13 |
| | S2 | 9.24 ± 0.14 | 9.88 ± 0.17 | 10.94 ± 0.01 | 8.00 ± 0.26 | 10.75 ± 0.06 | 8.41 ± 0.79 | 15.48 ± 0.00 | 8.97 ± 0.86 |
| | S3 | 30.83 ± 2.60 | 27.85 ± 2.53 | 34.89 ± 2.46 | 37.02 ± 1.83 | 40.81 ± 1.73 | 41.03 ± 0.73 | 39.01 ± 1.23 | 36.56 ± 1.17 |
| | S4 | 20.46 ± 1.70 | 26.87 ± 0.03 | 15.22 ± 0.00 | 15.68 ± 4.65 | 11.13 ± 0.89 | 12.97 ± 1.09 | 9.91 ± 1.14 | 13.56 ± 3.23 |
| | S5 | 36.94 ± 2.74 | 25.24 ± 4.07 | 38.16 ± 5.33 | 29.47 ± 1.83 | 35.81 ± 1.20 | 27.85 ± 3.05 | 35.26 ± 0.96 | 30.88 ± 2.42 |
| Cr | S1 | 5.72 ± 0.27 | 0.52 ± 0.29 | 1.02 ± 0.14 | 0.81 ± 0.14 | 1.26 ± 0.07 | 1.19 ± 0.08 | 0.16 ± 0.01 | 0.15 ± 0.01 |
| | S2 | 4.82 ± 0.33 | 4.53 ± 0.22 | 1.07 ± 0.14 | 1.18 ± 0.01 | 2.96 ± 0.07 | 3.13 ± 0.05 | 5.21 ± 0.01 | 3.33 ± 0.15 |
| | S3 | 73.73 ± 0.41 | 68.91 ± 0.33 | 73.04 ± 0.63 | 64.85 ± 2.82 | 82.92 ± 1.97 | 73.72 ± 2.16 | 82.21 ± 1.83 | 74.49 ± 1.85 |
| | S4 | 8.66 ± 0.72 | 9.73 ± 0.88 | 13.81 ± 2.12 | 17.67 ± 1.39 | 7.27 ± 0.29 | 6.84 ± 0.72 | 6.99 ± 0.41 | 7.01 ± 0.17 |
| | S5 | 7.07 ± 0.23 | 4.42 ± 0.00 | 11.07 ± 1.26 | 3.88 ± 1.56 | 5.60 ± 0.23 | 3.24 ± 0.69 | 5.43 ± 0.34 | 3.13 ± 0.49 |
| Zn | S1 | 0.12 ± 0.02 | 0.13 ± 0.02 | 0.05 ± 0.00 | 0.16 ± 0.04 | 0.04 ± 0.00 | 0.04 ± 0.00 | 0.07 ± 0.01 | 0.11 ± 0.02 |
| | S2 | 38.08 ± 0.66 | 28.72 ± 0.74 | 32.00 ± 0.00 | 37.31 ± 2.26 | 35.99 ± 0.00 | 42.57 ± 1.71 | 32.39 ± 0.01 | 39.73 ± 1.92 |
| | S3 | 53.65 ± 2.35 | 52.91 ± 0.54 | 56.40 ± 1.63 | 39.16 ± 1.81 | 51.50 ± 0.11 | 35.69 ± 0.56 | 54.81 ± 2.42 | 37.57 ± 1.94 |
| | S4 | 6.59 ± 0.57 | 3.91 ± 0.00 | 8.75 ± 0.75 | 7.94 ± 0.41 | 9.76 ± 0.30 | 6.97 ± 0.23 | 10.20 ± 0.94 | 7.76 ± 0.03 |
| | S5 | 1.56 ± 0.23 | 1.13 ± 0.00 | 2.80 ± 0.36 | 2.23 ± 0.09 | 2.70 ± 0.18 | 1.53 ± 0.16 | 2.53 ± 0.08 | 1.65 ± 0.09 |
| Pb | S1 | 0.04 ± 0.01 | 0.03 ± 0.01 | 0.03 ± 0.00 | 0.02 ± 0.01 | 0.03 ± 0.01 | 0.05 ± 0.01 | 0.01 ± 0.00 | 0.03 ± 0.00 |
| | S2 | 16.30 ± 0.40 | 14.15 ± 0.84 | 2.02 ± 0.00 | 3.30 ± 0.00 | 13.81 ± 0.01 | 12.43 ± 0.05 | 5.59 ± 0.00 | 7.18 ± 0.58 |
| | S3 | 43.27 ± 0.83 | 42.29 ± 3.90 | 53.57 ± 1.37 | 51.91 ± 1.96 | 45.66 ± 0.31 | 42.77 ± 2.62 | 52.97 ± 5.40 | 47.83 ± 3.52 |
| | S4 | 6.91 ± 1.61 | 5.93 ± 0.07 | 9.14 ± 1.20 | 7.16 ± 0.48 | 4.84 ± 0.10 | 8.34 ± 0.81 | 8.90 ± 1.33 | 6.80 ± 1.07 |
| | S5 | 33.48 ± 1.58 | 34.04 ± 2.60 | 35.24 ± 4.39 | 34.06 ± 2.71 | 35.67 ± 1.31 | 32.86 ± 2.65 | 32.53 ± 2.60 | 34.62 ± 0.41 |
| Ni | S1 | 0.24 ± 0.08 | 0.15 ± 0.07 | 0.16 ± 0.00 | 0.18 ± 0.01 | 0.11 ± 0.00 | 0.06 ± 0.00 | 0.10 ± 0.00 | 0.11 ± 0.01 |
| | S2 | 6.72 ± 1.22 | 4.60 ± 0.21 | 3.27 ± 0.00 | 3.25 ± 0.29 | 3.70 ± 0.00 | 3.75 ± 0.18 | 3.75 ± 0.00 | 3.57 ± 0.19 |
| | S3 | 76.64 ± 1.37 | 75.59 ± 3.56 | 81.18 ± 1.3 | 72.86 ± 2.62 | 85.09 ± 1.69 | 82.78 ± 2.19 | 83.18 ± 1.38 | 79.34 ± 4.15 |
| | S4 | 11.51 ± 1.30 | 14.25 ± 0.67 | 10.96 ± 0.68 | 17.41 ± 3.08 | 8.69 ± 1.54 | 8.32 ± 2.25 | 10.51 ± 0.36 | 11.11 ± 1.17 |
| | S5 | 4.90 ± 1.66 | 3.60 ± 1.26 | 4.43 ± 0.89 | 4.49 ± 0.63 | 2.41 ± 0.01 | 3.28 ± 0.10 | 2.47 ± 0.04 | 4.06 ± 0.18 |

^a Calculated based on the individual metal content in the original soil.

3.2.2. Cr

As shown in Table 6, a mixture of FeSO_4 and $\text{Ca}(\text{OH})_2$ effectively reduced the Cr mobility in the soil, and that process seemed less influenced by the soil washing. The added FeSO_4 has been widely reported to successfully reduce Cr(VI) to Cr(III) [40] and the latter is of little mobility and often exists in the form of Cr_2O_3 or $\text{Fe}_x\text{Cr}_{2-x}\text{O}_3$ [41]. Therefore, this mixture was so effective to completely overwhelm the potential positive or negative effects on the Cr mobility, induced by soil washing.

Table 6 also shows that the MI_{Cr} values in the soils treated by Exps. 2.1 and 2.2 were lower than those in Exps. 3.1 and 3.2, indicating that soil washing can result in a substantial decrease of the Cr mobility in the soil immobilized by Na_2HPO_4 or $\text{Ca}(\text{OH})_2$. In the original soil, about 5.72% of Cr was S1 (as listed in Table 7), most of which originated from weakly adsorbed $\text{Cr}_2\text{O}_7^{2-}$ and Cr^{3+} on the minerals [32]. The soil washing removed most of S1 (from 5.72% to 0.52%), and thus reduced MI_{Cr} from 3.676 to 0.359.

Besides, the Na_2HPO_4 or $\text{Ca}(\text{OH})_2$ was found to immobilize the weakly bound Cr^{3+} to considerably decrease S1 (1.02 and 1.26, respectively), leading to a decrease in Cr mobility in the original soil (from 3.676 to 2.537 or 2.950). However, the MI_{Cr} in Exps. 2.1 and 2.2 were higher than that in Exp. 1.9, suggesting that the Na_2HPO_4 or $\text{Ca}(\text{OH})_2$ may have an opposite effect when being applied on the washed soils. In the soils where the Na_2HPO_4 or $\text{Ca}(\text{OH})_2$ was added, the pH was raised from the acidic to the alkaline (from 5.5 to 8.7 or 9.9), which favors the oxidation of Cr(III) to form the more mobile Cr(VI) [42], or the formation of soluble Cr(III) hydroxide complexes, as well as the desorption of Cr(VI) from the soil particles due to the increase in the negative charges accumulated on the soil surface. Besides, the added chemicals also resulted in the dissolution of some chromium oxide, such as lead chromium oxides or zinc chromium carbonate hydroxide oxides. The XRD spectra of the treated soils, as illustrated in Fig. 2, shows that the lead chromium oxide in the soils treated by Exps. 3.1 and 3.2, and zinc chromium carbonate hydroxide oxides in Exp. 3.1 disappeared. Therefore, these processes may offset the efficiency of the immobilization on the weakly adsorbed Cr^{3+} species, especially after the majority of these Cr species were removed by soil washing. Moreover, as discussed above, the soil washing can also facilitate the destabilization of some less labile fractions via EDTA–surface complexes, and thus may accelerate the above-mentioned desorption or oxidation process. These destabilized Cr fractions may be mobilized over time during the ageing for chemical immobilization. As a result, these added immobilizing agents contrarily increased the Cr mobility in the washed soils, as listed in Table 6.

3.2.3. Zn

As shown in Table 6, the soil washing was found to increase the Zn mobility in all the treated soils with these three immobilizing agents. That is not surprising since the soil washing itself significantly increased the Zn mobility as above discussed. Therefore, the combination of washing and immobilization could not effectively immobilize Zn, compared with the chemical immobilization only. As discussed above, the mobilization of the destabilized Zn was not completed at the end of the soil washing due to its rate-limiting nature. The mobilization continued in the 7-day ageing, so the Zn mobility increased (as listed in Table 4), likely in the form of Zn–EDTA complexes. These complexes may be immobilized by the added $\text{Ca}(\text{OH})_2$ (in Exp. 2.2) via the precipitation or the exchange of the EDTA–complexed Zn^{2+} with Ca^{2+} . Due to thermodynamic constraints, however, the added Na_2HPO_4 cannot effectively immobilize Zn–EDTA (in Exp. 2.1). The metal fraction distribution, which shows a S1 increase in Exp. 2.1 (from 0.13% to 0.16%) but a decrease in Exp. 2.2 (from 0.13% to 0.04%), may indirectly support this hypothesis.

As listed in Table 7, the S2 was higher and S3 was lower in all the washed and immobilized soils (Exps. 2.1–2.3) than in the corresponding soils only immobilized (Exps. 3.1–3.3), although the soil washing reduced the S2 level in the original soil likely due to the dissolution of zinc carbonates by EDTA. This indicates that some portion of the destabilized Zn may be redistributed from S3 to S2 to increase their mobility with the aid of the immobilizing agents during the ageing. However, the detailed pathway and mechanism are still unclear, and further investigations are needed.

3.2.4. Pb

As shown in Table 6, an increase in the Pb mobility was found in the $\text{Ca}(\text{OH})_2$ -immobilized soils no matter whether it was washed or not, and such an increment became more pronounced in the washed soil (Exp. 2.2). Although the soil washing only slightly increased the Pb mobility in the original soil (MI_{Pb} from 0.006 to 0.007), the ageing process may enlarge such an increment (MI_{Pb} from 0.011 to 0.025) due to the continued mobilization of the destabilized Pb, especially when the less effective immobilizing agent, i.e., $\text{Ca}(\text{OH})_2$, was added. The S4 decrease in Exp. 3.2 as well as the disappearance of lead chromium oxide in XRD spectra illustrated in Fig. 2 indicates that the dissolution of soil organic matter and lead chromium oxide in $\text{Ca}(\text{OH})_2$ -based alkaline environment may result in so less effective Pb immobilization. Besides, the favorable formation of soluble Pb hydroxide complexes at that pH 9.9 may be another reason. However, the influence of soil washing on the effective immobilization by Na_2HPO_4 or a mixture of FeSO_4 and $\text{Ca}(\text{OH})_2$, appeared trivial.

Table 7 demonstrates that the added Na_2HPO_4 or the mixture of FeSO_4 and $\text{Ca}(\text{OH})_2$ decreased the S2 fraction of Pb in the original soil, probably due to the formation of pyromorphite-type minerals [43], the inner-sphere complexes, or co-precipitates with Fe/Mn oxides [19,44]. However, these immobilizers were often found to increase its S2 fraction in the washed soils, showing that the soil washing impacts a counterbalance effect on these changes.

3.2.5. Ni

As listed in Tables 6 and 7, although the soil washing removed some liable S1 fraction of Ni and reduced its mobility in the original soil, the washing treatment was found to increase the MI_{Ni} of the soils mobilized with Na_2HPO_4 or a mixture of FeSO_4 and $\text{Ca}(\text{OH})_2$ from 0.025 to 0.037 or from 0.020 to 0.036. In the washed soil, the Na_2HPO_4 or a mixture of FeSO_4 and $\text{Ca}(\text{OH})_2$ seemed completely nullify for the Ni mobility, and the added $\text{Ca}(\text{OH})_2$ even increased the MI_{Ni} (Exp. 2.2), although these three immobilizers were all found to decrease its mobility in the original soil to some extents. This phenomenon suggests that the soil washing may destabilize some Ni species, as listed in Table 5. Therefore, it restricted the effectiveness of the subsequent chemical immobilization, since these immobilizers were not so highly effective to completely overwhelm the negative effect induced by soil washing. As an exception listed in Table 6, the soil washing was found to reduce MI_{Ni} in the soils immobilized with $\text{Ca}(\text{OH})_2$. This may be due to the less efficiency of the $\text{Ca}(\text{OH})_2$ immobilization on Ni, which makes the removal of the S1 fraction by washing dominant.

Table 7 demonstrates an obvious increase in the S3 fraction of Ni in all the immobilized soils, probably due to the co-precipitation or surface complex between Ni and Fe/Mn oxides at a slightly alkaline environment [17]. Although the soil washing itself marginally alter the S3 level in the original soil, the S3 level in the washed and immobilized soil was lower compared with the treated soils by chemical immobilization only, hinting an above-mentioned counterbalance effect of the soil washing on the metal immobilization.

4. Conclusion

The soil washing decreased the overall metal mobility to different extents depending on the EDTA concentration and contact time. A longer contact time or a more concentrated EDTA solution often decreased the mobility of Pb, Ni and Cu in the washed soil, but increased the Zn mobility. The mixture of FeSO_4 and $\text{Ca}(\text{OH})_2$ was found to most effectively reduce the overall metal mobility in the immobilized soils, and its efficiency was less dependent on whether the soil was washed in advance. Metal fraction distribution analyses disclose that the studied soil had measurable labile fractions of Cu and Cr, and that the soil washing removed the majority of them. As a result, the soil washing appreciably reduced their mobility in the soil immobilized by $\text{Ca}(\text{OH})_2$, which was not highly effective to immobilize these two metals. On the contrary, the soil washing was found to increase the mobility of Zn and Pb in the soils immobilized by $\text{Ca}(\text{OH})_2$, likely owing to the continued mobilization of the destabilized metals during the ageing.

This interpretation is also indirectly supported by the metal fraction distribution analyses, which show that metal fractions were often redistributed during chemical immobilization: S4 decreased with an accompanied increase in the S2, S3, or S5 fractions likely due to the increased dissolved organic matter in an alkaline environment, while the soil washing was found to change the extent and direction of these redistributions. However, the pathway, pattern and mechanism are still not clear, and extensive investigations with the aid of new approaches, such as the isotope tracer technology [45], and precise quantification in mass balance schemes, may be therefore required in the future.

Therefore, the influence of soil washing on the subsequent immobilization performance in their combination is dominated by these three competitive processes: the removal of labile fractions, the destabilization of less labile fractions by soil washing, and chemical immobilization. If chemical immobilization is highly effective, the soil washing may hardly influence the chemical immobilization. If the metal labile fractions are non-ignorable and the immobilizer is less effective, the soil washing may facilitate the immobilization. If the metal labile fractions are trivial while immobilizing agents are not so highly effective, the soil washing may obstruct the immobilization, even resulting in an increase of metal mobility.

So, the sequential combination of EDTA soil washing and chemical immobilization may have advantages for the treatment of contaminated soils containing substantial amounts of labile metals, like in freshly contaminated sites. To secure effective remediation of heavy metal-contaminated sites, a comprehensive study on metal fraction distribution in the target soil is needed.

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