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The acid dissolution characteristics of cadmium fixed by a novel Ca-Fe-Si composite material

Aijun Yao^{1,5}, Xiang Guo¹, Man Zhao^{2,3}, Shizhong Wang^{2,3,5},
Yetao Tang^{2,3,5}, Rongliang Qiu^{2,4,5,*}

¹School of Geography and Planning, Sun Yat-sen University, Guangzhou 510275, China

²School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China

³Guangdong Provincial Key Lab of Environmental Pollution Control and Remediation Technology, Sun Yat-sen University, Guangzhou 510275, China

⁴Guangdong Provincial Key Laboratory of Agricultural & Rural Pollution Abatement and Environmental Safety, College of Natural Resources and Environment, South China Agricultural University, Guangzhou 510642, China

⁵Guangdong Laboratory for Lingnan Modern Agriculture, Guangzhou 510642, China

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ABSTRACT

Ca-Fe-Si material (CIS), a novel composite material rich in calcium, iron, manganese and silicon showed marvelous immobilization properties for heavy metal(loid)s in soils. To elucidate the acid stability of Cd fixed by CIS (CIS-Cd) and the underlying immobilization mechanisms, the acid dissolution characteristics of CIS-Cd were investigated by using acid titration method and X-ray diffraction (XRD) technique. The results showed that CIS-Cd had distinctive acid buffering capacity in different pH ranges. Based on the titration curve between dissolution rate of CIS-Cd and pH, CIS-Cd can be divided into non acid-stable Cd (9.4%), moderately acid-stable Cd (22.5%) and acid-stable Cd (68.1%). XRD analysis of CIS-Cd at different pH intervals and the correlation curves of dissolution rates of Cd and concomitant elements indicated that non acid-stable Cd was mainly bound by carbonate, silicate and sulfate (CdCO_3 , Cd_2SiO_4 and CdSO_4) or co-precipitated with the corresponding calcium salts. Moderately acid-stable Cd was mainly bound by magnesium-aluminum-silicon containing minerals or electrically bound by manganese iron minerals. Acid-stable Cd remaining undissolved at $\text{pH} < 2.42$ included CdFe_2O_4 and ferromanganese minerals strongly bound Cd. It was by multilateral fixation mechanisms that Ca-Fe-Si material possessed marvelous immobilization capability for Cd and strong resilience to environmental acidification as well. The findings implicated that proper combination of calcium-iron-silicon containing minerals could develop novel promising amendments with high efficiency in heavy metal(loid)s immobilization and strong resilience to environmental change.

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* Corresponding author.

E-mail: eesqrl@mail.sysu.edu.cn (R. Qiu).

Introduction

According to the national soil pollution survey bulletin published in 2014, 7% of sampled arable soils in China contained higher contents of Cd than the soil quality standard (National Soil Pollution Survey Bulletin of China, 2014). Cd as the top inorganic pollutant existed in farmland has aroused great concern from government and public. Compared with other heavy metal(loid)s, labile Cd in soil can be easily transferred and taken up by crops to enter the food chain and threaten human health (Loganathan et al., 2012). Finding efficient and cost-effective remediation measures to guarantee safe production on the large areas of farmland contaminated by heavy metal(loid)s especially Cd has become a top priority for sustainability of agriculture and public health.

In situ immobilization provides a feasible solution for remediating heavy metal(loid)s in large areas of arable land (Hamid et al., 2019), due to that it is efficient in remediation and environmental-friendly but less costly technique. Most amendments used for in situ immobilization mitigate the toxicity and the bioavailability of Cd by adsorbing, precipitating, chelation reactions et al in soils (Adriano et al., 2004; Seshadri et al., 2016; Jin et al., 2021). There are variety of amendments such as calcareous alkaline substances (Gu et al., 2011; Liu and Lian, 2019; Yan et al., 2021), clay minerals (sepiolite, bentonite, zeolite et al) (Garcia-Sanchez et al., 1999; Hamid et al., 2019), modified biochar, such as sulfur or sulfur-iron modified biochar possessing higher surface areas and functionality and active exchange sites (Rajendran et al., 2019; Kashif et al., 2020; Liu et al., 2020; El-Naggar et al., 2021., Wang et al., 2021); sulfur-containing materials (hair or cysteine), manganese compounds as an antagonist and an oxidant, and Fe containing minerals (maghemite, goethite et al) as adsorbents, or their combinations through coating or modification (Chowdhury and Yanful, 2013; Huang et al., 2018; Ullah et al., 2020) have shown the ability to immobilize soil Cd. However, the remediation efficiency and environmental stability of these materials are often found inadequate, frequent application is needed to avoid risk of second release. Recently, a novel Ca-Fe-Si composite material rich in Ca, Fe, Si, Mn, P, S et al. was found to have marvelous outstanding fixation properties for heavy metal(loid)s, the maximum adsorption capacity of CIS for Cd²⁺ can reach 93.46 mg/g (Yao et al., 2017; Yao et al., 2019), which can effectively immobilize metal(loid)s especially Cd in soils and guarantee the safe production of crops on Cd contaminated soils.

However, soil acidification was prevalent in southern China. Acid stability and dissolution characteristics of Ca-Fe-Si composite material fixed Cd (CIS-Cd) as well as the underlying immobilization mechanisms under acidified conditions remain unclear. In order to explore that, acid titration and X-ray powder diffraction (XRD) technique were used to investigate the dissolution characteristics of CIS-Cd under different acidification conditions, the immobilization mechanisms of CIS for Cd were discussed. The findings will help to develop novel amendments highly efficient in remediation and resilient to environmental change for safe production on farmland soils contaminated by heavy metal(loid)s.

1. Materials and methods

1.1. Preparation of Ca-Fe-Si material (CIS) fixed Cd

The tested Ca-Fe-Si material (denoted as CIS) is a patent material (ZL 201510602213.6). CIS sample was ground to pass 0.149 mm nylon sieve for further use. Added Cd(NO₃)₂ solution to 30.0 g of tested CIS to get the Cd content of CIS reaching 20.0 mg/kg, and a moisture content of 70%-80%. They were mixed thoroughly, sealed with plastic wrap, and stored under room temperature for 30 days. After being air dried, ground to pass 0.149 mm nylon sieve, the preparation of Ca-Fe-Si material fixed Cd (CIS-Cd) was finished. The contents of the main elements Ca, Fe, Mn, Mg, Al, P, S, K, Na, Si and Cd are 280.6, 109.7, 81.4, 32.7, 6.3, 4.3, 1.9, 0.86, 0.66, 35.7 and 16.2 mg/kg, respectively. The pH value of CIS-Cd was 11.88.

1.2. Acid titration experiments

Weighed 14 sets of CIS-Cd, each 0.2000 g, into 100 mL clean polythene centrifuge tubes, added 0, 25, 50, 100, 150, 200, 250, 300, 400, 500, 600, 700, 1000 and 1500 μL of 1 mol/L HCl solution, respectively, replenished ultrapure water to reach a volume of 20.0 mL. Duplicate treatments were conducted simultaneously. Control (blank) treatment without CIS-Cd addition but with same amount of acid and ultrapure water was set up at the same time. After 16 hr of continuous shaking at a speed of 220 r/min under 25°C, each treatment was centrifuged at a speed of 4,000 r/min for 5 min. The supernatant was collected and its pH was determined potentiometrically. To avoid loss of Cd, after pH determination, the electrode washing water was incorporated into the supernatant. The centrifuged solid-phase samples were rinsed with 20.0 mL of deionized water, centrifuged again at 4,000 r/min for 5 min, and the supernatants were combined. The supernatants were brought to volume, filtered with 0.22 μm membrane, the contents of Cd, Ca, Mg, Fe, Al, Na, K, S and other elements in the solution were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 5300dv, PE, USA). This was the content of dissolved elements during acid titration. The centrifuged solid-phase samples were vacuum dried and analyzed by X-ray powder diffraction (XRD, Empyrean, Panalytical, Netherland) using a scan range of 5°~80°. The total element contents of CIS-Cd were digested by using aqua regia-HClO₄ digestion method described by protocols GB/T 17141-1997 (NEPA, 1997) and determined by ICP-OES.

1.3. Quality control

Duplicate error was within 20% for all treatments. Standard soil reference material (SSRMGBW07443 (GSF-3)) was used to test accuracy of the methods. The measured metals in SSRM were within 85% to 110% of certified value. Reagent blanks were routinely analyzed to get rid of the background contamination. Limit of detection value of ICP-OES used was 1 mg/L. Readings obtained from a standard solution were reproducible within a variation of 5%. All the glass utensils or centrifuge tubes used in the experiments were soaked with 7%-10% (W/W) HNO₃ for 12 hr, washed completely with ultrapure water and dried for use.

1.4. Data analysis

IBM SPSS Statistics 23 package (SPSS Inc., Chicago, USA) was used for data processing and fitting. MATLAB R2016A was used for hierarchical clustering analysis according to the longest distance method. XRD patterns were analyzed using MDI Jade 6 software and plotted using origin pro 9.1. Data were presented as mean \pm D ($n = 2$). The correlation analysis was carried out using a Pearson's correlation test with a significance level of $P < 0.05$.

2. Results

2.1. Acid buffering curve of CIS-Cd

The acid buffering curve of CIS-Cd is illustrated in Fig. 1. In the acid titration, the presence of CIS-Cd raised the solution pH by 1–9 units compared to the control with no CIS-Cd addition. In the pH range of 11.88–10.27, the pH of CIS-Cd solution decreased slowly with the addition of acid. In the range of 10.27–8.64, the pH of the CIS-Cd solution began to accelerate to drop with the addition of H^+ . While when it came to the pH range of 8.64–2.42, the pH of CIS-Cd solution decreased sharply with the addition of H^+ , indicating that CIS had distinctive buffering capacity at different stage of acid titration. It should be different materials that buffered acid at different stage of titration.

2.2. Acid dissolution of CIS-Cd

Acidic dissolution characteristics of CIS-Cd can be characterized by elemental dissolution rate (ratio of the total amount of each element dissolved in acid titration to the total amount of corresponding element contained in CIS-Cd, respectively, expressed as percentage rate, %).

As shown in Fig. 2, the release of Cd^{2+} from CIS-Cd varied with the addition of H^+ . The release of Cd was slow in the pH range of 11.88–8.64, the dissolution rate of Cd at this stage was 9.43%, since this part of Cd could be released even under alkaline conditions when subjected to acidification, it is non acid-stable Cd. As acidity continued to increase, the Cd dissolution rate quickly increased from 9.43% to 31.89%

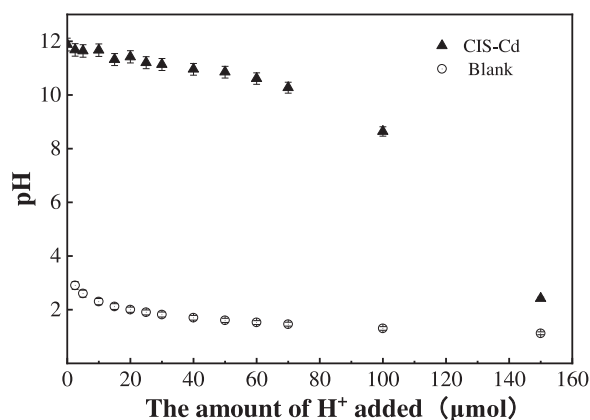


Fig. 1 – Acid buffering curve of CIS-Cd.

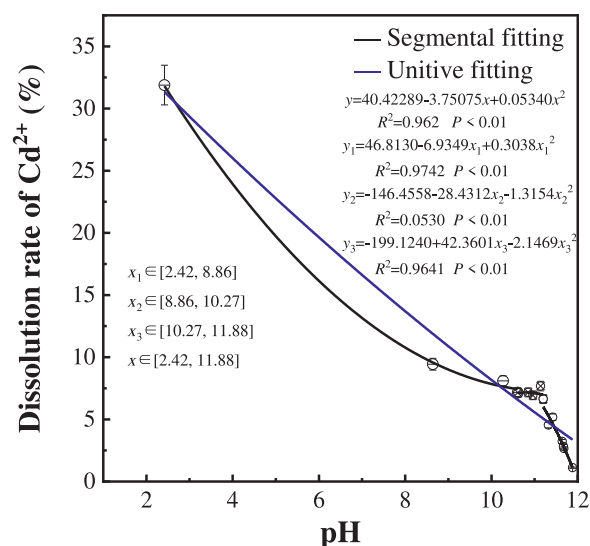


Fig. 2 – Variation of dissolution rate of CIS-Cd with pH.

in the pH range of 8.64–2.42, this part of Cd was moderately acid-stable Cd, which accounted for about 22.46% of total Cd ($31.89\% - 9.43\% = 22.46\%$). The Cd that remained undissolved at $pH < 2.42$ was acid-stable Cd, and this fraction occupied approximately 68% of total Cd. CIS-Cd showed distinctive releasing characteristics at different stages of acidification.

2.3. Releasing characteristics of other elements in CIS-Cd under acidification

Releasing characteristics of other elements in CIS-Cd during acid titration are shown in Fig. 3. The dissolution rates of most of the elements except for Na increased with decreasing pH.

The content of Ca in the CIS was the highest, which was as high as 280.6 mg/g and S was 1.9 mg/g, the content difference between the two elements was large, however, both of Ca and S had the highest dissolution rates under alkaline conditions and were very sensitive to pH changes. Dissolved Ca reached 66% of its total dissolution rate at $pH 10.27$, and 84% at $pH 8.64$, whereas dissolved S reached 82% of its total dissolution rate at $pH 10.27$, indicating that the Ca and S containing minerals were pH sensitive even under alkaline conditions and had the weakest acid stability. The dissolution rate of Na reached the highest at $pH 11.2$, but the dissolution rate did not increase with the decreasing pH, indicating its high solubility was independent of pH change.

The contents of Fe and Mn in CIS-Cd were second to that of Ca, but the highest dissolution rate of Fe and Mn were only 4.08% and 3.02% at extreme acidity of $pH 2.42$, indicating the high acid stability of Fe and Mn containing minerals. From the segmental regression relationship between dissolution rate and pH, the dissolution rate of Fe had no significant functional relationship with pH under acid to neutral conditions, but significantly correlated with pH under alkaline conditions, indicating dissolution of Fe containing minerals was acid sensitive under alkaline conditions but relatively pH-independent under acid to neutral conditions. Dissolution rate of Mn was significantly correlated with pH in the whole tested pH ranges,

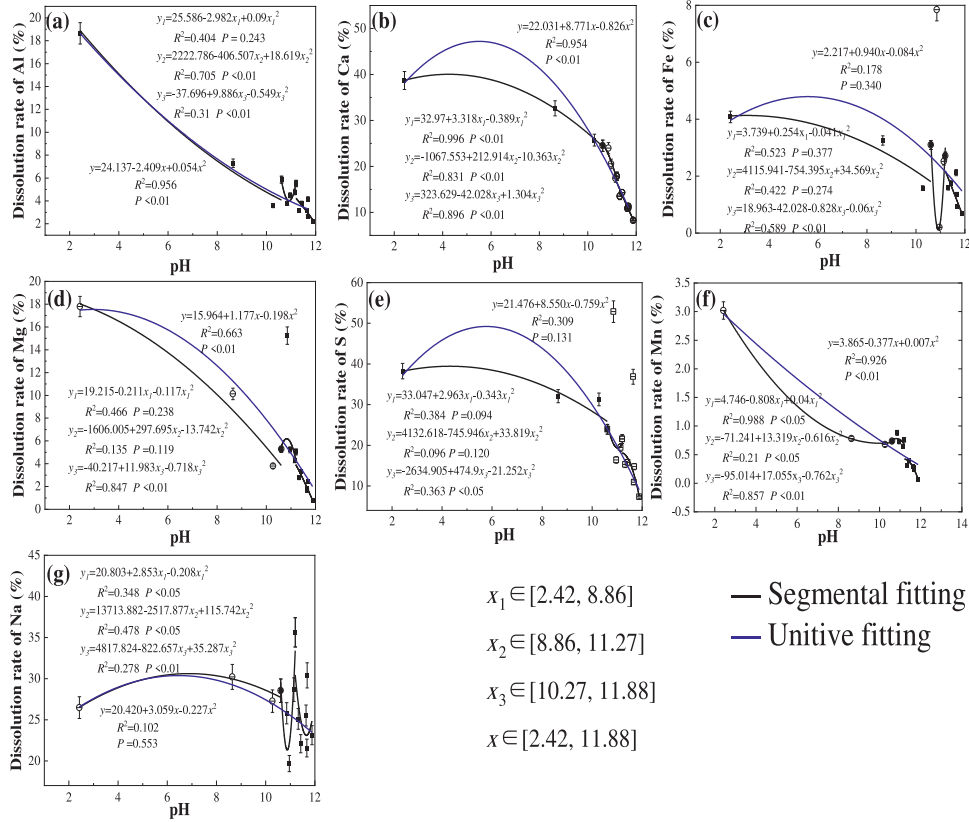


Fig. 3 – Variation of dissolution rate of Al(a), Ca(b), Fe(c), Mg(d), S(e), Mn(f) and Na(g) in CIS-Cd with pH.

though the dissolution rates of Mn containing minerals were low, they were acid sensitive in all pH ranges.

Mg and Al contents in the CIS-Cd were lower than those of Fe and Mn. From the regression fitting, dissolution of both of Al and Mg had a significant functional relationship with pH change, indicating their dissolution was pH-dependant. By using segmental regression fitting, dissolution rates of Al had significant functional relationship with pH under neutral to alkaline conditions but had no significant relationship with pH under acid conditions. Dissolution of Mg had no significant functional relationship with pH under acid to neutral circumstance, but had significant relationship with pH under alkaline conditions.

The total dissolution rate of elements in CIS-Cd (the percentage ratio of the dissolved element content to the total amount of same element in CIS-Cd at pH = 2.42) was in the order: Ca (38.71%) > S (38.27%) > Cd (31.89%) > Na (30.22%) > Mg (24.03%) > Al (18.65%) > Fe (7.85%) > Mn (3.02%). The dissolution sequence of above elements in response to acidification was in agreement with the study of Hartley et al. (2004). Among which, dissolution of Ca, Mg, Al, Mn and Fe was pH-dependant, while that of S and Na was pH independent.

The dissolution rates of each element in CIS-Cd were analyzed by cluster analysis using MATLAB software, and the results obtained are shown in Fig. 4. The elements in CIS-Cd can be classified into three groups, Ca-S-Na, Al-Mg-Cd and Fe-Mn, by acid releasing characteristic similarity. The dissolution

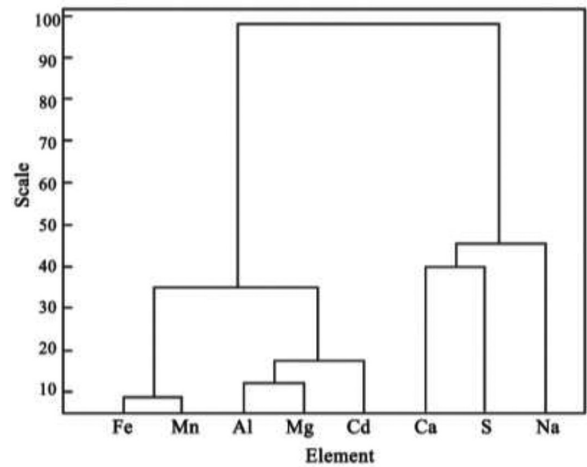


Fig. 4 – Cluster analysis of elemental dissolution of CIS-Cd in terms of acid releasing characteristic similarity.

rates of Ca, Na and S were the highest, Al, Mg and Cd were the intermediate, the lowest was Fe and Mn.

2.4. Concomitant dissolution characteristics of Cd and other elements

The concomitant relationship between the dissolution of Cd and other elements such as S, Mg, Al, Mn, Ca, Na, Mn and Fe in

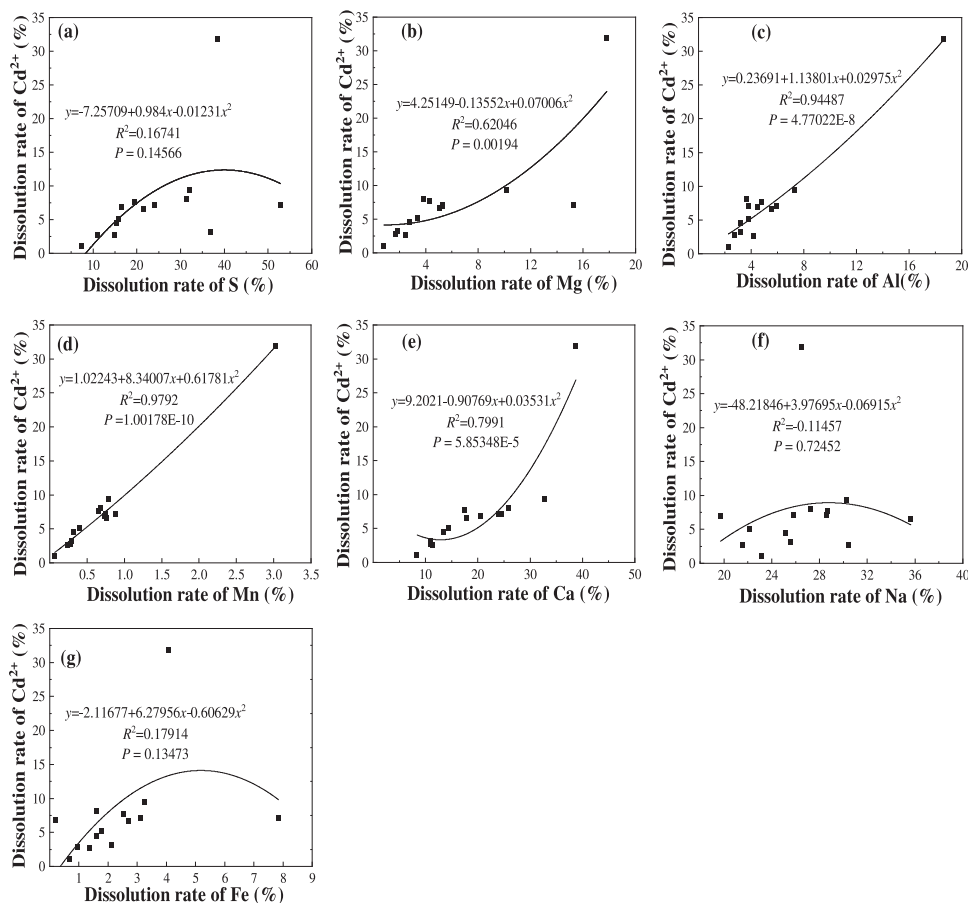


Fig. 5 – Correlation between dissolution of Cd and other elements in CIS.

CIS-Cd during acid titration is shown in Fig. 5. There was a significant functional correlation ($P < 0.05$) between dissolution of Cd and the dissolution of Ca, Mg, Al, Mn, indicating that dissolution of Ca, Mg, Al, Mn containing minerals controlled the dissolution of Cd. It can be observed that the dissolution of all these elements were pH-dependant. These minerals might immobilize Cd by forming insoluble compounds with Cd²⁺ or through adsorption, co-precipitation, electrical or chemical adsorption as well. The dissolution of S, Na, and Fe was not significantly correlated with that of Cd, indicating Fe immobilized Cd primarily by adsorption instead of forming insoluble compound with Cd or co-precipitating with Cd, while S and Na containing minerals were not major sink minerals for Cd immobilization.

To identify the Cd containing mineral species and their corresponding acid stable pH intervals, XRD analysis of the CIS-Cd under different acidification conditions was conducted.

2.5. XRD analysis on CIS-Cd under different acid conditions

Results of XRD analysis on minerals existed in CIS-Cd under different acidity conditions are shown in Fig. 6. It showed that original CIS contained calcite (CaCO₃),

calcium silicate (Ca₄Si₂O₅), gypsum (CaSO₄), wustite (FeO), srebrodolskite (Ca₂Fe₂O₅), iron manganese oxide (MnO)_{0.593}(FeO)_{0.407}, silicosulfide (SiS₂), aluminum phosphate Al(PO₄), calcium ferrihydrite (manganese silicon displaced) (Ca₂Fe_{1.4}Mg_{0.3}Si_{0.3}O₅), iron magnesium oxide (MgO)_{0.593}(FeO)_{0.407}, ilvaite (CaFe₂Fe(Si₂O₇)O(OH)), orthorhombic calcerite (CaAl₂Si₂O₈·4H₂O), quartz (SiO₂), kaolinite (Al₂Si₂O₅ (OH)₄), magnesium manganese oxide (MgO)_{0.725}(MnO)_{0.275}.

The stable minerals in CIS-Cd at different pH intervals analyzed by XRD are shown in Table 1. Calcium silicate, iridescent, calcium ferrihydrite, iron nitride, gypsum, calcite were stable only in alkaline environment. Magnesium manganese oxide and orthorhombic calcium zeolite (CaAl₂Si₂O₈·4H₂O) were stable under alkaline to neutral conditions. Minerals containing iron such as ferrihydrite, iron manganese oxide, iron magnesium oxide, silicosulfide, kaolinite and quartz were stable in alkaline to acidic environment.

Alkaline conditions favored the conversion of Cd²⁺ into carbonates and hydroxides, facilitating further precipitation of Cd (Liu and Lian, 2019). XRD results showed that CIS could immobilize Cd by forming poorly soluble minerals such as Cd₅(PO₄)₂SiO₄, CdFe₂O₄, Cd₂SiO₄, CdCO₃, CdSO₄, but their acid stability differed with pH. From the stable pH range of these Cd containing minerals (Table 1), their dissolution sequence

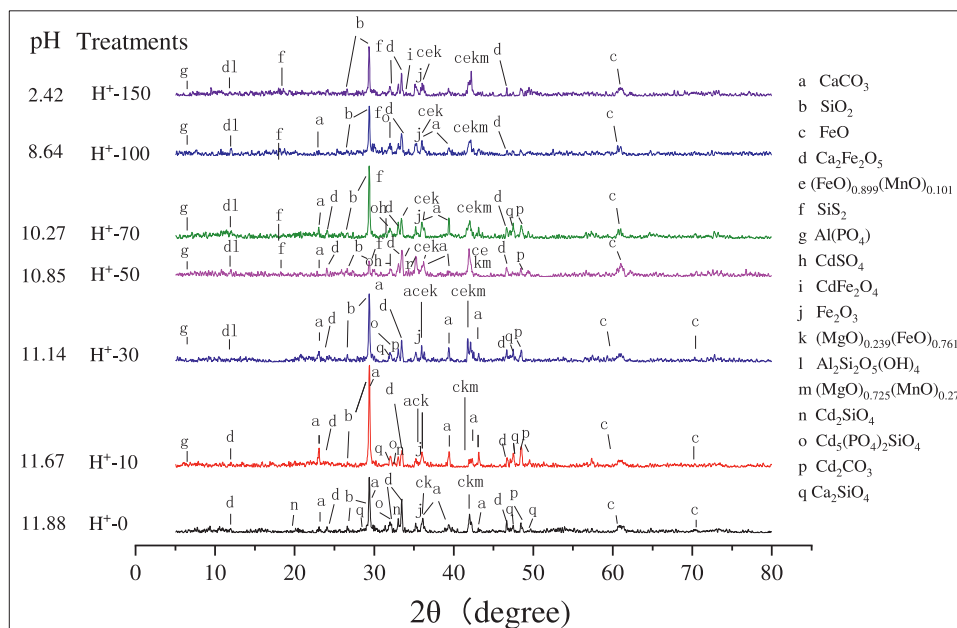


Fig. 6 – XRD spectrum of CIS-Cd at different pH conditions.

Table 1 – Major minerals existed in CIS-Cd and their stable pH ranges.

Minerals	Stable pH range
Calcium silicate (Ca ₄ Si ₂ O ₅)	11.48~11.08
Aluminum phosphate (Al(PO ₄))	11.48~11.08
Calcium ferrihydrite(manganese silicon displaced (Ca ₂ Fe _{1.4} Mg _{0.3} Si _{0.3} O ₅))	11.48~11.08
Ilvaite (CaFe ₂ Fe(Si ₂ O ₇)O(OH))	11.08~ 10.54
Gypsum (CaSO ₄)	10.54~ 9.24
Calcite (CaCO ₃)	11.48~7.68
Magnesium manganese oxide ((MgO) _{0.725} (MnO) _{0.275})	8.40~7.68
Orthorhombic calcium zeolite (CaAl ₂ Si ₂ O ₈ ·4H ₂ O)	8.40~7.68
Iron magnesium oxide ((MgO) _{0.593} (FeO) _{0.407})	11.08~ 2.42
Wustite (FeO)	11.48~2.42
Silicosulfide (SiS ₂)	11.48~ 2.42
Quartz(SiO ₂)	11.48~ 2.42
Srebrodolskite (Ca ₂ Fe ₂ O ₅)	11.48~2.42
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	9.24~2.42
Iron manganese oxide ((MnO) _{0.593} (FeO) _{0.407})	7.68~2.42
Iron magnesium oxide ((MgO) _{0.593} (FeO) _{0.407})	7.68~2.42
Dicadmium silicate (Cd ₂ (SiO ₄))	11.88-11.67
Cadmium sulfate (CdSO ₄)	11.14-10.27
Pentacadmium diphosphate orthosilicate (Cd ₅ (PO ₄) ₂ SiO ₄)	11.88-2.42
Cadmium diiron(III) oxide (CdFe ₂ O ₄)	< 2.42

followed the order: Cd₂(SiO₄) and CdCO₃ (pH stability interval: 11.88-11.67) > CdSO₄ (pH stability interval: 11.14-10.27) > Cd₅(PO₄)₂SiO₄ (pH stability interval: 11.88-2.42) > CdFe₂O₄ (stable even at pH < 2.42). Cd₂(SiO₄), CdCO₃ and CdSO₄ was the most acid sensitive, they will dissolve upon acid addition even under strongly alkaline conditions. CdFe₂O₄ was the most stable against acidification.

3. Discussions

3.1. Fixation mechanisms of CIS for Cd and its acid dissolution characteristics

The Cd dissolution curve indicated that CIS-Cd had a distinct acid releasing characteristics at different pH intervals. The slowly released Cd under alkaline conditions was non acid-stable Cd. This fraction accounted for about 9.54% of the total Cd. With the progress of acidification, the rapidly released Cd in the pH range of 8.86-2.42 was moderately acid-stable Cd, this fraction occupied about 22.46% of the total Cd. Those remained undissolved at pH < 2.42 were acid-stable Cd. This fraction occupied about 68% of the total Cd.

From the pH stability interval of Cd containing minerals formed in CIS and the correlation curves between the dissolution rates of Cd and concomitant elements (Fig. 5), the dissolution pH interval of non acid-stable Cd was consistent with that of Cd₂(SiO₄), CdCO₃, CdSO₄. In addition, the dissolution of non acid-stable Cd was mainly accompanied by the dissolution of Ca and S, it can be inferred that non acid-stable Cd was mainly in the form of Cd₂SiO₄, CdSO₄, CdCO₃ or co-precipitated with lime (CaCO₃), calcium silicate (Ca₄Si₂O₅), gypsum (CaSO₄). As acidification progressed, moderately acid-stable Cd began to release rapidly, this fraction of Cd was mainly accompanied by the dissolution of Mg, Al, suggesting that the moderately acid-stable Cd should be mainly bound by Mg and Al containing minerals such as magnesium oxide, orthorhombic zeolite and kaolinite. It was reported that pH played a critical role in the adsorption of magnesium oxide, orthorhombic zeolite, kaolinite for heavy metals (Sdiri et al., 2011; Chen et al., 2017; Farsi et al., 2020). As pH decreases, the adsorption capacity of these minerals for heavy metal ions decreases, easily causing the desorption of immobilized heavy

metals. pH can also affect the solubility of Cd by influencing the surface charge of variable charged soils (McBride, 1989), i.e., with the decreasing pH, the negative charge on the surface of iron manganese oxides decreases and increases the activity of electrically sorbed Cd (Mouta et al., 2008). CIS are rich in iron and manganese containing minerals. Under alkaline conditions, variable negative charges on the surface of iron manganese oxides can electrically adsorb Cd^{2+} , with the progress of acidification, the variable negative charge on the surface of iron manganese minerals gradually changed into positive charge, the adsorbed Cd was then released gradually, and this part of the pH sensitive Cd was electrically bound by iron aluminum manganese oxides. This part of Cd should be included in the moderately acid-stable Cd.

From Fig. 6, it can be seen that the stable pH interval of acid-stable Cd was in good agreement with that of $\text{Ca}_2\text{Fe}_2\text{O}_5$, AlPO_4 , CdFe_2O_4 , iron manganese oxide $(\text{FeO})_{0.899}(\text{MnO})_{0.101}$, $(\text{MgO})_{0.239}(\text{FeO})_{0.761}$, $(\text{MgO})_{0.725}(\text{MnO})_{0.275}$. Since iron and manganese oxide can exist and chemically adsorb Cd even at extremely acidic conditions ($\text{pH} < 2.42$), acid-stable Cd mainly included CdFe_2O_4 , AlPO_4 , $\text{Ca}_2\text{Fe}_2\text{O}_5$ as well as iron manganese oxides chemically bound form.

The results showed that CIS immobilized Cd by several mechanisms, including 1) forming poorly soluble precipitates Cd_2SiO_4 , CdCO_3 , CdSO_4 , $\text{Cd}_5(\text{PO}_4)_2\text{SiO}_4$, CdFe_2O_4 ; 2) co-precipitated with lime (CaCO_3), calcium silicate ($\text{Ca}_4\text{Si}_2\text{O}_5$), gypsum (CaSO_4); 3) bound by Mg and Al containing minerals or aluminum manganese oxides; 4) electrically sorbed or chemically sorbed by iron-manganese containing minerals. It was by such multilateral fixation mechanisms that enabled CIS to possess marvelous high efficiency in Cd immobilization and strong resilience to environmental acidification. Among which, iron manganese containing minerals showed much higher efficiency in Cd immobilization and stronger resilience to acidification than calcium and silicate containing minerals, but the latter showed much higher acid buffering capacity than the former. Under acidified conditions, non acid-stable Cd in CIS, mainly in carbonate, silicate, and sulfate bound form (CdCO_3 , Cd_2SiO_4 , CdSO_4) or co-precipitated with calcite (CaCO_3), calcium silicate ($\text{Ca}_4\text{Si}_2\text{O}_5$), gypsum (CaSO_4), will be dissolved first. Further acidification will lead to the dissolution of moderately acid-stable Cd (occupied approximately 22% of total Cd), which was mainly bound by magnesium-, aluminum containing minerals or electrically bound by iron manganese containing minerals. The acid-stable Cd (occupied approximately 68% of the total Cd), mainly included CdFe_2O_4 and ferromanganese minerals strongly bound Cd, was most resilient to acidification. It is noteworthy that compositions of CIS such as calcium, magnesium, silicate, phosphate, sulfate can not only attenuate the toxicity of Cd, but also provide nutrients to the growth of crops. CIS showed promising application potential for the remediation of soils contaminated by moderate to high levels of Cd.

The findings elucidated the acid stability characteristics and immobilization efficiency of different types of amendment (calcium-silicon containing materials, magnesium-aluminum-silicon containing clay materials, and iron manganese containing materials), proper combination of Ca-Fe-Si containing minerals could develop novel promising amendments with high efficiency for heavy metal(loid)s

immobilization and strong resilience to environmental change.

4. Conclusions

Calcium-iron-silicon composite material showed excellent acid buffering capability for environmental acidification. Acid titration solution chemistry and XRD results showed that iron and manganese containing minerals were much more efficient in Cd immobilization and more resilient to acidification than that of calcium and silicate containing minerals, magnesium and aluminum containing minerals were the intermediate. Under acidified conditions, non acid-stable Cd in CIS-Cd, accounting for approximately 9.54% of total Cd, mainly in silicate, carbonate and sulfate bound form (Cd_2SiO_4 , CdCO_3 and CdSO_4) or co-precipitated with calcite (CaCO_3), calcium silicate ($\text{Ca}_4\text{Si}_2\text{O}_5$), gypsum (CaSO_4), will be dissolved first. Further acidification will lead to the dissolution of moderately acid-stable Cd (occupied approximately 22% of total Cd), which was mainly bound by magnesium-, aluminum containing minerals or electrically bound by iron manganese containing minerals. The acid-stable Cd, occupied approximately 68% of the total Cd, mainly included CdFe_2O_4 and ferromanganese minerals chemically bound Cd. It was by such multilateral fixation mechanisms that Ca-Fe-Si material possessed marvelous high efficiency for Cd immobilization and strong resilience to environmental acidification.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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