

## In situ capping technology for controlling heavy metals release from contaminated sediment

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Received 17 October 2018; Accepted 16 June 2019

### ABSTRACT

The efficiency and the mechanism of calcite/sand as a capping layer to simultaneously prevent the Pb, Cr, and Mn releasing from the contaminated sediments were investigated using the simulated in situ capping batch experiments. The results showed that the order for the inhibition efficiency of the different capping materials is: calcite > calcite + sand > sand for the three metals. The capping materials of calcite (325 mesh) + sand could hinder the release of Pb, Cr, and Mn effectively, with the inhibition efficiencies of 77.90%, 81.16%, and 86.26%, respectively, which were approaching to the inhibition efficiencies of calcite (mesh 800). Toxicity characteristic leaching procedure test showed that the leaching amounts of Pb, Cr, and Mn from sediments with capping system were lower than that from the control. The least leaching concentrations were recorded in the sediments with the calcite (mesh 800) and concentrations for Pb, Cr, and Mn were 0.0049, 0.015, and 2.05 mg L<sup>-1</sup>, respectively, and for the calcite (mesh 325) + sand, the concentrations were 0.0074, 0.016, and 2.50 mg L<sup>-1</sup>, respectively. Tessier extraction test proved that the element fractions in the sediments with caps tended to transform the metal fractions of exchangeable, carbonate, Fe–Mn oxidize, organic to the metal fraction of residual.

*Keywords:* In situ capping; Calcite; Sand; Contaminated sediment; Heavy metal

### 1. Introduction

The heavy metal contamination in sediments has induced worldwide concern because of the environmental persistence, biogeochemical recycling, and the ecological risks in the presence of heavy metals [1]. With the rapid development of the world's industry, heavy metals originating from human activities are discharged into aquatic environments, and they are accumulated in sediment, and biomagnified, which results in numbers of serious environmental and health problems, such as a mutagenic and carcinogenic risks, to humans [2–4].

Just similar to soil remediation, there is a systematical remediation strategy to remedy the heavy metals contaminated sediments [5]. First, in situ remediations are adopted to increase the stabilization of heavy metals in sediments and to control the ecological risks of the elements [6,7]. Second, an ex-situ extraction could be used to separate the toxic metals from the sediments when the technologically and economically appropriate solutions are available [8]. The in situ technology provides low cost and easy operational solutions, which primarily focused on the improvement of metal stabilization; mainly by enhancing metal sorption, precipitation and complexation capacity on sediment particles [9,10].

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In situ capping is an effective method of controlling the endogenous pollution of the water bodies, which isolates the upper water body from the sediments and prevents transferring of the pollutants to the overlying water [11].

Traditional capping materials, such as clean sand, do not possess the ability to adsorb and degrade contaminants, but they can form a solid barrier between the sediment and the aquifer to considerably delay the contaminant breakthrough when the diffusive transport dominates [12–14]. More recently, the additives to encourage the degradation or sequestration of contaminants have been proposed as cap materials. The chemical composition of calcite is  $\text{CaCO}_3$ , which is a carbonate mineral with a tri-crystalline system. It has strong adsorption and immobilization properties for the phosphates and heavy metals cations and is suitable as active capping material for the in situ capping [15–19]. In general, the uptake of metals by calcite may proceed via different mechanisms, including adsorption (the coordination of metal ions to the mineral surface), coprecipitation (the incorporation of metal ions into the mineral structure by substituting for lattice atoms) and precipitation (the formation of secondary mineral phases) [20–22]. These uptake mechanisms might be operative in the sequestration of divalent trace metals by calcite and depend on the reaction variables such as metal type, concentration, calcite saturation state, reaction time, and pH [23–25]. Berg et al. [26] studied the effect of calcite cover on the release of phosphorus from sediments. The results showed that the 1 cm thick calcite cover system over the sediments could reduce the phosphorus release up to 80% for 3 months. The application of a calcite barrier had been investigated to prevent phosphorus release from eutrophic lake sediments, with the consideration of different materials properties of calcite; varying in grain size, specific surface area and roughness of the surface [26]. Lin et al. [27] investigated the performance of sediment capping with active barrier systems using calcite/zeolite mixtures to manage the release of phosphorus and ammonium simultaneously.

The objective of the present study was to investigate the efficiency and mechanism of calcite as a capping layer to prevent the release of Pb, Cr, and Mn simultaneously from

the contaminated sediments under the different covering styles conditions of calcite, such as particle size, coating thickness, and calcite coupled with sand.

## 2. Materials and methods

### 2.1. Experiment material

#### 2.1.1. Materials

The heavy metal contaminated sediment used in this study was taken from a river in northeastern of Jinan, China. In the 1990s, the industrial and mining companies around the river had discharged large quantities of wastewater that contains heavy metals to the river and which has resulted in the severe contamination in the river water and the sediments. The sediment samples were taken to the laboratory for sedimentation analysis and heavy metal release control simulations. Organic matter (OM) in sediment was measured by the method of residual titration of  $\text{K}_2\text{Cr}_2\text{O}_7$  after the treatment of the sample with  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$  [28]. Sediment pH was measured by a PHS-25 digital pH meter (Shanghai Leici Instrument Plant, China) in 1:2.5 (W/V) sediment-to-water suspensions [28]. The Standards, Measurements and Testing (SMT) protocol was used to determine the total phosphorus (TP) of sediment [29,30]. The total concentrations of the heavy metal were analyzed using the EPA 3050A Total Metal Analysis Method. The content of Pb, Cr, and Mn in the digest solution was determined by the atomic absorption spectrometry (AAS, TAS-990, Beijing Puxi company, China). The characteristics of the sediment including pH, water content, TP, Pb, Mn, Cr, and, organic matter is illustrated in Table 1. Calcite has a content of 100% calcite and was sieved to 325 and 800 mesh separately for further experiment.

### 2.2. Simulated in situ capping batch experiments

3.0 L plastic opaque barrels were used as batch reactors to simulate the in situ capping trials. In the glove boxes in a nitrogen-saturated environment, the contaminated sediment was sieved evenly on the bottom of the reactor. 0.6 kg of sediments (about 3.0 cm thick) were placed at

Table 1  
Main physical and chemical characteristics of the sediments

Parameter	Value	Limited value of heavy metals in the different levels, Environmental quality standard for soils, GB (15618-1995) <sup>a</sup>
Water content (%)	27.5	
pH	8.02	
TP (mg kg <sup>-1</sup> )	1.82	
Pb (mg kg <sup>-1</sup> )	1,080	III: 500
Mn (mg kg <sup>-1</sup> )	738	210 <sup>b</sup>
Cr (mg kg <sup>-1</sup> )	720	III: 400
ORP (mV)	-200 ~ +200	
Organic matter (%)	11.4	

<sup>a</sup>Environmental quality standard for soils in China divides into three levels: Level I is for the background concentrations of heavy metals, Level II is designed to guarantee the agriculture production and people health, and Level III is the limited values for maintaining the growth of the woods and crops.

<sup>b</sup>No regulated in the environmental quality standard for soils in China, while the background value of Mn here is 210 mg/kg.

the bottom of each reactor, and then the different capping materials were spread over the sediment layers (Table 2). Then the reactor filled with the water up to the 1.0 L fixed level, and the siphon method was applied to prevent the sediment particle suspension while adding water to the reactor. Then all the reactors were placed in a dark box. During the experiment trials, the reactors were blown in  $N_2$  to keep the overlying water in an anaerobic state, and to prevent the sediments from being influenced by the air. The trials were operated over 160 d, the samples of overlying water were collected at 5 cm below the free water surface at day 2, day 5, day 8, day 14, day 21, day 29, day 41, day 60, day 80, day 95, day 111, day 125, day 135, day 145, and day 160, respectively. Each time, after the water sample was collected, the same amount of tap water was refilled and the reactor was sealed, and  $N_2$  was continued to blow inside the space between the free water surface and the cover. The water samples were filtered with 0.45  $\mu\text{m}$  membrane, then the concentrations of Cr, Mn, and Pb in the water samples were determined by AAS (TAS-990, Beijing Puxi company, China). All the samples were analyzed in triplicate.

The cumulative amount of heavy metals released from the sediment is calculated by Eq. (1).

$$Q_n = \frac{V(C_n - C_0) + \sum_{i=1}^{n-1} V_i C_i}{W_s} \quad (1)$$

where  $Q_n$  ( $\text{mg kg}^{-1}$ ) is the cumulative amount of heavy metal released from the sediment for  $n$  days;  $V$  (L) is the available water volume in the reactor;  $C_n$  ( $\text{mg L}^{-1}$ ) and  $C_0$  ( $\text{mg L}^{-1}$ ) are the concentrations of the heavy metals in the overlying water at day  $n$  and the day 0, respectively;  $V_i$  (L) is the volume of sampling water at day  $i$ ;  $C_i$  ( $\text{mg L}^{-1}$ ) is the concentration of the heavy metal in the overlying water at day  $i$ ; and  $W_s$  (kg) is the initial mass of the sediment in the reactor.

The average release rate of heavy metals in sediment is calculated by Eq. (2) as follows:

$$V_Q = \frac{Q_n}{T \times S} \quad (2)$$

where  $V_Q$  ( $\mu\text{g (kg m}^2 \text{d)}^{-1}$ ) is the average release rate of heavy metals during trial period;  $Q_n$  (mg) is the release flux of heavy metals during the trial period;  $T$  (d) is the time of continuous release of heavy metals;  $S$  ( $\text{m}^2$ ) is the contacting surface area between the capping layer and the sediment.

The inhibition efficiency of the different capping materials is calculated by Eq. (3) [31] as follows:

$$\text{IR} = \frac{Q_s - Q_f}{Q_s} \quad (3)$$

where IR is the inhibition efficiency of the capping materials after the release equilibrium;  $Q_s$  ( $\text{mg kg}^{-1}$ ) is the amount of heavy metals released from the sediments without capping materials;  $Q_f$  ( $\text{mg kg}^{-1}$ ) is the amount of heavy metals released from the sediments with different capping materials.

### 2.3. Toxicity characteristic leaching procedure test and heavy metal speciation analysis

At the end of in situ capping batch experiment, that is, day 160, the sediments located beneath the caps calcite (mesh 800), calcite (mesh 325), calcite (mesh 325) + sand, sand, and control) in each batch reactor was sampled. The sample collected from each batch reactor was divided into two segments. One segment was tested for toxicity characteristic leaching procedure (TCLP) to evaluate the heavy metal leaching from the sediments after capping for several months according to the Method 1311 [32]. The other segment was evaluated by Tessier extraction method to analyze the speciation of heavy metals in the sediment below the capping materials [33].

In the TCLP test, 1.0 g of the sample was weighted into the polypropylene bottle, and then 20 mL of HAc (0.1 M, pH  $2.88 \pm 0.05$ ) was added. Then the bottles oscillated at 30 rpm and  $25^\circ\text{C}$  in a constant temperature bath oscillator for 18 h. At last, the leachate was separated by centrifugation. Before being analyzed by AAS, the leachate was acidified to pH  $< 2.0$  by the concentrated nitric acid and stored at  $4^\circ\text{C}$  in the refrigerator [34,35].

In the test of Tessier extraction method, the desired fractions of trace metals are defined by five fractions: exchangeable, carbonate, iron–manganese oxides (Fe–Mn oxides), organic and residual. The Tessier speciation process is a five-step sequential extraction: step (a) exchangeable fraction: 1.0 g of sediment samples (dry weight) was extracted at room temperature for 1 h with 40 mL, 1 M  $\text{MgCl}_2$  (pH 7.0) with continuous agitation. Step (b) Carbonate fraction: the residue from the step (a) was leached with 40 mL, 1 M NaAC adjusted to pH 5.0 with HAC for 5 h. Step (c) Fe–Mn oxides fraction: the residue from the step (b) was extracted with 80 mL, 0.04 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% (v/v) HAc at  $93^\circ\text{C} \pm 3^\circ\text{C}$  for 6 h. Step (d) Organic fraction: the residue from the step

Table 2  
Characteristics of in situ capping materials in the batch experiments

No.	Capping materials	Thickness (cm)	Note
1	Calcite (325 mesh)	3.0	
2	Calcite (800 mesh)	3.0	
3	Calcite (325 mesh) + sand (80 mesh)	3.0	Mixed evenly
4	Sand (80 mesh)	3.0	
5	Without capping materials		Control sample

(c) was extracted with 3 mL, 0.01 M  $\text{HNO}_3$  and 5 mL 30% (v/v)  $\text{H}_2\text{O}_2$ . This mixture was heated to  $85^\circ\text{C} \pm 2^\circ\text{C}$  for 2 h. Then the second aliquot of 5 mL 30%  $\text{H}_2\text{O}_2$  was added to the mixture and heated at the same temperature for 2 h. After the mixture cools to the room temperature, 15 mL 3.2 M  $\text{NH}_4\text{Ac}$  in 20% (v/v)  $\text{HNO}_3$  was added. Finally, the sample was diluted to 100 mL and agitated continuously for 30 min. Step (e) Residue: the final residue was microwave digestion with 9.0 mL HCl and 3.0  $\text{HNO}_3$ . According to the five steps mentioned above, the selective extractions were conducted in centrifuge tubes (PE, 50 mL), and the supernatant was removed with a pipette and analyzed for trace metals [36,37].

### 3. Results and discussion

#### 3.1. Release of heavy metals in the sediment

The cumulative releases of Pb, Cr, and Mn in sediments are shown in Fig. 1. The cumulative release of metals in control sediments was much more than those in sediments with caps. It is noted that the metal release could be divided into two phases according to the metal release rate, and the release rate in the first phase was faster than that in the second phase. To show this clearly, the average release rates of Pb,

Cr, and Mn in sediments over the experiment periods and in the rapid releasing phase were summarized in Tables 3 and 4, respectively. The average release rates of Pb, Cr, and Mn in control sediments over the experiment periods were 17.81, 13.75, and 23.44  $\mu\text{g} (\text{kg m}^2 \text{d})^{-1}$ , respectively, which were much more than those in the sediments with caps. The rapid releasing periods were normally focused as several days at the beginning of the experiments. The rapid release rates of Pb, Cr, and Mn in control sediments were 1,225.00; 750.00; 1,374.00  $\mu\text{g} (\text{kg m}^2 \text{d})^{-1}$ , respectively, which were also much higher than those in sediments with caps.

Table 3

Average release rates of Pb, Cr, and Mn in sediments over the experiment periods (Unit:  $\mu\text{g} (\text{kg m}^2 \text{d})^{-1}$ )

	Pb	Cr	Mn
Calcite (325 mesh)	6.88	4.69	3.63
Calcite (800 mesh)	3.56	2.03	2.06
Calcite (325 mesh) + sand (80 mesh)	5.31	2.59	3.22
Sand (80 mesh)	6.97	7.03	4.75
Control	17.81	13.75	23.44

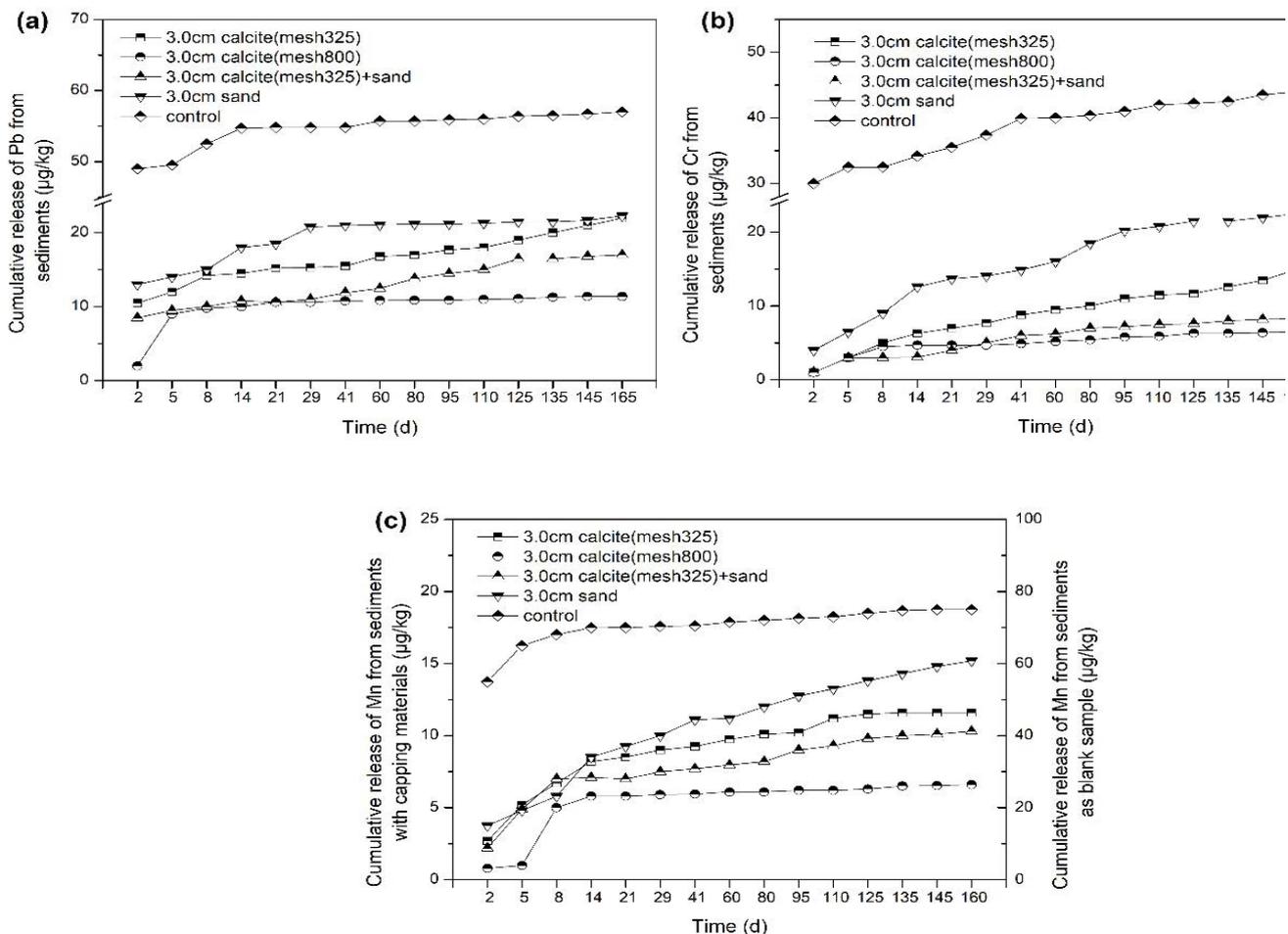


Fig. 1. Cumulative release of Pb, Cr, and Mn from sediments as time over the experiment period.

Compared with the control, the calcite cap series (calcite or calcite + sand) considerably hindered the Pb releasing from the sediments. The average release rate of Pb in the sediments with calcite cap series was 3.56–6.88  $\mu\text{g} (\text{kg m}^2 \text{d})^{-1}$  during the whole test period, only counting for 19.99%–38.63% of Pb release compared with the control sediment sample. The maximum inhibition efficiencies of Pb by the caps of calcite (mesh 800), calcite (mesh 325) + sand were 78.07%, and 77.90%, respectively.

As for the Cr releasing from the sediment was considered, the average release rate from the control sample was 13.75  $\mu\text{g} (\text{kg m}^2 \text{d})^{-1}$ . The average release rates of Cr in the sediments with caps of calcite (mesh 800), and calcite (mesh 325) + sand were 2.03, 2.59  $\mu\text{g} (\text{kg m}^2 \text{d})^{-1}$ , respectively, which only accounted for 14.76%, 18.82% of that in the control sediment, respectively. The inhibitory efficiencies of calcite (mesh 800) and calcite (mesh 325) + sand were 85.24% and 81.16%, respectively.

For Mn releasing from the sediments, the average release rate in sediments with capping materials of calcite (mesh 800) and calcite (mesh 325) + sand was 2.06, 3.22  $\mu\text{g} (\text{kg m}^2 \text{d})^{-1}$ , which only accounted for 8.78%, 13.74% of that in the control sample. The inhibition efficiencies for Mn in sediments with caps of calcite (mesh 800) and calcite (mesh 325) + sand were 91.21%, and 86.26%, respectively.

All in all, as for the inhibition efficiency of the different capping materials is concerned, the results showed that the expectable trend is: calcite > calcite + sand > sand, for all the three metals were considered. The species of metals in the sediments would vary depending on the coupling of pH and redox potential in environments. The heavy metals used in this test generally exist as cations ( $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ ) and under certain conditions of pH 8.5 and ORP  $\pm 200$  mV presents as hydrolyzed species ( $\text{Cr}(\text{OH})^{2+}$ ,  $\text{Pb}(\text{OH})^+$ , etc.) [38]. Therefore, the ion charge could play an important role in the adsorption of heavy metals in the calcite surface [21]. It is noted that for a given total quantity of capping materials (calcite and calcite + sand), the calcite alone as capping material will provide much more sorption sites at the calcite surface than calcite + sand [21].

### 3.2. Effect of particle size and materials on the release of heavy metals

In situ capping, many factors are affecting the release effect of heavy metals, such as temperature, pH, dissolved nutrients in overlying water, capping material particle size, capping method and so on [23,25]. This study mainly focused on capping particle size and capping materials.

As is shown in Fig. 1, the calcite with the particle size of 800-mesh has a better inhibitory effect on the tested metals in the batch experiments. While, the cumulative release amounts of Pb, Mn, and Cr from the overlying water in calcite (mesh 325) were much more than those from calcite (mesh 800). It can be seen that the capping particle size has a great influence on the metal element release in the sediment. The smaller the calcite particle size is, better the effect of the capping system can get. The reason may be that the small size calcites could provide much more sorption sites due to high specific surface area at the conditions of same thick caps. Some studies had shown that the stability of

partitioned metals increases with sorption time, as evidenced by a decrease in the rate and extent of metal desorption [25], which also can be seen from Fig. 1. This indicates that in certain systems, absorbed metal species may transform to more stable materials that are less susceptible to release back into solution. Mechanistically, several different processes may be involved in the increase in stability of metal partitioning with time; these include metal incorporation into the mineral lattice during recrystallization of the mineral sorbent [39–41]. The primary crystal of calcite with small particle size could lead to the smaller size of the recrystallization product. Therefore, this could result in a much more specific surface area, providing much more sorption sites and easy pathways for metal cations going into the mineral lattice by solid-state diffusion [42,43].

Fig. 2 shows the cumulative release of heavy metals from the sediments with different caps at 160 d. It is clear that the order of the heavy metal cumulative release amounts was calcite (mesh 800) > calcite (mesh 325) + sand > sand. The effect of sand as capping material was poorer than that of calcite or calcite + sand just because the function of the sand cap was mainly dependent on its physical blocks or physical sorption. While the metal cumulative release amount in sediments with calcite (mesh 325) + sand was a little bit lower than that in sediments with calcite (mesh 800). Considering the engineering applications and economic factors, the calcite (mesh 325) + sand could be suitable as the capping materials for the heavy metal contaminated sediment.

### 3.3. Toxicity characteristic leaching procedure test and heavy metal speciation analysis

In Fig. 3, according to the TCLP test, the leaching concentrations of heavy metals in the sediments beneath caps were much lower than that in the control. The leaching concentrations of Pb, Cr, and Mn from sediments with calcite (mesh 800) were 0.0049, 0.015, and 2.05  $\text{mg L}^{-1}$ , respectively. For the cap of calcite (mesh 325) + sand, the concentrations were 0.0074, 0.016, and 2.50  $\text{mg L}^{-1}$ , respectively. The values recorded for each tested metals were far below the regulated level, 5.0  $\text{mg L}^{-1}$  (USEPA) [44]. It indicated

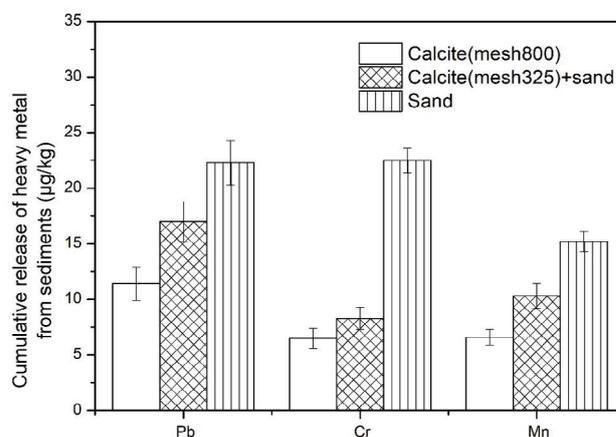


Fig. 2. Cumulative release of heavy metals from the sediments with different caps at 160 d.

that the capping materials such as calcite, or calcite + sand could have already adsorbed some metals through pore water in the underneath sediment. Therefore, the release amount of the metals was less than that in the control.

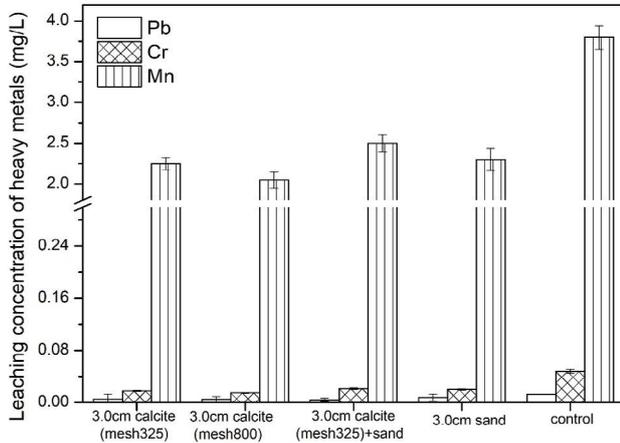


Fig. 3. Leaching concentration of heavy metals from sediments with different caps using TCLP.

Fig. 4 shows the percentage of heavy metal fractions in sediments with different caps at day 160. The results showed that the proportion of the extractable and active fractions were smaller in the sediments with caps than that in the

Table 4

Average release rates of Pb, Cr, and Mn in sediments at rapid releasing phase and the releasing periods (Unit for average release rates:  $\mu\text{g} (\text{kg m}^2 \text{d})^{-1}$ )

	Pb	Cr	Mn
Calcite (325 mesh)	1–2 d	1–8 d	1–8 d
	262.50	28.75	53.79
Calcite (800 mesh)	1–8 d	1–8 d	1–14 d
	67.50	27.71	27.32
Calcite (325 mesh) + sand (80 mesh)	1–2 d	1–5 d	1–8 d
	212.50	27.50	49.25
Sand (80 mesh)	1–2 d	1–2 d	1–2 d
	325.00	100.00	93.75
Control	1–2 d	1–2 d	1–2 d
	1,225.00	750.00	1,374.00

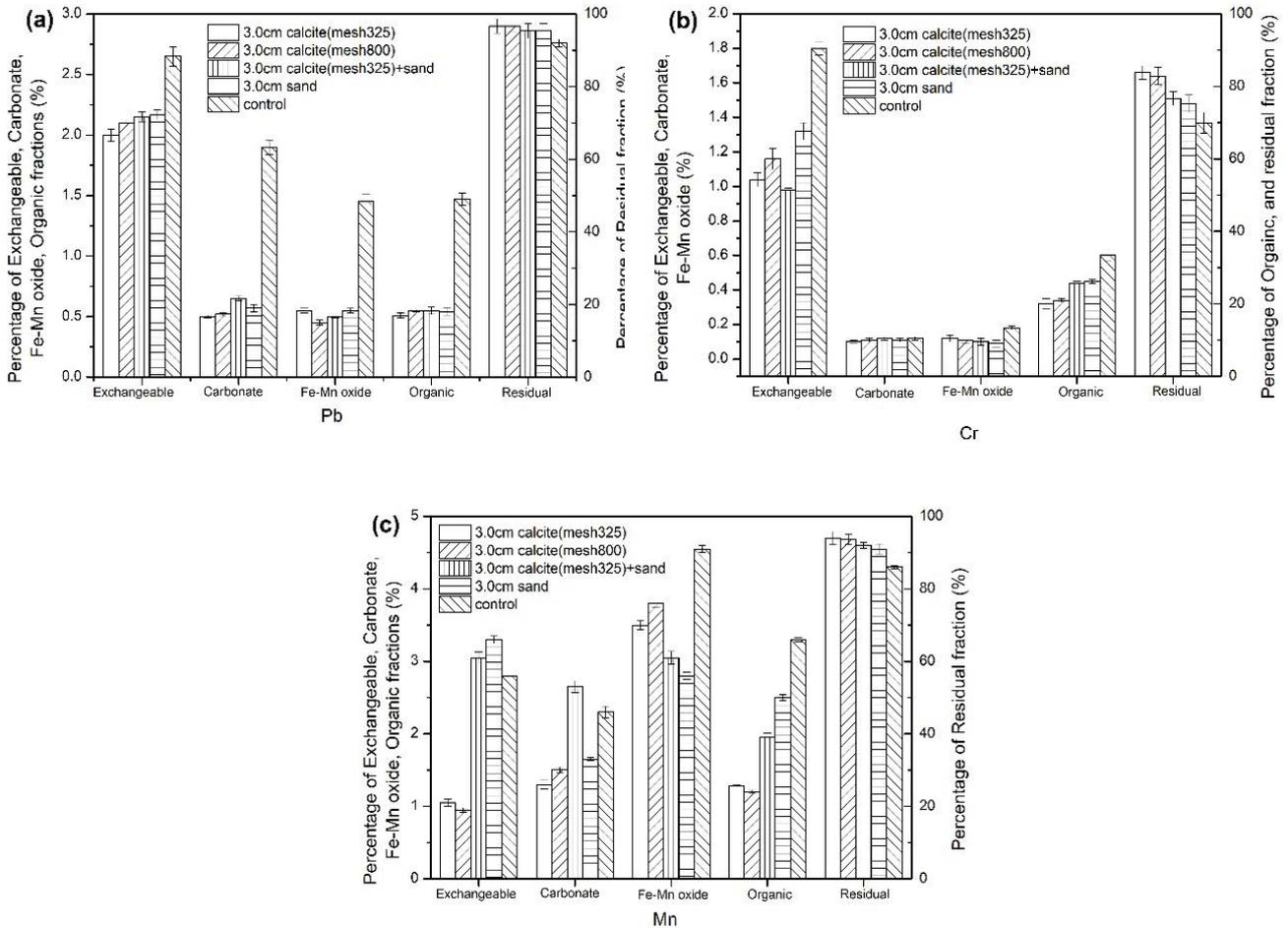


Fig. 4. Percentage of heavy metal fractions in sediments with different capping materials at day 160.

control. Also, the proportion of the residual fractions in the sediments with calcite as capping material was much more than that in the control sediments or the sediments with sand as capping material. It proved that there is a transformation tendency that the metal fractions would change from the fractions of exchangeable, carbonate, Fe–Mn oxidize, organic to the fraction of residual in the sediments with caps. The aquatic pH, ORP, and mineral characteristic could influence the metal absorbing on the sediments, especially the aquatic pH [45–47]. Sediment pH increase due to the calcite leads to a rapid increase in net negative surface charge and thus increases sediment's affinity for metal ions, which might be one of the reasons that the residual fraction in sediments with calcite cap was higher than sand and control [48].

#### 4. Conclusion

Considering the engineering applications and economic factors, the 3.0 cm thick cap of calcite (mesh 325) + sand was a suitable capping material to inhibit the heavy metal release from sediment, with the inhibition efficiencies of 77.90%, 81.16%, and 86.26% for Pb, Cr, and Mn, respectively. TCLP test showed that the leaching amounts of Pb, Cr, and Mn from the sediments with capping materials were lower than that of the control sediments. The transformation of the heavy metals in the sediments under different caps were different from each other, while the fractions transformation had the same trend that the changes were from the extractable and available fractions to the residual fractions.

#### Acknowledgments

This research was supported by Natural Science Foundation of Shandong Province (No. ZR2018MEE045), Shandong Provincial Department of housing and urban rural construction (No. 2017-K2-002), and Shandong Key Scientific and Technical Innovation Project (No. 2018YFJH0902). Yanhao Zhang was very grateful for the support of the China Scholarship Council.

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