

The deposition characteristics of coupled lead ions and suspended silicon powders along the migration distance in water seepage

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Keywords: heavy metal; silicon powder; metallographic microscopy; particle-size distribution; migration distance

Acknowledgments:

Funding for this research was provided by the National Natural Science Foundation of China (51678043; 51878035).

Abstract: The deposition characteristics of lead ions (Pb^{2+}) in the presence of silicon powders (SPs) were investigated in water seepage in a long one-dimensional sand column experiment. The injected SPs possess a very wide particle-size distribution (PSD). The concentrations of deposited Pb^{2+} and SPs and the migration distance along the water flow direction were measured by sampling. The PSDs of the deposited SPs in different sections were obtained by laser diffraction after transport test completion, and microstructure photos were also acquired through metallographic microscopy. Test results show that the presence of SPs may promote or inhibit Pb^{2+} migration, which is closely related to the concentration of injected Pb^{2+} , particle size and concentration of injected SPs, seepage velocity, and change in the absolute zeta potential in the surface charge. Larger SPs are first deposited within a relatively short distance from the injection surface of the sand column compared with smaller SPs. The median diameter of the deposited SPs near the injection end is larger than that of the injected SPs and gradually decreases with increasing distance, which represents a clear particle-separation characteristic due to the flowing water.

Keywords: heavy metal; silicon powder; metallographic microscopy; particle-size distribution; migration distance

1. Introduction

Rapid industrial production has led to large-scale deposition of metal-contaminated waste into soil and water and emission to the atmosphere, causing widespread ecosystem damage. As a result, wastewater treatment is becoming increasingly complex, and the transport of heavy metal ions (e.g., Pb^{2+} , Cd^{2+} , Cr^{2+} , Zn^{2+} , and Cu^{2+}) in groundwater has become the focus of considerable research interest in environmental geotechnology (Tansel and Rafiuddin, 2016; Hudcova et al., 2018; Wang et al., 2019).

The presence of mobile solid particles, such as colloids, clay particles, bacteria and silicon

powders (SPs), can provide additional media for the transport of heavy metal ions, thereby resulting in an increase or decrease in the transport rate of heavy metal ions (Syngouna and Chrysikopoulos, 2016; Kamrani et al., 2018). Clearly, a better understanding of the cotransport of heavy metal ions and SPs is essential for the remediation of contaminated soils. Karathanasis et al. (1999) showed that the existence of colloids enhanced metal ion transport and that Zn^{2+} was more mobile than Cu^{2+} . Malkovsky et al. (2015) revealed colloid-facilitated transport of uranium by groundwater from the ore zone to the surface of Earth. Recently, Abbar et al. (2019) investigated the cotransport of heavy metals and kaolinite particles in sand columns and evaluated the potential role of kaolinite in heavy metal transfer and the influence of flax geotextiles on the transfer of these pollutants.

The interactions of heavy metal ions with the soil matrix and their transport processes in pores can differ substantially (Raikova et al., 2019; Valsala and Govindarajan, 2019). Wu and Li (1998) reported that the mobility of several typical heavy metal ions followed the order of $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$ in neutral leachate (pH=7) but followed the order of $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+}$ in more acidic leachate. Tang et al. (2013) indicated that water-soluble organic carbon could compete for adsorption sites or form soluble complexes with heavy metal ions to reduce their adsorption onto soil media to facilitate the transport of heavy metal ions. Kumpiene (2015) investigated the microbial functional diversity, biochemical activity, heavy metal ion availability and soil toxicity of Cd^{2+} -, Pb^{2+} -, and Zn^{2+} -contaminated soils to restore soil ecological functions. Ma et al. (2016) showed that the rapid transport of soil colloids facilitated As(V) transport by inhibiting As(V) adsorption onto sand. Lee et al. (2019) revealed that the outflow concentration of heavy metal ions, such as Cr^{2+} and Pb^{2+} , in the pore solution increases with increasing colloidal particle concentration, while Cd^{2+} and Cu^{2+} lagged behind the release of colloidal particles; that is, the physical and chemical effects in the solution notably impacted heavy metal ion migration promoted by different suspended particles.

The presence of SPs can facilitate or inhibit heavy metal ion transport, depending on the interactions between heavy metal ions and SPs and their deposition mechanism onto the solid matrix of the porous medium, including influencing factors such as the ionic concentration, solution pH, double layer repulsive force, van der Waals force and critical salt concentration, especially the particle size of SPs (Chrysikopoulos and Katzourakis, 2015; Valsala and Govindarajan, 2019). These factors are influenced by the physical-chemical changes in the various suspended matter in seepage flow. For example, positively charged heavy metal ions can be easily adsorbed onto negatively charged SPs, which will conversely affect the deposition coefficient and dispersion process of SPs. Moreover, SPs with a small particle size can facilitate heavy metal ion transport due to the size exclusion effect (Bennacer et al., 2017; Russell and Bedrikovetsky, 2018), whereas SPs with a particle size larger than the pore size of the porous medium can become entrapped due to pore constrictions, which can therefore inhibit heavy metal ion transport. Wang et al. (2012) investigated the effect of the particle size on the retention and transport of nanoparticles in saturated porous media and examined the applicability of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory to describe the deposition of small nanoparticles on sand surfaces. Alem et al. (2015) proposed that, regardless of the hydraulic operating conditions, the median diameter of the particle-size distribution (PSD) of the recovered particles clearly increased over time due to physical clogging of the porous media.

The restriction mechanisms on the movement of individual suspensions (e.g., SPs or heavy metal ions) such as straining and filtration have been extensively examined previously. Ahfir et al. (2017) investigated the removal performance of suspended particles with a diameter range of 2–30 μm in porous media based on median diameter variations of the deposited suspended particles along a column and breakthrough curve evolution in the effluent. Li et al. (2018) simulated the microscale

changes in colloidal particle transport and deposition in porous media and replicated the flow field by reconstructing the pore structure, the main purpose of which focused on the deposition probability and the spatial distribution of deposited particles. The deposition process is always inseparable from the detachment mechanism. In this aspect, the experimental works of Cui et al. (2017) aimed to delineate the detachment characteristics of deposited quartz powder particles in porous media, and they revealed that changing the flow direction was more effective than changing the flow rate through a two-dimensional sandbox packed with quartz sand. Despite the many studies on the coupled transport of heavy metal ions and suspended particles in flowing water (Bradford et al., 2009; Kim and Walker, 2009), the deposition mechanisms of heavy metal ions together with suspended particles along the migration distance remain to be elucidated.

In this paper, the deposition characteristics and migration distance of lead ions (Pb^{2+}) in the presence of SPs were investigated in porous media in a long one-dimensional laboratory column experiment at three injection concentrations of Pb^{2+} , two particle sizes of SPs, and two Darcy velocities. The deposited Pb^{2+} and SPs along the column were measured, and the PSDs and microstructure photos at different migration distances were obtained after test completion. The test results indicated that the presence of SPs may promote or inhibit Pb^{2+} migration, which is closely related to the concentration of injected Pb^{2+} , the particle size and concentration of injected SPs, the seepage velocity, and the change in absolute zeta potential in the surface charge.

2. Materials and method

2.1 Experimental apparatus

The test apparatus used in the experiments is made of Plexiglas (Fig. 1(a)) with a long seepage distance. The inner diameter of the hollow cylindrical chamber is $D=8$ cm, and the length is $L=90$ cm. The length-to-diameter ratio is $L/D=11.25$, which can be regarded as a completely one-dimensional

sand column test. To facilitate sand sample filling and sampling for measuring the deposition concentration after testing, the cylindrical chamber is divided into three equal sections, each of which is 300 mm long. The three sections are connected by bolts with rubber rings to ensure good sealing (Fig. 1(b)).

The suspension (Pb^{2+} , SPs or Pb^{2+} mixed with SPs) in the water tank was pumped into the cylindrical chamber at a constant velocity using a peristaltic pump (BT600-2J, LongerPump Co., Baoding, China; control range: 120–1200 mL/min). The flow velocity was measured with a digital flow meter installed at the column inlet. The mixed solutions were maintained in suspension with the help of a motorized stirrer in the water tank. The water flowed vertically from the top to the bottom of the chamber, and the gravity force slightly accelerated the transport and deposition of SPs due to a coincident direction with the hydrodynamic forces.

Mesh screens 0.5 mm in diameter were placed at both the inlet and outlet of the chamber to prevent the loss of quartz sand particles. Leachate was collected using 30-mL plastic tubes at regular time intervals using a fraction collector (Huxi CBS-A 100, China) for measuring the concentrations of Pb^{2+} and SPs. The concentration of Pb^{2+} was determined using the graphite furnace method (TAS-990G; Persee General Instrument Co., Beijing, China) based on the concentration–absorbance relationship. The turbidity of SPs was measured using a turbidity meter (Type 2100N, HACH Co., USA), and the concentration of SPs was then calculated according to the concentration-turbidity relationship determined a priori.

2.2 Porous medium, Pb^{2+} and SPs

Natural quartz sand (mainly composed of the mineral constituent SiO_2 ; $\rho_s=2.65 \text{ g/cm}^3$) prepared by mechanical crushing was used as the porous medium. It had a white, lustrous surface with a high acid and alkali resistance. Its particle size uniformly ranged from 1–2 mm, and the mean value was

$d_g=1.5$ mm. The impurities and chemical substances on the quartz sand surface, such as iron and aluminum oxides, were removed by rinsing with 0.01 mol/L NaOH and HNO₃ solutions for 10 min prior to the experiment, and the quartz sand was then repeatedly washed with deionized water until the water pH remained constant.

Heavy metal ions of Pb²⁺ with an atomic weight of 207.2 were used. Due to the low solubility of Pb²⁺ and its high adsorption ability, SPs (or SiO₂ particles) can more notably influence Pb²⁺ transport. Pb²⁺ solutions with different concentrations were prepared by diluting a 100 µg/mL Pb(NO₃)₂ solution with deionized water. Given that Pb²⁺ ions in solution commonly result in a slightly acidic state, the Pb²⁺ solution was adjusted to pH=5.5 by adding an appropriate amount of 0.01 mol/L NaOH or HNO₃ solution.

Two commercial spherical SPs were prepared by dry grinding of natural high-quality color quartzite (Fuhong Mineral Products Co., Shanxi, China) insoluble in acidic and alkaline solutions. The median diameters of the two SPs were $D_{50}=13.4$ and 24.7 µm. Fig. 2 shows the measured PSDs by laser diffraction (LA-950 Mode, HORIBA, Japan; wet method). The two particle-size ranges were $d=1-60$ and $1-120$ µm. The injected SP actually had a very wide PSD, which reflects the situation in practical engineering whereby the mobilized solid particles may be very inhomogeneous. The two SPs were red and black, and the density of both SPs was $\rho_{sp}=2.2$ g/cm³.

2.3 Column experiments

To ensure complete saturation of the porous medium, 20 mL of deionized water (pH=7) was first added to the cylindrical chamber, and the outlet was adjusted to ensure no bubbles escaped from the bottom. The quartz sand was packed in layers, divided into 10 parts, according to the total amount; each layer was approximately 90 mm high. After each quartz sand layer was placed, the sand was stirred using a glass rod and compacted to a set thickness with a compacting hammer. Then, the next

quartz sand layer was added, and each time, the deionized water level was kept 2 cm above the top of the sand column. The final average porosity of the saturated sand column was $n=41.67\%$.

Prior to the experiment, the sand column was washed by injecting deionized water at a steady water flow velocity that was higher (e.g., $v=0.348$ cm/s) than that in the subsequent test (e.g., $v=0.260$ cm/s) until the effluent turbidity was nearly zero. The laboratory experiments were conducted to investigate the transport of either Pb^{2+} or SPs and the cotransport of Pb^{2+} with SPs. The injection concentration of SPs was set to $C_{\text{inj}}=0.5, 2$ and 4 mg/mL. According to the situations likely to be encountered in geoenvironmental engineering (Agbozu and Bassey, 2016; Tansel and Rafiuddin, 2016), the Pb^{2+} solution concentration was set to $C_M=100, 200$ and 400 ng/mL. The Darcy velocity was set to $v=0.087$ and 0.260 cm/s. The temperature was controlled at $T=22\pm0.2$ °C.

Because of the high coordination capacity of ethylenediaminetetraacetic acid disodium (EDTA), it readily forms stable chelates with Pb^{2+} adsorbed on the surface of SPs. In this experiment, 15 mL of a 0.05 mol/L EDTA disodium salt solution was used as the extraction reagent, which resulted in a high extraction efficacy ($> 90\%$) (Fangueiro et al., 2002; Qiao et al., 2017). The leachate was shaken for 4 h in a constant-temperature oscillator (HY-4, Changzhou, China; vibration amplitude: 0–20 mm; vibration frequency: 0–300 rpm). Subsequently, Pb^{2+} and SPs were separated using a desktop low-speed centrifuge at a rotation speed of 4500 rpm (L3-6K, Hunan Co., China). The supernatant was collected to measure the Pb^{2+} absorbance.

After completion of the transport tests, samples were collected from the different sections, and the sampling thickness of each section was approximately within 1 cm. Then, the concentrations of the deposited Pb^{2+} and SPs were measured, and the PSD of the SPs was obtained by laser diffraction (the wet method). In addition, a 5-megapixel metallographic microscope (CX40M, Ningbo Sunny Instrument Co., China) was used to examine the deposition state of SPs, which could easily

distinguish the difference between the colored SPs and white quartz sand, as evident in the microstructure photos.

3. Theoretical transport model of a single suspension

For a one-dimensional case, the transport equation of a single suspension (e.g., only heavy metal ions or SPs) can be written as (Ahfir et al., 2017; Bedrikovetsky et al., 2017):

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} - u \cdot \frac{\partial C}{\partial x} - \frac{\rho_s}{n} \cdot \frac{\partial \sigma}{\partial t} \quad (1)$$

where C is the suspension concentration [ML^{-3}], t is the time [T], x is the transport distance [L], D is the hydrodynamic dispersion coefficient [L^2T^{-1}], which is defined as $D = \alpha_d \cdot u$, where α_d is the hydrodynamic dispersivity [L], and u is the average internal velocity [LT^{-1}], n is the porosity [-], σ is the attachment concentration [MM^{-1}], which refers to the mass of the suspension adsorbed per unit mass of the solid matrix of the porous medium, and ρ_s is the solid matrix density [ML^{-3}].

The deposition rate (or the release rate) in Eq. (1) has the following form (Bai et al., 2019):

$$\frac{\partial \sigma}{\partial t} = \lambda \cdot (S - \sigma) \quad (2)$$

where λ is the reaction rate constant [T^{-1}] and S is the equilibrium adsorption concentration, which can be expressed as (Bai et al., 2019):

$$\frac{\partial S}{\partial C} = \kappa_d \cdot e^{-\beta_1 \frac{C}{C_L}} \quad (3)$$

where κ_d is the transient equilibrium constant [M^{-1}L^3] and $\kappa_d = \beta_1 \cdot S_{\max}/C_L$. β_1 is the dimensionless attenuation factor of the initial deposition process (i.e., $\sigma=0$ when $t=0$), S_{\max} is the maximum attachment concentration, and C_L is the characteristic concentration, which is assumed to be $C_L=1$ (whose dimension is the same as that of C).

From Eq. (2), the attachment concentration can be deduced as $\sigma = S(1 - e^{-\lambda t})$ for the initial deposition process. Actually, the reaction rate constant λ essentially reflects the mass conversion between the flowing water and deposited suspension on the solid matrix under hydrodynamic forces,

which is closely related to the seepage velocity. For a column test, the ratio of the mass of migrating matter flowing through cross-section x at time t to the total mass injected into the porous medium is defined as:

$$M_b = \frac{\int_0^t C(x,t) \cdot u \cdot (nA) \cdot dt}{m} \quad (4)$$

where M_b (%) is the penetration rate, A is the cross-sectional area of the sand column [L^2], and m is the total mass of the suspended matter injected into the porous medium [M].

The deposition rate is defined as $M_a = 1 - M_b$ (%), which denotes the amount of suspended matter deposited in the range of $(0, x)$ in the column. The dimensionless time V_p is defined as the ratio of the total volume of water flowing through the column to the void volume of the column (i.e., the pore volume; $V_p = (unAt)/(nAL) = ut/L$), where L is the column length [L].

4. Results and discussion

4.1 Transport process of Pb^{2+}

Fig. 3 shows the breakthrough curves (BTCs) of only Pb^{2+} at the different injection concentrations ($C_M = 100, 200$ and 400 ng/mL) and Darcy velocities ($v = 0.087$ and 0.260 cm/s). Clearly, the steady values increase with increasing injection concentration C_M , and the times needed to reach stability also correspondingly increase. On the other hand, the outflow concentration slightly increases with increasing Darcy velocity ($v = 0.087$ cm/s \rightarrow 0.260 cm/s), which actually reveals a small deposition effect at a higher velocity.

Using Eqs. (1)–(3), the BTCs of Pb^{2+} can be theoretically predicted (see Fig. 3), which are in good agreement with the test results in terms of the trend, with a coefficient of determination of $R^2 > 0.90$. The adopted parameters are summarized in Table 1 referring to the test results of the authors. According to the concept of the theoretical model, the parameters (β_1, κ_d) are not related to the hydrodynamic process (Bai et al., 2019), and parameter α_d is also simply set to a constant value (Bai

et al., 2017; Bennacer et al., 2017). Thus, only the reaction rate constant λ varies due to the difference in seepage velocity. Therefore, determining the calculation parameters becomes very simple and clear. The transport processes are calculated using the PARDISO solver in COMSOL Multiphysics (COMSOL Co., Ltd.). The control parameters in the calculations are as follows: the temporal discretization step is 3 s, the spatial discretization step is 0.02 m, the damping factor is 0.9, the iteration number is 4, and the relative tolerance is 0.0001.

For the test results using the impulse-injection pattern obtained by the authors at a higher injection concentration (Pb^{2+} , $C_M=100\text{--}400$ mg/mL), the BTCs at $v=0.087$ and 0.260 cm/s are approximately the same, seemingly indicating that the Darcy velocity has a negligible effect on the transport of heavy metal ions. This phenomenon is slightly different from the test results shown in Fig. 3 (herein, $C_M=100\text{--}400$ ng/mL). Actually, during heavy metal ion transport, a portion dissolves in water and is transported by it, while some is adsorbed onto the solid matrix. Clearly, at a high injection concentration, the heavy metal ions dissolved in water are dominant due to the relatively limited adsorption amount on the solid matrix, which will have little effect on the effluent concentration in a short time (e.g., the impulse-injection pattern or the initial period in Fig. 3). In contrast, a large influence is observed in the case of continuous injection (Fig. 3), which is manifested as a distinct deposition and subsequent release process with decreasing injection concentration. The theoretical results also confirm this characteristic (see Fig. 3).

Compared with the outflow concentration of Pb^{2+} in the absence of SPs (Fig. 3), the steady outflow concentration of Pb^{2+} in the presence of SPs (Figs. 4 and 5) is complex. In other words, the presence of SPs may promote or inhibit Pb^{2+} migration. The final results seem to be closely related to the concentration of injected Pb^{2+} , the particle size and concentration of injected SPs, and the seepage velocity. For instance, the steady concentration of Pb^{2+} in the presence of SPs ($C_{\text{inj}}=0.5$ mg/mL; Fig.

4(a)) for a slightly smaller particle size (e.g., $D_{50}=13.4\ \mu\text{m}$) and at a lower injection concentration of Pb^{2+} (e.g., $C_M=100\ \text{ng/mL}$) and higher seepage velocity (e.g., $v=0.260\ \text{cm/s}$) is nearly 1.1 times that in the absence of SPs. This indicates that SPs can significantly facilitate Pb^{2+} transport due to the size exclusion effect (Alem et al., 2015; Bai et al., 2017).

However, with increasing injection concentration of Pb^{2+} (e.g., $C_M=400\ \text{ng/mL}$; please compare Figs. 3 and 4(a)), the presence of SPs inhibits Pb^{2+} transport due to the accelerated deposition of SPs. For example, the steady concentration of Pb^{2+} in the presence of SPs ($C_{\text{inj}}=0.5\ \text{mg/mL}$; Fig. 4(a)) for a slightly smaller particle size (e.g., $D_{50}=13.4\ \mu\text{m}$) is nearly 0.5 times that in the absence of SPs (Fig. 3) at a Pb^{2+} injection concentration of $C_M=400\ \text{ng/mL}$ and a seepage velocity of $v=0.260\ \text{cm/s}$. At this time, Pb^{2+} adsorption onto SPs reduces the repulsive force between SPs and the solid matrix according to the DLVO theory due to the decrease in absolute zeta potential in the surface charge (Wang et al., 2012; Sugimoto et al., 2014; Chrysikopoulos, et al., 2017; Chen et al., 2018), resulting in an increase in the deposition amount of SPs onto the solid matrix. Hence, the coupling effect of Pb^{2+} and SPs should be considered, which is attributed to the decrease in the double electric layer on the SP surface (i.e., the decrease in surface potential energy). Clearly, the promotion effects of SPs increase with increasing injection concentration (please refer to the difference between Figs. 4(a) and 4(b)), while they significantly decrease with increasing particle size (please refer to the difference between Figs. 4 and 5).

4.2 Deposition of Pb^{2+} and SPs along the migration distance

As a typical result, Fig. 6 shows the measured Pb^{2+} deposition concentrations along the migration distance when the particle size of the co-injected SPs is $D_{50}=13.4\ \mu\text{m}$, including the results in the absence of SPs (i.e., $C_{\text{inj}}=0$). The test results reveal that the Pb^{2+} deposition concentration on the solid matrix rapidly decreases with increasing migration distance. When the migration distance is

reduced to $x=90$ cm (i.e., the length of the sand column), the deposition concentrations are already very low. In addition, with increasing seepage velocity of the water flow (e.g., $v=0.087 \rightarrow 0.260$ cm/s), due to the continuously increased hydrodynamic forces, the Pb^{2+} deposition concentration also notably decreases with decreasing suspended SPs in the water flow (please compare Figs. 6 and 7). Similar results are also obtained when $D_{50}=24.7$ μm , which is not shown herein due to the limited space. However, the test photos in Fig. 1(b) clearly show the transport evolution of SPs over time. On the whole, with increasing particle size of the SPs, the SP deposition amount will increase significantly (Fig. 1(b)), while the Pb^{2+} deposition amount will conversely decrease. In other words, when the SP particle size is larger than a certain value, SP adsorption onto heavy metal ions will be weakened, namely, the inhibition effect will be significantly reduced.

Fig. 6 shows that Pb^{2+} deposition increases with increasing injection concentration (e.g., $C_M=100$ ng/mL \rightarrow 400 ng/mL). At this time, more Pb^{2+} will be adsorbed onto the surface of SPs and migrate or be deposited in the form of coupled Pb^{2+} and SPs with the flowing water, which is reflected by the SP deposition distribution with the migration distance, as shown in Fig. 7. It should be noted that the concentration of the injected Pb^{2+} in this test is arguably low (i.e., $C_M=100\text{--}400$ ng/mL), so most Pb^{2+} will be adsorbed onto the surface of SPs, thus forming a combination of coupled Pb^{2+} and SPs. However, when the Pb^{2+} injection concentration notably increases, Pb^{2+} will not only occur in combined form but will also occur as free Pb^{2+} in water and be transported by the flowing water. At this time, as shown in Figs. 4 and 5, the Pb^{2+} concentration in the leachate will notably increase.

Generally, the heavy metal ions adsorbed onto SPs will change the dielectric properties of the SPs, resulting in positively charged surfaces. As such, the adsorption of SPs onto the porous medium matrix increases, and the deposition probability of SPs also increases. However, in this study, it seems that the Pb^{2+} injection concentration has little effect on SP deposition during the migration process

(see the green and red test dots in Fig. 7), which is probably related to the low Pb^{2+} injection concentration (i.e., $C_M=100\text{--}400$ ng/mL). In other words, adsorption of a small amount of heavy metal ions is not enough to significantly change the surface charge characteristics of SPs. At this time, the migration process of SPs can still be described by the transport theory of a single suspension (i.e., Eqs. (1)–(3)). In contrast, the coupling effect of SPs on heavy metal ion transport must be considered. Hence, heavy metal ions will migrate and be deposited in two forms, i.e., dissolved in the flowing water and absorbed onto the SPs.

Using Eqs. (1)–(4), the BTCs of SPs can be theoretically predicted, and furthermore, the distributions of the deposited SPs along the migration distance are also obtained (see the solid lines in Fig. 7). The adopted parameters are listed in Table 1 according to the test results. Fig. 7 also shows the predicted curves of the deposited SPs during transport of only SPs (i.e., dashed lines). Clearly, there is a good agreement between the predicted and experimental results denoted by the dots, with a coefficient of determination of $R^2>0.91$. These suitable agreements indicate that the deposition-release model proposed in this paper can well reflect the migration process of a single suspended substance by seepage. Clearly, the reaction rate constant of SPs interacting with the solid matrix is far larger than that of Pb^{2+} interacting with the solid matrix (Table 1), which essentially reflects a more notable hysteretic effect of the SPs attached on the matrix by the clogging effect. It can be deduced that heavy metal ion transport is closely related to SP transport due to the strong adsorption on heavy metal ions with positive charges. In other words, the magnitude of the mutual influence between two types of suspended matter on their transport and deposition characteristics depends on the physical and chemical properties.

Based on the test results in Fig. 6, the Pb^{2+} deposition rate in the whole column with the SP injection concentration, C_{inj} , can also be given by Eq. (4) (see Fig. 8). Clearly, with increasing SP

injection concentration (e.g., $C_{inj}=0, 0.5, 2, 4$ mg/mL), the Pb^{2+} deposition amount gradually increased. Here, $C_{inj}=0$ indicates the Pb^{2+} deposition rate in the absence of SPs. Apparently, with increasing Pb^{2+} injection concentration ($C_M=100, 400$ ng/mL), the Pb^{2+} deposition amount decreases. Moreover, heavy metal ions will be dissolved in water and migrate with the water flow. Therefore, the deposition rate of heavy metal ions decreases slightly with increasing seepage velocity, and the heavy metal ions dissolved in water will gradually become dominant with increasing injection concentration.

As mentioned before, with increasing SP particle size (e.g., $D_{50}=13.4 \rightarrow 24.7$ μm), the SP deposition amount increases. However, due to the reduction in the specific surface area of SPs, their adsorption capacity of Pb^{2+} will be weakened, resulting in a decrease in the Pb^{2+} deposition rate. In addition, the increasing trend of the Pb^{2+} concentration with increasing SP injection concentration will also be weakened, which results in a decreasing trend in the Pb^{2+} deposition rate (Fig. 8(a)).

4.3 Particle-size distributions of the SPs with the flowing water

For SPs with smaller particle sizes (e.g., $D_{50}<10$ μm), the preferential flow caused by the size exclusion effect can accelerate the movement of heavy metal ions (e.g., Pb^{2+}) along with that of SPs (Bai et al., 2017; Katzourakis and Chrysikopoulos, 2019). However, for SPs with larger particle sizes (e.g., $D_{50}=13.4$ and 24.7 μm), the migration process will experience notable deposition due to the pore blocking effect of the porous medium, and eventually, heavy metal ion migration will be inhibited rather than promoted. The microstructure photos after the transport tests (Figs. 9–11) reveal that the SPs with larger particle sizes are first deposited within a relatively short distance from the injection surface of the sand column (e.g., $x=1$ cm), while the SP deposition amount gradually decreases with increasing distance. At a certain point, the deposition amount rapidly decreases (e.g., $x=30, 60$ cm), which is consistent with the measured deposition concentrations along the migration

distance of the sand column (Fig. 7).

The so-called straining effect is sensitive to the ratio of the solid particle diameter D_{50} to the porous medium grain diameter d_g (Ahfir et al., 2017; Bai et al., 2017). In the experiments, $D_{50}/d_g=0.0089-0.0165$ (i.e., $D_{50}=13.4$ and $24.7\ \mu\text{m}$, and $d_s=1.5\ \text{mm}$), and as a result, the straining effect becomes dominant relative to the preferential flow (Xu et al., 2006; Johnson et al., 2010; Alem et al., 2015). Large-sized SPs can lead to pore narrowing (see Figs. 9(a), 10(a) and 11(a)), which enhances the SP deposition probability by the straining effect, especially at a low velocity (e.g., $v=0.087\ \text{cm/s}$; Fig. 9(a)). Comparing Figs. 9 and 10 reveals that with increasing seepage velocity (e.g., $v=0.087\rightarrow 0.260\ \text{cm/s}$), the SP deposition amounts at the same distance decrease and advance to locations farther away from the injection end. That is, at a low velocity, the porous medium captures most of the injected larger-sized SPs at the entrance. At a high velocity, the water flow carries the particles deeper into the porous medium, producing more gradual changes in the deposition profile. Certainly, at the same seepage velocity, the migration distance of larger-sized SPs will be readily limited to a narrow range (Fig. 11; $D_{50}=24.7\ \mu\text{m}$).

Fig. 2 shows the PSD of the two selected SPs (i.e., $D_{50}=13.4$ and $24.7\ \mu\text{m}$) in the different sections of the sand column after transport test completion. Fig. 2 shows that with increasing distance from the injection end, the particle size of the deposited SPs gradually decreases, exhibiting a clear particle-separation characteristic due to the flowing water. For example, for the injected SPs of $D_{50}=13.4\ \mu\text{m}$ comprising a wide range of $d=1-60\ \mu\text{m}$, the median diameter is $D_{50}=26.4, 17.6, 11.3,$ and $9.5\ \mu\text{m}$ when $x=1, 30, 60,$ and $89\ \text{cm}$, respectively, while for the injected SPs of $D_{50}=24.7\ \mu\text{m}$ with a range of $d=1-120\ \mu\text{m}$, the median diameter is $D_{50}=42.7, 17.8, 15.0,$ and $11.5\ \mu\text{m}$, respectively. Clearly, at the injection end (e.g., $x=1\ \text{cm}$), the median diameter of the deposited SPs will be even larger than that of the injected SPs, which will gradually decrease with increasing migration distance,

and finally, the median diameter will be smaller than that of the injected SPs near the outflow (e.g., $x=89$ cm).

5. Conclusions

The test results indicate that the Pb^{2+} deposition concentration rapidly decreased with increasing migration distance. On the whole, with increasing SP particle size, the SP deposition amount will significantly increase, while the Pb^{2+} deposition amount will conversely decrease. Actually, the presence of SPs may promote or inhibit Pb^{2+} migration, which seems to be closely related to the concentration of injected Pb^{2+} , the particle size and concentration of injected SPs, the seepage velocity, and the change in absolute zeta potential in the surface charge.

Pb^{2+} deposition increases with increasing SP injection concentration; in addition, more Pb^{2+} will be adsorbed onto the surface of SPs and migrate or be deposited as coupled Pb^{2+} and SPs with the flowing water. The heavy metal ions adsorbed onto the SPs will change the dielectric properties of the SPs, resulting in positively charged surfaces. The theoretical predicted results are in good agreement with the test results, indicating that the deposition-release model presented in this paper can suitably reflect the transport process of a single suspension by seepage.

The microstructure photos reveal that larger SPs are first deposited within a relatively short distance from the injection end of the sand column, while SP deposition gradually decreases with increasing migration distance. Clearly, the median particle size of the deposited SPs near the injection end will be larger than that of the injected SPs and then gradually decrease with increasing migration distance, which represents a clear particle-separation characteristic due to the flowing water.

Acknowledgments

Funding for this research was provided by the National Natural Science Foundation of China (51678043; 51878035).

Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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