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Study on the mechanism of distribution, preservation and occurrence state for the remediation of Cr(VI) from chrome slag soil-water belt

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ABSTRACT: *The pollution of Cr(VI) in chrome slag soil-water belt is a very serious pollution problem due to industrial expansion in China. In this paper, the transmission characteristics of stabilizing nanoscale zero-valent iron (nZVI) in chrome slag soil-water belt are investigated by carrying out a simulatively penetrating experiment, in which use of soil column is made for， the elution process test of Cr(VI), the long-time maintained experiment and the chemical state analysis of Cr in the washed soil column. The results showed that the chrome slag soil-water belt-a and c were liable to be penetrated. The chrome slag soil-water belt-b had relatively slow penetration rate. The concentration of Cr(VI) in the leachate in the long-time maintained experiment was bigger than short-time test. When the reaction proceeded with 0.37g/L of nZVI, the final fixed rate of Cr(VI) in the chrome slag soil-water belt-c was 97.55%. It makes sense to use excessive nZVI to maintain the reducing effect of reaction system. On the whole, distribution of Cr in various states is different in different soil samples. The residual state accounts for the largest proportion, followed by the adsorption state and the organic combination state. The residual state increases with the depth of soil column. For the carbonate bounded state, it reaches maximum proportion at mid-depths. However, the proportion of organic bounded state keeps decreased with the increase of soil depth. The research results in this paper provide an important reference for the practitioner regarding the remediation of soil and groundwater pollution.*

KEYWORDS: *SOIL-WATER BELT; CHROME SLAG; CR(VI) ; NZVI*

1. Introduction

The pollution of soil-water zone in the industrial site as side-products of industrialization is tremendous and persistent [1, 2]. The pollutants of the soil-water zone include the inorganic substance such as acid, alkali, salt, heavy metal and radioactive element, as well as the organic contaminant such as phenols, prussiate, organic pesticide, petroleum, detergent and pathological substances [3, 4]. Cr(VI) can be frequently detected in the contaminated soil and groundwater caused by leather tanning, electroplating, wood processing pollution [5-7]. According to bulletins on the nationwide investigation of soil pollution conditions in 2014, Cr pollution in China exceeded the standardized threshold in the national soil sampling points by 1.1%. The Cr(VI) pollution poses serious environmental problems and is dangerous to human health due to they can form the un-biodegradable compounds [8]. Thus, the remediation of Cr(VI) - contaminated soil is much needed.

Conventional feasible remediation techniques for the removal of heavy metals from soil and groundwater can generally be divided into three categories: physical methods, chemical methods and biological treatment. The physical method mainly contains filtration, sediment, centrifugation, magnetic process, flotation, new soil replacement, deep tillage, solidification, steam extration and thermal desorption method [9-14]. The main chemical method for the remediation of soil pollution are chemical, oxidation, chemical reduction, chemical elution, solvent-extraction and electrokinetic remediation [15-19]. It is worth noting that Fe0(ZVI) and nZVI are the frequently-used reductive agent when employing chemical reduction method [20, 21].

The biological method of the remediation encompasses phytoremediation, animal repair and microbial recovery technique [22-24]. However, these treatment methods suffer from high cost, large-scale applications challenges remain, causing secondary pollution [25, 26]. Among the large numbers of treatment methods, nZVI were wildly used in the in-situ remediation [27]. This thesis is concerned with the remediation principle about Cr(VI) pollution by means of nZVI in soil-water zone. The in-situ reduction technology with nZVI belongs to in-situ chemical reduction, of which ZVI shows reduction effects for many metal ions. In recent years, ZVI is common used for the reduction treatment of heavy mental pollutant such as Cr, U, Se, Co, Cu, Hg, As [28-30]. Furthermore, its applicable depth is relatively larger. The advantage of this technology becomes more obvious with the greater depth as the anaerobic environmental is beneficial to the stability of the reducing agents. The reduction technology with nZVI can be used for removal of wide range of pollutants, and also possesses good removal efficiencies of many kinds of heavy metal and organic chloride. Besides, the repair process took place quickly with high efficiency. In most cases, the contaminants can be transferred to non-poisonous compounds within several days.

For the ion transport of heavy metals in soil and groundwater, He Feng et al. conducted a soil penetration test using a variety of osmotic media (coarse and fine glass beads, clean sand, and sandy soil) [31]. Studies have shown that the rate of migration is affected by many factors, including the particle size of nZVI, dispersion, agglomeration tendency and other properties, as well as the amount of dosage, the quality of stabilizer.

For the sustainability during the remediation process of polluted soil by heavy metals, researchers normally focused on the dispersal of the reducing agents. Such as the mechanism study on the dispersion and stability of nZVI [32]. Up to now, researchers prepared nZVI usually by employing CMC (Carboxymethyl Cellulose) aqueous solution. Some studies indicated that nZVI particle exhibited a constant migration rate in different mediums, which was controlled by first-order kinetic mechanism [33]. Researchers discovered that the nature of ordinary nZVI particles was active, which easily induced oxidation or agglomeration, including physical bonding (soft agglomeration) and chemical bonding (hard agglomeration) [34-36]. Hence, the technology for stabilization, decentralization and homogenization of nZVI particles is of high importance. In recent years the common dispersion stabilizer are CMC, pectin and Fe3O4. CMC is a kind of water solubility cellulose ether. Coelho used magnetite Fe3O4 to stabilize nZVI, reduced the cluster effect of nZVI [37]. Regina C. C. Costa discovered that Fe3O4 promote the pure iron powder enhanced its activity [38].

The occurrence of heavy metals in soil remediation not only affects the soil chemical properties, but also its biological effectiveness [39, 40]. Research shows that the occurrence of heavy metals is subject to internal factors and external factors. The internal factors mainly include the nature of the soil water belt, initial valence of Cr and initial chemical forms while the external factors include the pH, temperature of the system, Exogenous chemical groups, and other parameters [41].

However, there were few studies on the migration of Fe0 in soil-water zone, long term maintain, mode of occurrence. The real application of this type of technology in chromium residue contaminated site soil-water zone is still lacking.

This text studied the transferring mechanism, preservation and occurrence state of Cr(Ⅵ) in chromium residue contaminated site soil-water zone. A variety of soil column experiments were carried out to simulate the operating conditions in actual soil sites, which can reflect the reciprocal actions of ions and the effect of hydrodynamics parameter on balancing in reactor. The objectives of the study were to (1) research the transmission characteristics of stabilizing nZVI in chrome slag soil-water belt, (2) achieve the elution process rule of soil-water sample columns, (3) obtained the long-time maintained experiment rule of Cr(Ⅵ) in the soil-water column, (4) evaluated the changes of Cr speciation in the after-amended soil.

This text manifested the important scientific significance in the application of nZVI restore Cr(Ⅵ) in chromium residue contaminated site soil-water zone for understanding its migration, preserve and deposition mechanism.

2 MATERIALS AND METHODS

2.1 Samples and the experimental columns

The test facility were consists of the soil-water column, the suspension container (isolation of oxygen), the pressure water pump and the gathering unit of filter liquor. The contaminated soil sample was placed into a glass column (internal diameter = 5 cm, height = 45 cm). Each column was filled with approximately the same amount of soil (300 g), while the effective height of the soil in the column is 40 cm. At the bottom and the top of column, a quartz sand layer of 10 cm was installed. The chromium-containing soil samples were collected from the chrome slag soil-water belt-a, b, c. And table 1 shows the characters of the samples in this study.

Table 1 Physical and chemical characteristic of the soil samples

Sample	Natural void ratio	Specific gravity	*Organic content (g/kg)*
belt-a	0.82	2.81	*0.9*
belt-b	0.41	2.68	*24.6*
belt-c	0.72	2.74	*6.1*

2.2 The test method of the transmission characteristics of stabilizing nZVI in soil-water belt

The background solutions used in the eluting test are NaCl and NaHCO3 (0.84 mM NaCl + 0.16 mM NaHCO3, pH 7.5). Before elution test, de-ionized water was flowed through the soil column to saturate the soil and reach equilibrium. The elution test was carried out by injected the stabilizing nZVI suspension (0.12 g/L) into the soil column. CMC and galacturonic acid with the mass ratio of 1:1 were adopted as the complex stabilizer to stabilizingnZVI. The dosage of complex stabilizer was 1.5 g/L. The concentrations of Fe in the leachate were measured, and then achieved the breakthrough curves based on the above results.

2.3 The test method of the elution process rules of Cr(Ⅵ) in soil-water column

The concentration of Cr(VI) in pre-assembly soil-water system of each column is 0.1 g/kg. Each column was leached upwards from the base with a continuous flow of stabilizing nZVI suspension. The flow rate was adjusted to be 0.15 mL/min and the volume of stabilizing nZVI suspension was controlled in 3 L. The nZVI concentration injected of this test is 0.12 g/L, with pH=6.0. The concentration of Cr(VI) in leachate were measured.

2.4 The test method of long-time maintained system experiment

In this section, the chrome slag soil-water belt-a, b, c were studied comparatively. Firstly, stabilizing nZVI suspension with the concentration of 0.37 g/L and 0.60 g/L(total flow 0.7 L) were upward injected one time. The initial pH of suspension liquid is 6.0. Secondly, 0.7 L of DIW (the de-ionized water) was eluted the soil column from bottom to top after stewing 120 h, while the flow rate was adjusted to be 0.15 mL/min. Lastly, the concentration of Cr(VI) in leachate were measured.

2.5 The test method of the occurrence distributions of Cr(Ⅵ) during the reaction with nZVI

The soil column leaching tests remain unchanged with foregoing test. The process was stopped when the test was carried out to 4 BV. After the tests, the columns were separated and extruded. Take out the soil samples including the front and back 1cm from the different depth sections (5 cm, 10 cm, 15 cm, 20 cm and 25 cm). The column was described as the inflow side because of the upward mode. The soil samples from the specified depth rangewere thorough mixed, and then analyzed the six occurrence chemical forms of Cr, including: the exchangeability state, the adsorption state, the organic combination state, the carbonate combination state, the sulphide bound state, the residual state. The occurrence distributions rule of Cr(Ⅵ) during the reaction with nZVI were achieved. Based on the above result, the proportion of every occurrence chemical forms of Cr can be calculated.

3. Results and Discussion

3.1 The transmission characteristics of stabilizing nZVI in simulative soil-water belt

The results obtained from soil column leaching tests are shown in the form of breakthrough curves (figure 1).

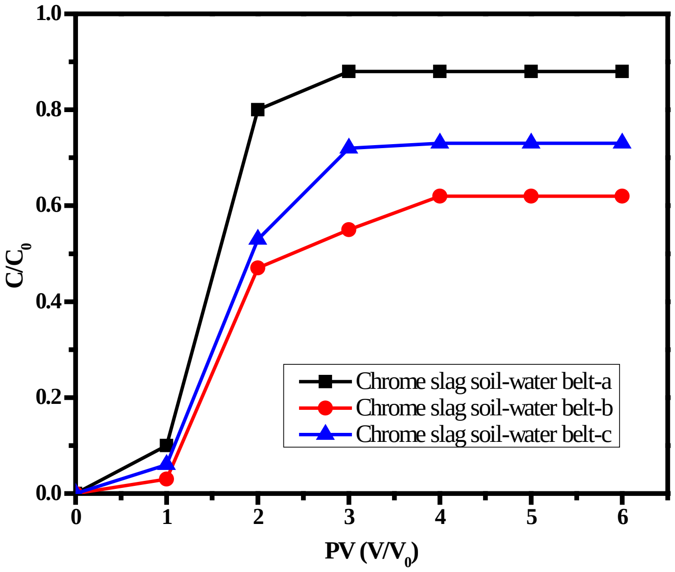

Figure 1 The breakthrough curve stabilization nZVI in various soil medium

As shown in figure 1, the results of fitted breakthrough curves of stabilization nZVI showed significant difference between from each other. As shown in figure 1, the relative concentrations (C/C0) of the three soil samples in leachates were increased with effluent volume. The chrome slag soil-water belt-a began to penetrate at 0.95 PV (C/C0 = 0.14), and attained the highest stable value at 2.00 PV (C/C0 = 0.88). While the chrome slag soil-water belt-b began to penetrate at 1.43 PV (C/C0 = 0.04) and showed an apparent plateau in the breakthrough curve (C/C0 = 0.55-0.62). As shown in the breakthrough curve of belt-c, the point at 0.96 PV (C/C0=0.11) indicated the chrome slag soil-water began to penetrate, and achieved the highest stable value at2.00 PV(C/C0 = 0.80).

The breakthrough curve of the chrome slag soil-water belt-a was located left relatively compared to belt-b, indicatedthe chrome slag soil-water belt-a was easy to penetrate. As we all known that, the heterogeneity of soil, and the chemical composition will interfere with the migration of heavy metal. The heterogeneity soil solutes are more likely to penetrate than homogeneous soil. In addition, the higher concentration of nZVI, the greater diffusion was shown, making it easier to penetrate.

The disturbance effect of the exchangeable ion received from soil more than non-adsorptive ion. The porosityin non-homogeneous soil will caused partial preferential flow appeared and put the penetrate time forward at some parts of soil-water belt. The chrome slag soil-water belt-b in test containing more small diameter clay, and it’s penetrate feature was more similar to clay. Because of the grinding pretreatment, the character of the soil in the chrome slag soil-water belt-c was close to the sand, the penetration rate is slightly higher than silty sand. However, a few advantages hydraulic conditions can be found due to its complex chemical composition and micro-inhomogeneous particle distribution.

3.2 The elution process rules of Cr(Ⅵ) in soil-water belt

Fig. 2 displays the elution process rules of Cr(Ⅵ) in different soil-water belt samples.

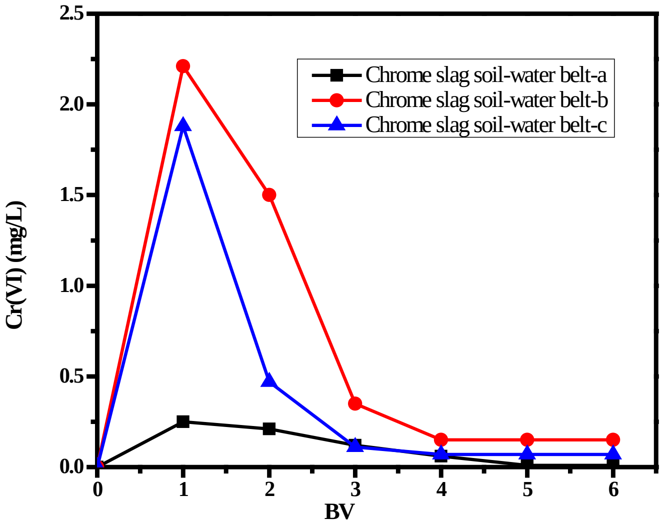

Figure 2 Different soil samples of Cr(VI) in the soil column elution process

As shown in figure 2, the concentration of Cr(VI) in the leachate of the chrome slag soil-water belt-a increased more slowly during the whole elution process, suggesting most of Cr(VI) was reduced by stabilizing nZVI. Compared with belt-a, the concentration of Cr(VI) of belt-b and belt-c were increased in the initial stage, and then decreased gradually in later period and reached apparent plateau (3 BV - 6 BV). The concentration of Cr(VI) in the lechate from the chrome slag soil-water belt-b were 2.21 mg/L and 0.35 mg/L at 1 BV and 3 BV, respectively. While the corresponding values were 1.88 mg/L and 0.11 mg/L, respectively.

The concentration of Cr(VI) in the leachate was affected by the viscosity of soil. The high-viscosity of soil will be blocking Fe0 in the reaction system which lead to more Cr(VI) was detected in the leachate. The peak dispersion caused by the inhibition of Fe0 from soil-water system in terms of the hysteresis release effect. Generally, the existing of inhibition will leads to the width of the peak broadening, which also applies to the phenomenon of trailing tail.

3.3 Long term maintenance test

The tests were performed by injecting nZVI into saturated soil columns with long-term maintenance, and the loess soil and chromium residue soil were studied respectively and comparatively. At the same time, the effect on reducing maintenance due to the excessive nZVI was also investigated (as shown in figure 3). It can be seen from Fig. 3, the curves were basically similar for the tests of long-term maintenance, but the numerical values in the intermediate process were varied greatly. The concentration of Cr(VI) in the filtrate was high at 1 BV, while decreased to a low level and maintained constant at 4 BV. Moreover, because of the "top-down" model was adoptedfor injecting, there are great varieties among the different types of soils.

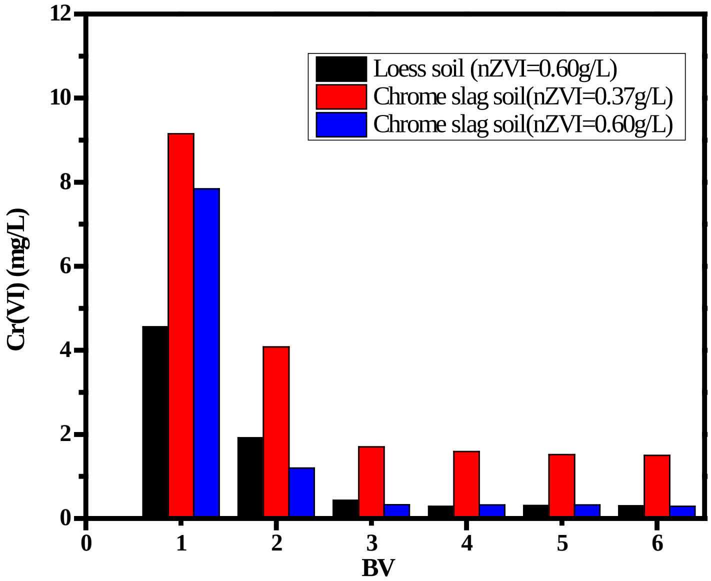

Figure 3 Different soil samples of Cr(VI) in the soil column during long time maintain elution process

3.4 The distributions of various species Cr(Ⅵ) were taken out during the reaction with nZVI

The transformation and distributions of Cr in different depth of soil were analyzed. Samples were taken from the depth of 5 cm, 15 cm and 25 cm at the liquid side. The 6 chemical forms of Cr, including exchangeability, adsorption, organic combination, carbonate combination, sulphide and residual, in the samples were analyzed.

As shown in figure 4 and figure 7, after the elution test, the residual state of Cr in the slag soil-water belt-a were 56.0%,63.5%,69.6% for the sampling depth of 5 cm, 15 cm, 25 cm, respectively. The organic combination state of Cr were 10.3%,6.3%,8.4% respectively. The relative concentrations of carbonate combination and sulphide bound state of Cr were very low.

As shown in figure 5 and figure 7, after the elution test, the residual state of Cr in the slag soil-water belt-b were 47.3%,58.5%,65.1% for the sampling depth of 5 cm, 15 cm, 25 cm, respectively. The organic combination state of Cr were 16.0%, 9.1%, 8.9% respectively. The relative concentrations of adsorption state and carbonate combination of Cr were very low.

As shown in figure 6 and figure 7, after the elution test, the residual state of Cr in the slag soil-water belt-c were 56.9%,63.5%,72.3% for the sampling depth of 5 cm, 15 cm, 25 cm, respectively. The adsorption state of Cr were 10.8%,7.3%,8.1% respectively. The relative concentrations of carbonate combination and organic combination state bound state of Cr were very low.

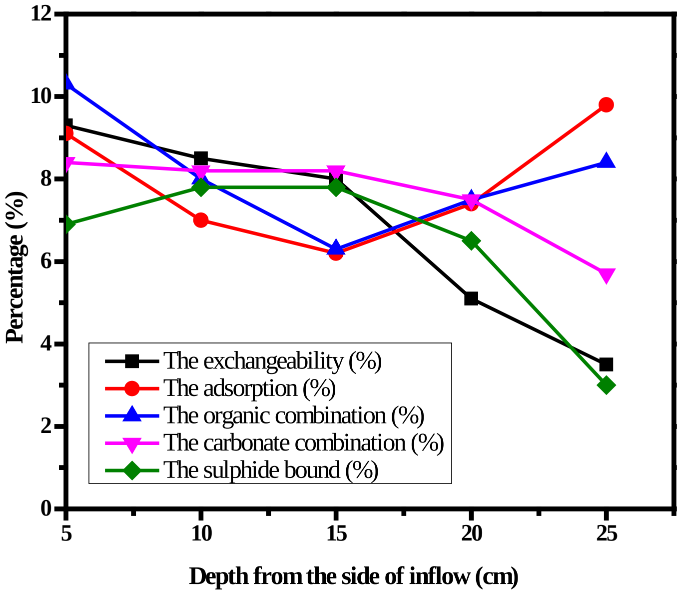

Figure 4 the chemical speciation of Cr in chrome slag soil-water belt-a during the reaction process

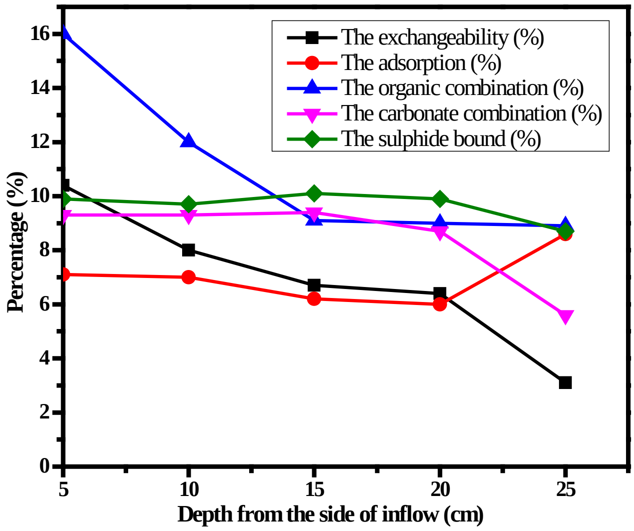

Figure 5 The chemical speciation of Cr in chrome slag soil-water belt-b during the reaction process

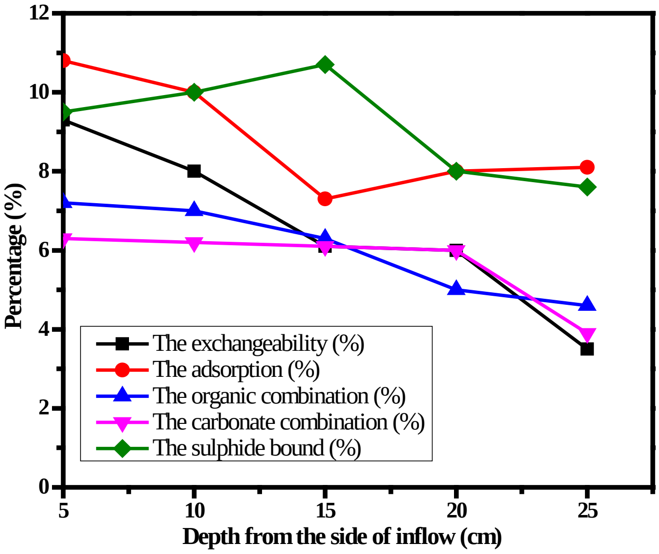

Figure 6 The chemical speciation of Cr in chrome slag soil-water belt-c during the reaction process

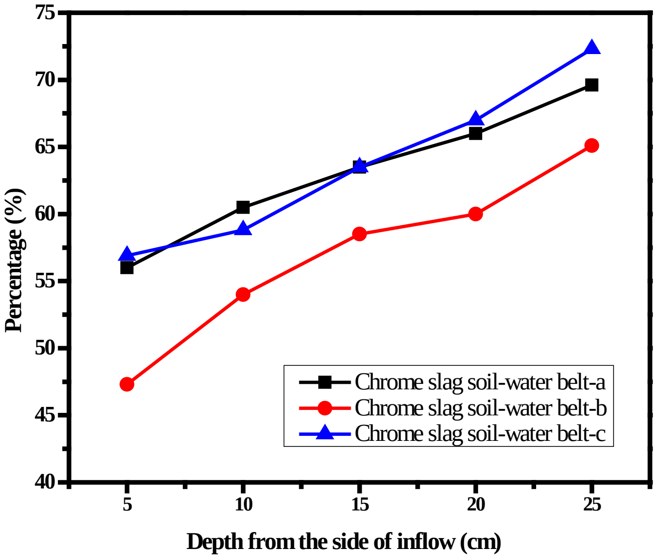

Figure 7 The chemical speciation of Cr in chrome slag soil-water belt during the reaction process

As shown in figures 5-6, there are some variations in the proportion of Cr in belt-b and belt-c. And the proportion sequencing of the occurrence distributions of Cr in different soil belt are shown in Table 2.

Table 2 Some kinds of the geometrical shape of Cr in the soil distribution proportion of sorting

Sample	Exchangeability	Adsorption	Organic combination	Carbonate combination	Sulphide	Residual
belt-a	6	2	3	4	5	1
belt-b	6	4	3	5	2	1
belt-c	6	3	5	4	2	1

The depth of the test is determined by the depth of location distance to the liquid side, which is similar to the depth of the natural soil in the field test, reflecting the vertical migration of Cr in the soil.

In terms of the depth rule in the morphological changes of Cr in soil, the proportion of residue state increased with the depth deepening. And the proportion of carbonate bond state is more in the middle depth and less in the lower and deeper parts. The organic binding state decreases with the depth deepening.

4. Conclusions

In this paper, the transmission characteristics of stabilized nZVI in chrome slag soil-water belt were studied according to the simulated penetrate experiment of soil column with the soil in water saturated state. The elution process rules of Cr(VI) in the soil column were obtained by transmit the stabilized nZVI suspension in the soil column. The long-time maintained experiment of soil column was conducted, theelution process rules of Cr(VI) in the long-time stabilized soil column were obtained. The chemical states of Cr in soil samples at various depth were analyzed. The rules of occurrence distributions of Cr(VI) were obtained under the effect of nZVI.

The results showed that the chrome slag soil-water belt-a, c were liable to be penetrated, and the penetration rate of the chrome slag soil-water belt-b was relatively slow. The concentration of Cr(VI) in the leachate after long-time maintained experiment were all bigger than short-time test. When the reaction was processed with 0.37 g/L of nZVI , the final fixed rate of Cr (VI) in the chrome slag soil-water belt-c was 97.55%. It makes sense to use excess of nZVI to maintain the reducing effect of reaction system.

The occurrence distributions of Cr in different soil are distinct, but on the whole, the residual state accounts for the largest proportion, followed by the adsorption state and the organic combination state. The deeper the residual state is, the larger its proportion gets. The deeper the carbonate bounded state is, the larger its proportion of mid-depth gets. However, the proportion of organic bounded state was decreased with the increase of soil depth.

The current study provide a valuable exploration for the Cr(VI) restoration by nZVI. The research will provide the references for nZVI stabilizing technology and make clear preliminary parameters and mechanism of Cr (VI) restoration in chrome slag soil-water belt by nZVI technology.

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