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1 **Simultaneous Stabilization of Pb and Improvement of Soil Strength using nZVI**

2 **Abstract**

3 This study demonstrates the feasibility of nanoscale Zero-Valent Iron (nZVI) for simultaneous
4 stabilization of Pb and improvement of soil strength via batch experiments. The soil samples
5 were prepared using slurry and pre-consolidation method at nZVI doses of 0.2%, 1%, 5%, and
6 10% (by dry weight). The physicochemical and geotechnical properties of Pb-contaminated
7 soil treated by nZVI were analyzed. The results indicate that the contamination of Pb(II)
8 resulted in a notable reduction in the undrained shear strength of soil from 16.85 kPa to 7.25
9 kPa. As expected, the Pb in exchangeable and carbonate-bound fractions decreased
10 significantly with the increasing doses of nZVI. Meanwhile, the undrained shear strength of
11 Pb-contaminated soil enhanced substantially as the increase of nZVI, from 25.83 kPa (0.2%
12 nZVI treatment) to 69.33 kPa (10% nZVI treatment). An abundance of bubbles, generated from
13 the oxidation of nZVI, was recorded. The mechanisms for simultaneous stabilization of Pb and
14 soil improvement primarily include: 1) the precipitation and transformation of Pb-/Fe- hydrated
15 oxides on the soil particles and their induced bounding effects; 2) the increased drainage
16 capability of soil as the occupation of nZVI aggregates and bubbles in the macropores space
17 and 3) the lower soil density derived from the increase in microbubbles retained in the soil.
18 This study is provided to facilitate the application of nZVI in the redevelopment of
19 contaminated soil.

20

21 **Keywords:** nZVI; lead, contaminated soil; physicochemical property; undrained shear strength

22

1 **1 Introduction**

2 Nanoscale Zero-Valent Iron (nZVI) is a well-established nanoparticle that has been used
3 widely in the remediation of contaminated soil and groundwater (Bartke et al., 2018). The
4 purpose of using nZVI is to remove or to stabilize the pollutants so that to reduce the potential
5 threats caused by the pollutants to the ecology (Chen et al., 2017). Considerable endeavors have
6 been made to improve the efficiency of NZVI in field application, such as degradation of
7 various pollutants, mobility in subsurface, and revealing the fate and impacts of NZVI on
8 ecology (Huang et al., 2016; Vilardi et al., 2018).

9 Nevertheless, civil engineers consider both the pollutants and the injected nZVI as non-native
10 components of soil. Their concerns stem mainly from the geotechnical properties of remedied
11 contaminated soil because these properties are important in the follow-up construction on the
12 contaminated site or the reuse of contaminated soil, such as backfill at another site. The
13 introduction of nZVI and its derived removal of contaminants in soil could potentially disturb
14 the micro-structures of soil and lead to alteration of its geotechnical properties. This means that
15 the application of nZVI in remediation of contaminated site may pose potential threat to
16 serviceability, and reliability of a facility. Just like the ecological and human health risk posed
17 by contamination, the geoenvironmental risk may break out at some point in the future,
18 considering the high reactivity of nZVI and its long-term effect on the physicochemical
19 properties of soil (Clayton, 2001). Thus, it is significant to investigate the behavior and
20 mechanism of nZVI treatment in changing of geotechnical properties of soil. However, few
21 studies have thoroughly addressed the effects of nZVI in this regard.

22 Most authorities accept that chemical contaminants are capable of changing properties of soil,
23 either by directly changing the chemical or physical state of the soil, or through indirect changes,
24 such as influencing biological activity and groundwater, which in return, modifies its properties
25 (Ma et al., 2018; Xu et al., 2018). Rogers et al. (2004) found that the contamination of Pb^{2+} and
26 Fe^{3+} had a significant effect on the initiation and development of the lime-clay reactions during
27 both short-term modification and longer-term solidification. Dror et al. (2015) summarized that
28 engineered nanomaterials have the potential to inflict irreversible changes on the physical and

1 chemical properties of pristine soils. Gil-Diaz et al. (2014) concluded that an immobilization of
2 Pb^{2+} and Zn^{2+} by nZVI posed no negative effects for physicochemical and biological properties
3 of soil. However, their researches did not reveal the changes in its geotechnical properties
4 associated with their physicochemical counterpart, such as the shear strength of the soil which
5 is the most important parameter in the design of civil engineering projects, neither did it reveal
6 the mechanism of the effects. The reader should note that the changes in physicochemical and
7 biological properties of soil do not always result in significant changes in the its geotechnical
8 properties. For instance, Cuisinier et al. (2011) reported that no evidence showed any impact of
9 chloride on the geotechnical behavior of their tested soils. Nasehi et al. (2016) performed an
10 investigation of the effects of nZVI and nanoscale hydrated lime on the geotechnical
11 characteristics of a diesel-contaminated soil. They suggested that the introduction of nZVI to
12 the diesel-contaminated soil led to an increase in Unconfined Compressive Strength (UCS),
13 maximum dry density, optimum water content, and shear strength parameters. Nevertheless,
14 the mechanism of nZVI in soil improvement remains ambiguous given that oxidation,
15 adsorption, and precipitation may be involved in the removal of diverse contaminants.

16 This study is an investigation of the stabilization of lead by nZVI in a clayey soil and its
17 effects on the geotechnical properties of soil. Particularly, lead (Pb), a heavy metal of well-
18 known toxicity, prevalence and responsible for liver and kidney damage, anemia, infertility,
19 and mental retardation among other consequences, is employed as an artificial contaminant
20 (Huang et al., 2018). Different doses of nZVI were added to the Pb-contaminated soil. The
21 mobilization effect on lead ions, physicochemical characterization, and shear strength of the
22 soil were examined to analyze the effects of nZVI on the physicochemical and geotechnical
23 properties of the Pb-contaminated earth. The results of this study can facilitate the application
24 of nZVI in the remediation of contaminated sites where remedied soil will be used as backfill,
25 such as remediation of brownfield and dredged sediment.

26 **2 Methodology**

27 **2.1 Soil Preparation**

1 The researcher collected the soil samples from a construction site in Areia Preta, Macau
2 (N22°12'35.84", E113°33'27.96"). According to the Unified Soil Classification System (USCS,
3 ASTM D2487-17), the Atterberg limits of the preconsolidated soil were found to be 61, 32, and
4 29 for the liquid limit, plastic limit, and plasticity index respectively. The particle size
5 distribution, when analyzed by the Malvern Particle Size Analyzer indicated that the D60, D30,
6 and D10 values were 8.5, 3.08, and 1.01 mm respectively. The soil was classified as MH: silt
7 with high plasticity.

8 The slurry and pre-consolidation method was employed to prepare the soil samples
9 (Choudhary et al., 2016). Firstly, the soil was first cut into small chunks and immersed in
10 distilled water for two days, after which the soil fractions were passed through a No. 16 sieve
11 (1 mm opening) to achieve a soil slurry. The water content of the obtained slurry was increased
12 up to twice of the liquid limit with vivid agitation for approximately 10 minutes to obtain a
13 homogeneous state. Subsequently the slurry (approximately 17 kg for each) was subjected to
14 pre-consolidation in a container under an overburden pressure of 200 kPa (Indraratna and
15 Redana, 1998). When the settlement of pre-consolidation was stable (usually took two weeks),
16 soil samples with a height of 84 mm and diameter of 38 mm were trimmed.

17 For the preparation of Pb-contaminated soil, artificial pollutant of lead nitrate ($\text{Pb}(\text{NO}_3)_2$)
18 (AR, powder solid state) at the lead mass ratio of 400 mg/kg (dry soil mass) was added to the
19 soil slurry (the weight of the soil slurry was approximately 120 kg). To achieve a homogeneous
20 state, the spiked soil slurry was mechanically stirred for approximately 10 mins. Then, the
21 spiked slurry was matured for two weeks to achieve equilibrium of adsorption and desorption
22 prior to pre-consolidation or further treatment. As for the preparation of nZVI treated soil
23 samples, 0.2%, 1%, 5%, and 10% (mass ratio of nZVI to the spiked dry soil) nZVI were added
24 respectively to the aged Pb-spiked soil slurry and agitated vividly prior to pre-consolidation.
25 The nZVI was supplied by Shanghai Xiangtian Nano Materials Co., LTD. The average diameter
26 of nZVI used in this study was about 50 nm, with a specific area of 30 m²/g (provided by the
27 manufacturer).

1 Figure 1 summarizes the experimental procedure. For all the natural, Pb-contaminated and
2 nZVI treated soil samples, sequential extraction procedure, shear strength tests, and
3 characterization were carried out to investigate the mechanism of the effect of nZVI treatment
4 on the physicochemical and geotechnical properties of the treated clayey soil.

5 **2.3 Shear Strength of Soil**

6 The Laboratory Vane Shear Test (Wykeham Farrance, 27-WF1730) was conducted to
7 evaluate the undrained shear strength of the soil samples, as per the Standard Test Method for
8 Laboratory Miniature Vane Shear Test for Saturated Fine-Grained Clayey Soil (American
9 Society for Testing Material, ASTM D4648/D4648M-13). Particularly, two kinds of vane blade
10 with the same width of 12.7 mm, yet the different heights of 19 mm and 12.7 mm were
11 employed. The rotation rate of the vane during testing was maintained at approximately 6°/min.

12 **2.4 Characterization and Testing**

13 The mineralogy of the soil was characterized by X-ray diffraction (XRD) on Rigaku
14 Smartlab (anode Cu, in configuration $\theta/2\theta$, with an acceleration tension of 45 kV and a current
15 of 200 mA), at a scanning rate of 2.0 °/min. Prior to the XRD test, the soil samples were
16 smashed and crushed into soil chip with a thickness of approximately 0.5 mm after freeze
17 drying for 24 h. The pore structure characteristics of the soil were quantitatively described by
18 Mercury Intrusion Porosimetry (MIP) using a Mercury Porosimeter AutoPore IV 9510
19 (Micromeritics Instruments Co., USA). Before the MIP measurements, the soil samples were
20 dried using the vacuum freeze-drying method for 24 hours. Washburn's equation was involved
21 to calculate the relationship between the mercury pressure and pore structure characteristics
22 (Abell et al., 1999). The soil particle size distribution was characterized by a laser particle size
23 analyzer (Malvern, Mastersizer 3000) in distilled water solution, assisted by the continuous
24 ultrasound dispersion (40W, 40kHz) and electric mixing (3000 rpm).

25 The availability of Pb in soil samples was analyzed after applying the Modified Sequential
26 Extraction Procedure proposed by Tessier et al. (1979) using Inductively Coupled Plasma Mass
27 Spectrometry (ICP-MS, Agilent 7700X). Soil pH was measured according to the International
28 Standard Soil Quality-Determination of pH (ISO 10390: 2005). The total carbon (TC) of soil

1 samples was analyzed by Analytik Jena (Multi N/C 3100 and 1300) after undergoing air drying
2 at 35 °C for 12 hours. Zeta potential and electrical conductivity of soil samples were collected
3 by a zeta potential analyzer using phase analysis light scattering (Brookhaven ZetaPALS) at a
4 soil concentration of 1g/L in distilled water.

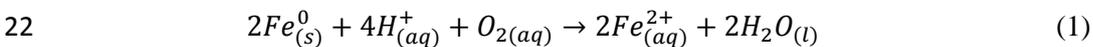
5 **3 Results and Discussion**

6 **3.1 Phenomenon and Theory**

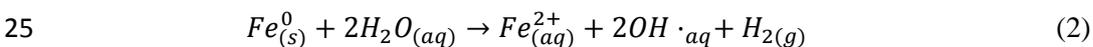
7 Changes of physicochemical and geotechnical properties of soil are invariably associated
8 with the microscopic change of the soil body. In this study, the specific behavior occurred
9 during the preparation of the soil sample which was recorded to examine the effect of nZVI on
10 the geotechnical properties of soil.

11 In this study, a mass of bubbles with a size of a few micrometers was observed in the soil
12 slurry after nZVI treatment (before pre-consolidation), as shown in Figure 2. Accordingly, a
13 copious quantity of microbubble prints remained in the soil sample following said process, as
14 shown in Figure 2 (c). For all nZVI-treated soil samples, the phenomena of nZVI aggregations
15 was detected in the wake of acute agitation of the soil slurry and nZVI. The appearance of
16 micro-bubbles and fissures intensified when the dose of nZVI was increased.

17 This specific phenomenon provides unequivocal evidence of the interaction between nZVI
18 and the clay slurry. In fact, this is reasonable because the nanosized Fe⁰ exhibited a markedly
19 increased extent of corrosion under both the anaerobic and aerobic conditions (Reardon, 1995;
20 Reardon et al., 2008). In an aerobic condition, nZVI is easily oxidized to ferrous iron, with
21 protons being consumed in the process (Li et al., 2006):

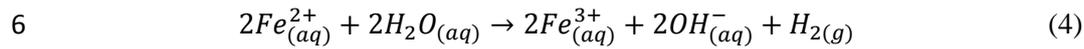
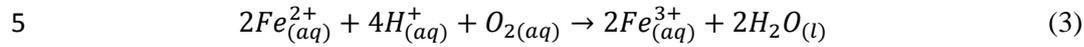


23 When oxygen is exhausted or in the absence of oxygen, fresh nZVI tends to experience a
24 rapid oxidation phase upon entering the aqueous phase:

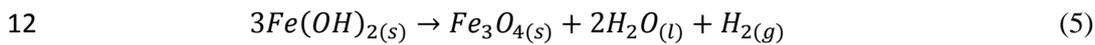


26 In this reaction (2), two molecules of water are consumed for every mole of iron corroded.
27 Meanwhile, one molecule of hydrogen gas and two molecules of hydroxy radicals are generated.

1 In addition to the ferrous ions and hydrogen gas, hydroxyl ions are also generated which will
2 increase the media pH, while hydrogen ions are consumed. Moreover, if oxygen is sufficient in
3 the slurry, ferrous ions will undergo further oxidative transformation to become ferric ions until
4 the oxygen is exhausted (Lefevre et al., 2016):



7 Continued corrosion of iron and generation hydroxyl ions lead to saturation and precipitation
8 of $Fe(OH)_2$ on the soil particles in the slurry, itself a relatively insoluble solid phase. In the
9 absence of oxygen (or anoxic conditions) and at low temperatures, $Fe(OH)_2$, is controlled by
10 the pH value of the system but is predicted thermodynamically to convert to magnetite or other
11 iron minerals (Liu et al., 2015):



13 Based on the previously stated theoretical foundation, the speculated is that iron minerals are
14 formed from ferrous and ferric ions in the aqueous phase of the soil slurry and may precipitate
15 on the soil particles and subsequently bond them together, with nZVI aggregates centralized.
16 Clearly, these micro-bubbles are generated primarily from the oxidation of nZVI in the aqueous
17 phase and are retained in the soil sample. In addition to that, the nitrogen and carbon dioxide,
18 generated by the reduction of nitrate by nZVI and oxidation of natural organic matters in soil,
19 respectively, may also contribute partially to the generation of micro-bubbles (Vilardi and Di
20 Palma, 2017; Vilardi et al., 2017, 2018). The increased the drying shrinkage occurred due to
21 the reduced water content lead to the occurrence of massive fissures grown on the surface of
22 nZVI-treated soil slurry.

23 **3.2 Microstructure**

24 A laser particle size analyzer was used to quantify the physical changes of soil particle size,
25 as demonstrated in Figure 3. In all cases, the soil particles stuck together in anomalous clumps
26 after undergoing pre-consolidation in the container, with the particle sizes varying from 400
27 nm to 1 mm. No distinct nZVI particle was observed in the soil particles. The decomposition

1 of soil particles by lead nitrate led to an increase in clay and silt clay fractions, which reduced
2 the average size of soil particles. Analogously, the introduction of nZVI resulted in a significant
3 decrease in the size of nZVI treated soil particles. The particle size gravitated toward a
4 decreasing value with increasingly large doses of nZVI. The thinking is that the oxidation and
5 the subsequent growth of iron particles from the nano-level to micron level instigated the
6 reduction in particle size. For the 10% nZVI-treated soil sample, the sand fraction in the soil
7 went up to 16%. Such increase can be ascribed to the prevailing of the increased pozzolanic-
8 like reaction of the nZVI-induced iron minerals' precipitation among the soil particles (Nasehi
9 et al., 2016).

10 As already noted, a mass of microbubbles and residual bubble prints were observed. They
11 were generated primarily from the oxidation of nZVI in the aqueous phase, as well as the
12 reduction of nitrate. Actually, for the remediation of the contaminated site by the injection of
13 chemical remediation materials, bubbles are the common coproducts during the mineralization
14 of contaminants, such as those involved in In-situ Chemical Oxidation (ISCO) using hydrogen
15 peroxide (H_2O_2), Micro-Nano Bubbles (MNBs) and persulfate (Liu et al., 2014). Soil pore
16 characteristics, including the total volume, size distribution, and shape of soil pore spaces are
17 important indicators that determine workability and friability of soil (Munkholm et al., 2016;
18 Obour et al., 2017). However, little is known about the link between remediation-derived soil
19 pore characteristics, and physicochemical and geotechnical properties of soil.

20 To improve the understanding of bubbles and their effect on the geotechnical properties of
21 soil, its pore structure characteristics were quantitatively described by MIP, as shown in Figure
22 4 and Table 1. The results indicate that the pore size diameter of all soil samples mainly ranged
23 from 10 nm to 10 μm , which can be classified as mesopore (2-50 nm) and macropore (> 50 nm)
24 (Anovitz and Cole, 2015). The introduction of lead nitrate resulted in an evident increase of
25 average pore diameter, which is in accordance with its appearance (as shown in Figure 2a).
26 When the amount of added nZVI was 0.2% in the mass ratio of dry soil (Pb-contaminated soil),
27 the average pore diameter mushroomed from 90.4 nm to 178.4 nm. Accordingly, a sharp drop
28 in the total pore area was recorded. With the increase in added nZVI, the average pore diameter

1 decreased, with a corresponding increase in total pore area. Furthermore, the increase in nZVI
2 was met with a reduction in the amount of macropores (>50 nm) and a rise in mesopores (2-50
3 nm). The 10% nZVI-treated soil samples held the highest total pore area. On the other hand,
4 along with the decrease in the amount of macropores and the increase in mesopores, both the
5 density and porosity of nZVI-treated soil samples gradually increased. However, the 0.2%
6 nZVI treated soil samples presented the lowest values of density and porosity among all the
7 samples, while the 10% nZVI treated soil sample showed a tiny drop in the values of density
8 and porosity. The speculated theory is that a dynamic equilibrium exists between the decrease
9 in macropores space caused by the occupation of nZVI aggregates and the increase in
10 microbubbles retained in the saturated soil (Soares et al., 2018).

11 **3.3 X-ray Diffraction (XRD)**

12 The X-ray diffraction (XRD) patterns of the soil samples are displayed in Figure 5. The
13 selected soil was composed primarily of quartz (PDF#85-1054, ICSD Minerals), laumontite
14 $\text{Ca}_4(\text{Al}_8\text{Si}_{16}\text{O}_{48}(\text{H}_2\text{O})_{18})$ (PDF#80-0150, ICSD Minerals), and greenalite $\text{Fe}_6\text{Si}_4\text{O}_{10}(\text{H}_2\text{O})_{18}$
15 (PDF#72-0177, ICSD Minerals). The main characteristic peaks revealed a slight discordance
16 among the soil samples, implying that distortion occurred in the lattice of minerals after the
17 introduction of nZVI. The assumption is that the frameworks of certain mineral crystals were
18 doped by Fe(II), Fe(III), and Pb(II) of larger atomic radius, resulting in the appreciable changes
19 in lattice parameters (Castaldi et al., 2008), as shown in Table 2. Lattice parameters of
20 laumontite mineral in the soil samples altered irregularly with the introduction of lead nitrate
21 as well as the nZVI. A minute difference in weak characteristic peaks can be perceived at 2-
22 Theta of 17.8° , 27.6° , 35.7° , and 36.6° , which can be credited to the iron mineral crystals of
23 magnetite Fe_3O_4 (PDF#89-0950), ferrosilite FeSiO_3 (PDF#76-0887, ICSD Minerals), hematite
24 Fe_2O_3 (PDF#85-0987, ICSD Minerals), and goethite FeOOH (PDF#81-0464) respectively
25 (Huang et al., 2013). The presence of deuterogenic and different iron minerals will constitute
26 the highly-disordered multilayer of amorphous core shell construction on the surface of nZVI
27 and soil particles with a thickness of approximately several nanometers (Arancibia-Miranda et
28 al., 2014).

1 For the nZVI in the oxidation system, on the one hand, the reduction of Pb^{2+} will be
2 suppressed because of isolation resulting from the multilayer core shell construction (Xue et al.,
3 2018). On the other hand, the corrosion byproducts can greatly promote the co-precipitation
4 and adsorption of Pb^{2+} and improve the stabilization capability of nZVI. However, the
5 characteristic peaks associated with reduced lead and related lead oxides were not clearly
6 presented in the diffractogram of nZVI-treated soil samples, which may have been a
7 consequence of 1) the Pb being of a trace amount in the soil, as well as 2) the crystalline
8 structures of reduced lead and related lead oxides being amorphous.

9 **3.4 Metal Immobilization**

10 Because heavy metals do not undergo microbial or chemical degradation, the total
11 concentration of these metals persists for a long time after their introduction in soils. The
12 ecological toxicities of heavy metals in soil are primarily controlled by their available fraction
13 because they are readily mobile and bioavailable within the environment and can potentially be
14 taken up by plant roots to enter the food chain (Hou et al., 2013; Roy and McDonald, 2015). In
15 this sense, the immobilization of heavy metals in soil offers a promising strategy for achieving
16 the redistribution of contaminants from the solution phase to more geochemically stable phases,
17 thereby reducing their bioavailability and transportation in the environment (Bolan et al., 2014).
18 Many studies have demonstrated the excellent immobilization capacity of nZVI for various
19 heavy metal ions, in both soil and groundwater (Gil-Díaz et al., 2017). The widely accepted
20 thinking is that the mechanism of nZVI for immobilization of Pb in an aqueous system is
21 controlled by a sorption process, reduction of Pb^{2+} to Pb^0 , and (co)precipitation (Wang et al.,
22 2016; Gil-Diaz et al., 2017).

23 In this study, the effects of nZVI on the immobilization of Pb in soil samples were examined
24 by comparing the distribution of lead in different soil fractions. Figure 6 displays the
25 concentration distribution tendency of the quantity of lead retained in the soil samples. With
26 the introduction of lead nitrate, the lead in the exchangeable (EX), carbonate-bound (CB),
27 organic matter-bound (OM), and the residual (RS) fractions increased significantly, compared
28 with that in the natural soil. As expected, the lead in the more easily available fractions, namely

1 EX and CB, was evidently decreased by the introduction of nZVI. Then increasing in the nZVI
2 amount, a diminishing concentration in the EX, CB, and OM fractions was observed. These
3 more easily available fractions have higher leachability and bioaccessibility than others
4 (Alloway, 2013; Zong et al., 2016). Thus, the application of nZVI can effectively immobilize
5 the lead in soil and lower the risk to humans and environmental organisms. By contrast, the
6 lead in Fe/Mn oxides-bound and residual fractions increased when nZVI added. This was
7 reasonable because of the increase in irons, and part of Fe/Mn oxides-bounded lead converted
8 to a more strongly bound complex. Moreover, part of this decomposition of organics, resulting
9 from the introduction of nZVI, may lead to a descending concentration of lead in the organic-
10 bound fraction, as shown in Table 1, and subsequently, an increased lead concentration in other
11 fractions. In all cases, most of the volume of lead was bound by organic matter and Fe/Mn
12 oxides, followed by a residual fraction, exchangeable fraction, and carbonate-bound fractions.

13 **3.5 Undrained Shear Strength**

14 To reveal the variations and features of geotechnical properties of soil, as a consequence of
15 contamination and remediation, was the main objective of this study. In the interests of
16 evaluating the effects of nZVI on the geotechnical properties of soil, undrained vane shear
17 strength (S_u) was investigated. The shear strength of a soil is defined as the maximum shear
18 stress that it can sustain under loading (Türkel, 2007). According to Stavi et al. (2016), the
19 moisture content of a soil is a crucial parameter in controlling the shear strength of clays. Figure
20 7 shows the results of vane shear strength together with the corresponding moisture content.

21 The results indicate that the S_u of natural soil dropped sharply after the introduction of lead
22 nitrate, from 16.82 kPa to 7.25 kPa. Correspondingly, the moisture content increased from
23 50.78% to 56.89%. Meanwhile, the zeta potential of soil dropped analogously from -16.14 mV
24 to -6.31 mV (Table 1), pointing to a notable decrease in soil stability. This phenomenon may
25 be another signal that explains the obvious decrease of S_u .

26 On a positive note, the S_u of Pb-contaminated soil was improved remarkably when treated
27 with nZVI. Figure 6 shows us that even the 0.2% amount of nZVI can strengthen the soils'
28 undrained shear strength from 7.25 kPa to 25.38 kPa. The S_u of soil was increased with the rise

1 in nZVI, but the acceleration rate decreased when the mass ratio of nZVI to dry soil was 10%.
2 Correspondingly, the moisture content of soil exhibited a negative trend to the S_u when the dose
3 of nZVI treatment was increased from 0.2% to 5%. That is, the soil moisture content decreased
4 with the increasing doses of nZVI. This can be presumably ascribed to the padding of nZVI
5 and its volume expansion by oxidation in the soil pore, which resulted in an extrusion of the
6 water. However, an unexpected situation for the 10% nZVI-treated soil was that a soaring of
7 its moisture content to 55.77%, along with further enhancement of the S_u of the soil sample up
8 to 69.33 kPa, was recorded. This can be put down to being a consequence of the changes in
9 both soil constituent and structure. On the one hand, the addition of 10% nZVI is at a high
10 percentage load with the forceful capacity of oxidation reaction to change the soil constituent
11 (Gil-Diaz et al., 2014); the increased water holding capacity can be partially attributed to the
12 generation of iron oxide-hydroxides such as ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), schwertmannite
13 ($\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}) \cdot n\text{H}_2\text{O}$), and goethite ($\alpha\text{-FeOOH}$) (Velimirovic et al., 2018; Zhang et al.,
14 2016). On the other, an increase in microbubbles enabled itself to readily adsorb moisture and
15 humidity (Lawrence and Jiang, 2017). Luxurious nZVI may give rise to a hardened soil, making
16 it difficult to drain under the consolidation pressure of 200 kPa and thus contributing to an
17 exceptionally high moisture retaining capacity (Burgess et al., 2016). Furthermore, with regard
18 to the microbubbles and their bubble prints in the soil samples, the presumption was that these
19 micron-level bubble-prints were the residual channeled network of voids for the drainage
20 boundary (Acharya et al., 2015). However, the density and porosity of nZVI-treated soil
21 decreased synchronously. The changes of the soil components by nZVI treatment can be
22 responsible for this abnormal condition. As a rule, low density of a soil is usually associated
23 with low strength (Lawrence and Jiang, 2017). Because of the consuming oxidation of nZVI in
24 the soil, the Pb-contaminated soil turned out to be lightened and firmed.

25 Based on these above discussions, the conclusion can be drawn that the application of nZVI
26 can simultaneously stabilize Pb and improve the soil strength in the short-term, as a result of
27 which it can lower the risks involved in geotechnical engineering (Griffiths et al., 2012). The
28 Pb-contaminated soil became light, dense, and reinforced after nZVI treatment. The increase in

1 undrained shear strength can be primarily assigned to the precipitation and transformation of
2 nZVI-induced iron minerals on the soil particles and their bonding together.

3 **4 Conclusion**

4 The application of nZVI in treating subsurface contaminants should be considered carefully
5 because their intrusion may lead to the changes of geotechnical properties of soil, ultimately
6 inducing potential geoenvironmental risks. In this study, the author investigated the effects of
7 nZVI on the immobilization of lead and the undrained shear strength of soil. The results indicate
8 that the introduction of Pb(II) in the natural soil resulted in a visible reduction in shear strength
9 from 16.85 kPa to 7.25 kPa.

10 On a positive note, with the increasing doses of nZVI from 0.2% to 10% (dry weight), the
11 shear strength of lead-contaminated soil substantially increased from 25.83 kPa to 69.33 kPa.
12 Moreover, increased dose of nZVI generally lead to increases in particle size (larger than 0.063
13 mm), amount of mesopore (2-50 nm), and decreases in the amount of macropore (>50 nm),
14 moisture content and Pb bound to exchangeable and carbonate fractions. The oxidation of nZVI
15 in the soil slurry gave rise to abundant micro-fissures, and bubbles equally appeared in the soil
16 slurry and were retained in the soil samples, leaving bubble prints. The mechanisms for
17 simultaneous stabilization of Pb and soil improvement can be primarily ascribed to the
18 precipitation and transformation of Pb-/Fe- hydrated oxides on the soil particles and their
19 induced bounding effects. Moreover, the increased drainage capability of soil as the occupation
20 of nZVI aggregates and bubbles retained in the soil also contributed to the soil improvement.

21 Although nZVI aggregations were evident in the soil slurry, the feasibility of nZVI for
22 simultaneous stabilization of Pb and improvement of soil strength is here confirmed. With
23 respect to the wide application of nZVI and the follow-up infrastructure construction on the
24 contaminated site (such as brownfields), the results of this study can facilitate the remediation
25 of metals-contaminated soil and recovery of contaminated soil for civil engineering. However,
26 the long-term effect of nZVI treatment on the geotechnical properties of soil and structural
27 stabilities should be revealed in future study.

28 **Acknowledgements**

1 The authors wish to thank financial supports from the Macau Science and Technology
2 Development Fund (FDCT) (Code: 125/2014/A3), the University of Macau Research Fund
3 (MYRG2015-00112-FST), Shenzhen Peacock Plan (KQTD2016022619584022), Shenzhen
4 basic research plan (JCYJ20160429191638556), and Guangdong Provincial Key Laboratory of
5 Soil and Groundwater Pollution Control, Southern University of Science and Technology.

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- 23

1 Figures List:

2 Figure 1. Flow chart of experimental procedure.

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4 120%, before the pre-consolidation) and b) laboratory vane shear test of 5% nZVI treated soil
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6 Figure 3. Particle size distribution of the soil samples.

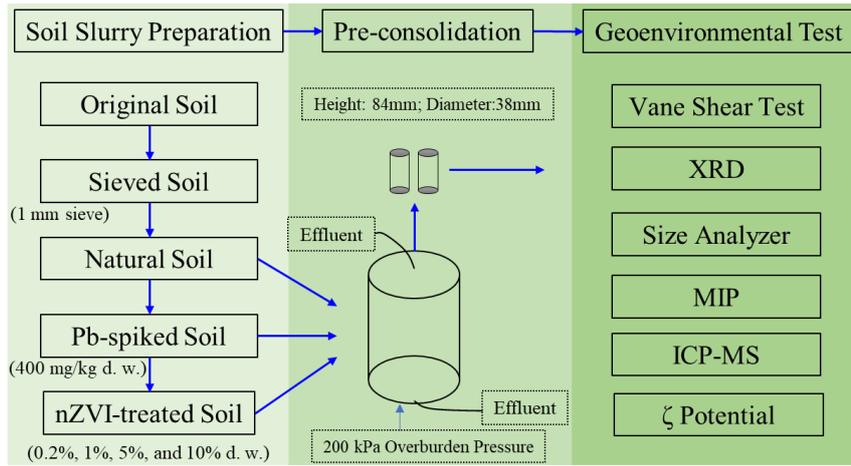
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14 Figure 7. Undrained shear strength results from laboratory vane shear test and moisture content.

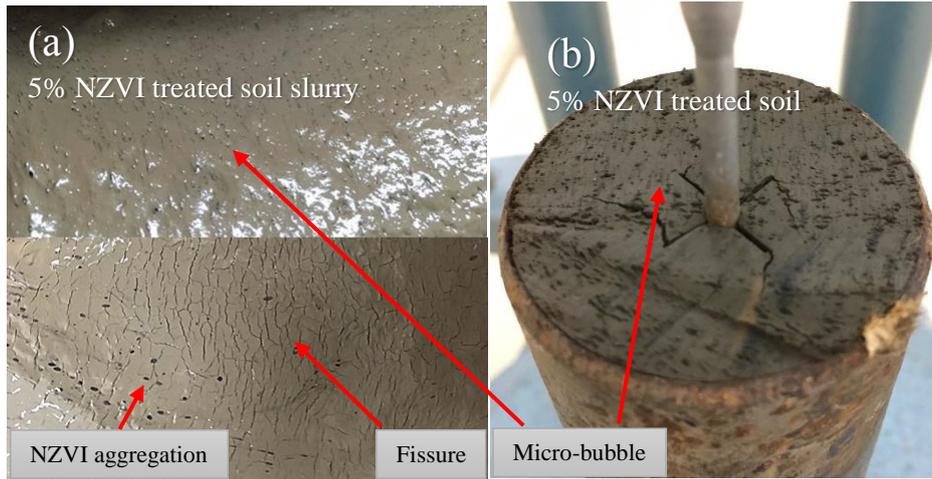
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Figure 1. Flow chart of experimental procedure.

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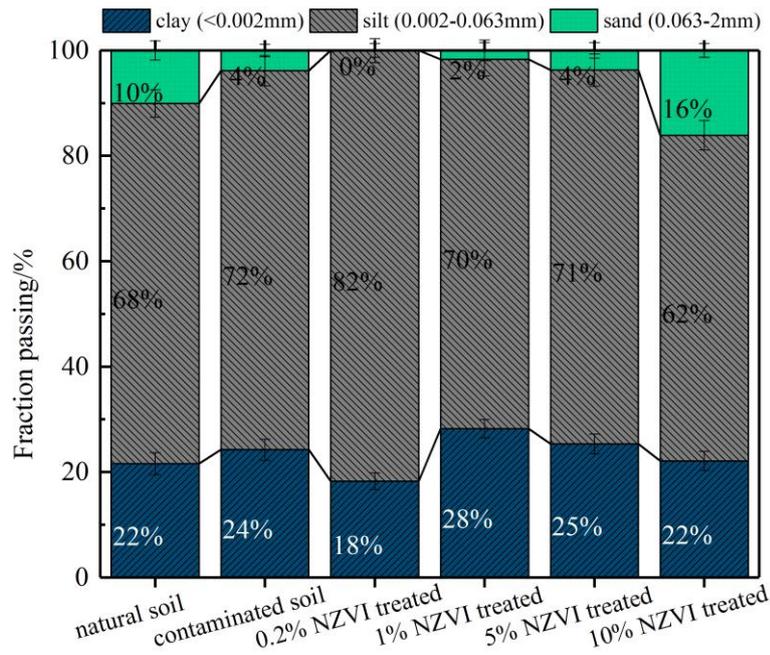
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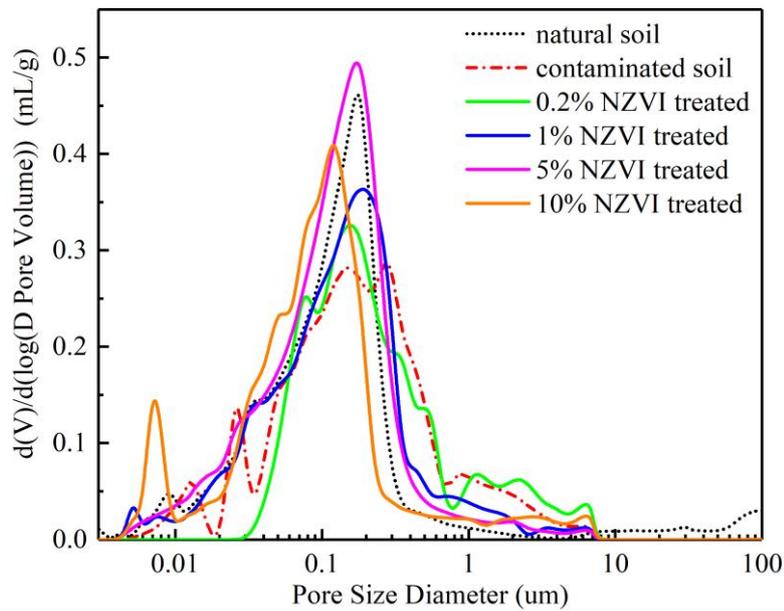
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1 Figure 3. Particle size distribution of the clayey soil under different treatment conditions.

2 Error bars represent relative standard deviations (n = 3).

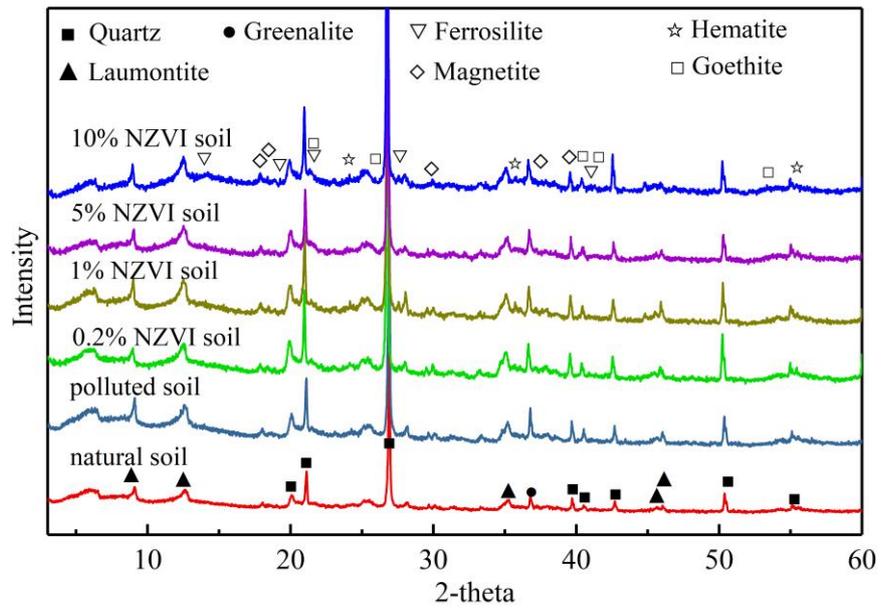
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4 Figure 4. Pore size distribution of soil samples determined by MIP in the range 3 nm to 360

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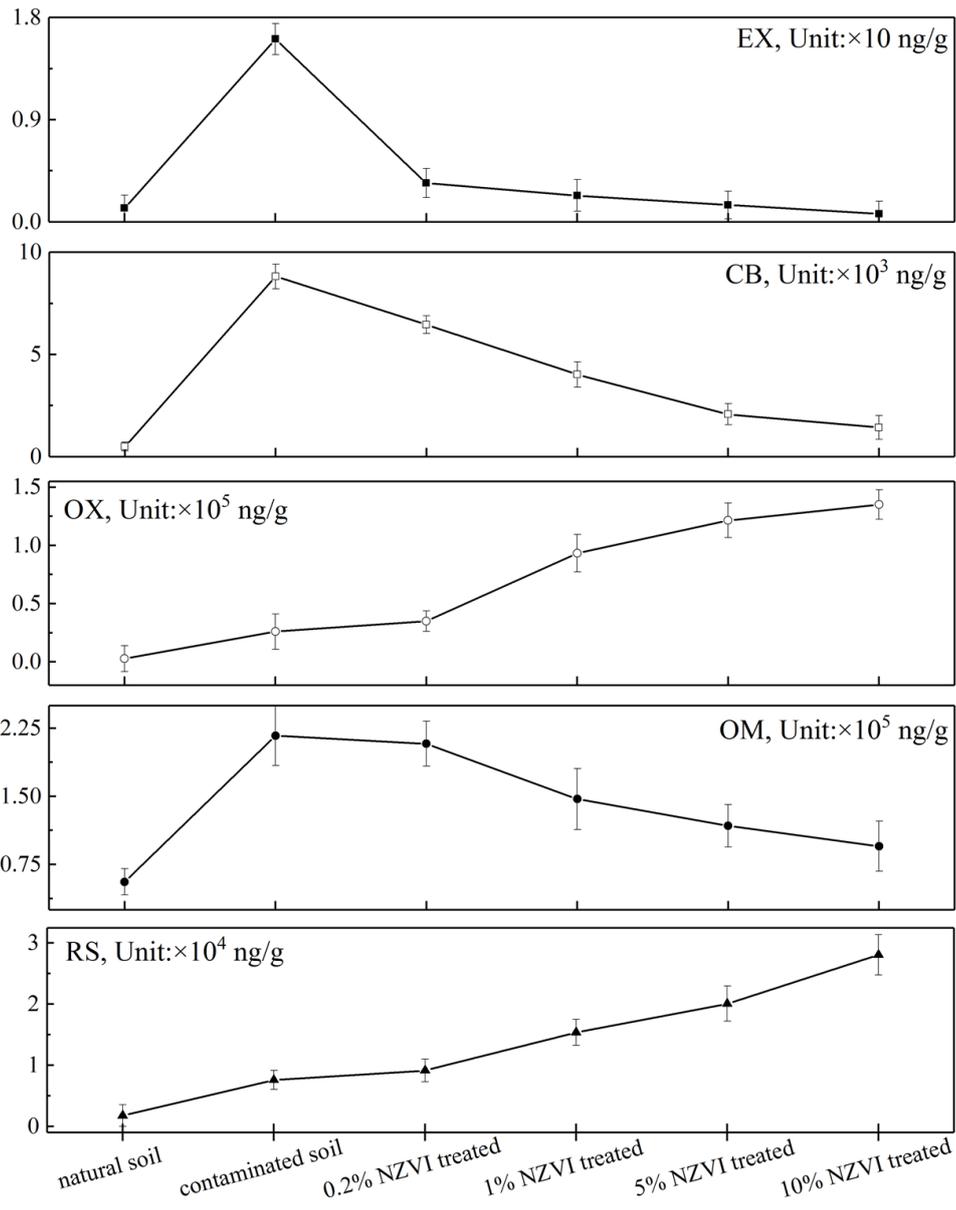
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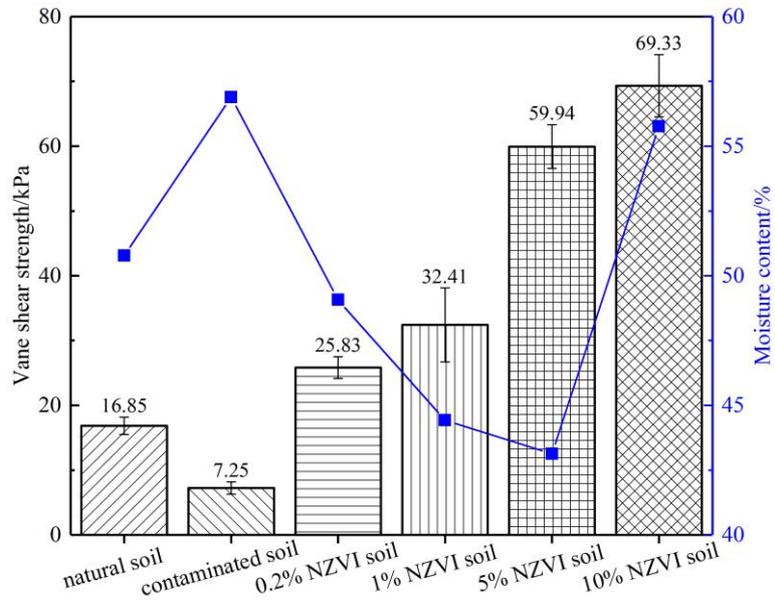
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2



1 Figure 6. Sequential relative concentration distribution tendency of Pb in the soil samples
 2 (EX, exchangeable fraction, $\times 10$ ng/g; CB, carbonate-bound fraction, $\times 10^3$ ng/g; OX, Fe/Mn
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 4 fraction, $\times 10^4$ ng/g) with error bars representing relative standard deviations (n = 2).

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1 Figure 7. Undrained shear strength results of the laboratory vane shear test versus moisture
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1 Table 1. Physicochemical and mechanical properties of clayey soil under different treatment
 2 conditions.

Item	Natural Soil	Contaminated Soil	0.2% nZVI Treated	1% nZVI Treated	5% nZVI Treated	10% nZVI Treated
Moisture Content /% ^a	50.8	56.9	49.1	44.4	43.1	55.8
Stabilization Efficiency of Pb ²⁺ in Exchangeable Fraction/%	-	-	78.8	85.5	90.8	95.6
Stabilization Efficiency of Pb ²⁺ in Carbonate-bonding Fraction/%	-	-	26.7	54.4	76.5	83.8
Degree of Saturation (Sr) /%	98.3	95.1	98.9	91.7	94.4	97.2
Vane Shear Strength /kPa	16.9	7.3	25.8	32.4	59.9	69.3
Total Carbon /mg·kg ⁻¹	832.1	808.2	797.9	741.5	724.1	705.4
Standard Deviation of TC /mg·kg ⁻¹	1.2	1.5	2.0	2.5	1.7	2.2
pH ^b	8.05	8.09	8.34	8.23	8.05	8.00
ζ Potential /mV ^c	-16.14	-6.31	-8.06	-11.60	-8.88	-18.10
Electrical Conductivity / mS/cm ^c	53	46	46	57	95	165
Bulk Density at 0.50 psia /g·cm ^{-3 d}	1.4	1.2	1.0	1.2	1.1	1.2
Apparent (Skeletal) Density /g·cm ^{-3 d}	2.8	1.9	1.4	1.9	2.0	1.9
Porosity /% ^d	49.0	38.4	29.7	38.6	42.7	37.6
Total Pore Area/m ² ·g ^{-1 d}	22.7	14.7	6.6	19.0	21.7	27.9
Average Pore Diameter (4V/A) /nm ^d	66.3	90.4	178.4	69.6	69.1	45.7

3 Note:

4 ^a refers to the soil samples after unload from the container;

5 ^b soil pH was measured using a glass electrode in a 1:5 (volume fraction) suspension of soil in water,
 6 according to the “international standard specifies an instrumental method for the routine determination
 7 of pH” (ISO 10390: 2005);

8 ^c Zeta potential and electrical conductivity of soil samples was measured at the soil concentration of 1g/L
 9 in distilled water;

10 ^dSoil density and porosity were calculated by Mercury Intrusion Porosimetry (MIP).

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Table 2. Lattice parameters of the laumontite mineral in soil samples.

Parameter	Natural soil	Contaminated soil	0.2% nZVI treated	1% nZVI treated	5% nZVI treated	10% nZVI treated
a (Å)	15.1902	14.9745	14.8368	14.6733	14.9459	14.8368
b (Å)	13.1902	13.1358	13.16531	13.3037	13.2284	13.1650
c (Å)	7.4170	9.7608	7.5406	7.8429	6.6367	7.5406
β	113.38	106.77	110.37	110.63	113.53	110.37
XS(Å)	429(66)	940(576)	1332(452)	1124(557)	514(178)	311(70)

2 Note: The lattice parameters of laumontite was analyzed using the software of MDI Jade 6.5 and guided
3 by Fridriksson et al. (2003).

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