



# Article Long-Term Performance of Cement-Stabilized/Solidified Pb-Contaminated Soil under Simulated Erosive Environments

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Abstract: The performance of stabilization/solidification(S/S) monoliths is vital for the long-term effectiveness of potentially toxic-element-contaminated soil treatments, which arevulnerable to environmental conditions (e.g., strongly acidic or alkaline conditions). This study numerically investigated the long-term performance of S/S monolith materials in erosive environments with pHs ranging from 2.65 to 10.00 over three years. It was found that the leachability and availability of Pb decreased continually over the three years due to the transformation of the chemical fractions of Pb from acid-soluble fractions to reducible and oxidizable fractions. Environmental pH greatly affected the strength and permeability of the S/S monoliths, which increased in weakly acidic and alkaline conditions (e.g., pH 5.00–10.00), while they were significantly reduced in strongly acidic conditions (e.g., pH 2.65–3.65). The strength of the S/S monolith decreased from 19.7 MPa to 0.2 Mpa after three years when the environmental pH was 2.65. A model was established to predict the long-term strength evolution of the S/S monolith. The dissolution of hydration products in the S/S monolith materials caused by acid erosion directly attenuated the strength and permeability of the S/S-treated soils. Long-term exposure to acidic environments could lead to the failure of S/S treatments. Thus, more attention should be paid to the long-term effectiveness of S/S monoliths in erosive environments.

**Keywords:** potentially toxic element; stabilization/solidification; long-term performance; contaminated soil

# 1. Introduction

Potentially toxic-element pollution is one of the most serious environmental problems in China and poses a threat to environmental quality and human health [1–3]. In recent years, with increasing requirements and demands for environmental quality, the remediation of potentially toxic-element-contaminated soil has grown rapidly in recent years. It was reported that China's soil-remediation market reached USD 2.9 billion in 2018 [4]. It is worth noting that stabilization/solidification(S/S) leads in the soil-remediation technology market in China, with a market share of 48.5% [5]. S/S technology originated in the late 1950s and was subsequently applied in the field of soil remediation, and eventually developed into the most widely used remediation technology in the US Super Fund Project [6,7].

Even though S/S technology has the advantages of being low-cost and having wide application to different types of pollutants, its long-term effectiveness is usually neglected. The long-term effectiveness of S/S technology should receive more attention because



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). S/S-treated soil suffers from environmental erosion, for example, acid rain and sulfate erosion [8]. In southern regions of China, such as the Pearl River Delta, acid rain has a wide range of impacts and a high frequency. The pH of acid rain is mainly concentrated in the range of 2.0–7.0 [9]. Hydrogen ions, carbonate, sulfate and other substances in acid rain have serious impacts on the occurrence and leaching characteristics of potentially toxic elements [7]. The core of S/S technology lies in the encapsulation and stabilization by cementitious materials, usually cement, of pollutants, such as potentially toxic elements [10,11]. Wang et al. [12] found that hydration reaction of cement and other cementitious materials could last for many years. It is only a matter of time before potentially toxic elements will be red is solved and released from S/S monolith to the environment. Accurate prediction of the performance of S/S monoliths under different environmentalerosion conditions is crucial to evaluate the long-term effectiveness of soil remediation strategies [13,14]. Acid rain, sulfate, groundwater, carbonization and other reactions in the surrounding environment affect the microstructures, mineral compositions and other mechanical-physical-chemical properties of S/S products, thus directly influencing the long-term effectiveness of S/S monoliths [15–17].

With the increase incontaminated-soil remediation projects, it is important to know for how long various remediation methods, especially S/S treatments, can be effective in the environment, particularly for reused S/S soil, such as roadbed backfilling, backfilling materials and in situ remediation [15–17]. Nevertheless, due to time and cost constraints, the long-term performances of S/S monoliths, including real-life strength, permeability and leachability performances, have not been paid much attention [16]. Previous studies have focused on evaluating the short-term strength, permeability and leachability of S/S treated waste, mostly within 28 days [18–21]. Only a few studies have considered the evolution of the mechanics, mineral compositions and leachabilities of S/S products over longtime scales [12]. In a previous study, the leaching concentrations of potentially toxic elements from S/S monoliths decreased with curing time [22]. Wang and Al-Tabbaa [23] investigated the leaching and strength properties of samples at 0.2, 2.4, 5 and 17 years and found that cement hydration was completed in 17 years. An increasing number of experimental studies have also indicated that a large number of potentially toxic elements in MgO-based S/S monoliths would leach 36.74–48.18% after 104 years by simulating leaching results [4]. It was reported that there was no apparent degradation in the performance of an in-situ stabilized contaminated site in three years [24]. However, erosive environments will alter the structures and worsen the effectiveness of S/S treatments [25,26]. It should be noted that the currently existing empirical models of geo-environmental performance are based on short-term data, due to the severe lack of long-term monitoring data for in situ or indoor test results of S/S samples [27,28]. Therefore, prediction models are needed to provide a more accurate assessment of the long-term performance of S/S-treated contaminated soil.

In this study, the long-term performance evolution and associated models of S/S products in different environments were studied, and parameters for the long-term performance assessment of S/S-treated potentially toxic-element-contaminated soil are provided. In summary, the research objectives of this work were: (1) to explore the performance evolution of S/S monoliths in different erosive environments; (2) to investigate the long-term variations in the speciation and leachability of potentially toxic elements in S/S products over three years; (3) to establish models of strength and permeability coefficients for S/S monoliths in different environments; and (4) to perform microstructural and mineralogical analyses for assessment of long-term performance change in S/S products.

## 2. Materials and Methods

# 2.1. Materials

In order to obtain better experimental accuracy, artificially Pb-contaminated soil prepared with silty clay was used in this study. The silty clay used in the experiments was collected from Hubei Province, China. The main mineral contents of the silty clay were quartz, albite, montmorillonite, kaolinite/kaolin, muscovite and plagioclase. The

physical and mechanical indexes are shown in Table 1. Detailed information about the preparation of the Pb-contaminated soil can be found in previous studies and briefly summarized as follows [29–31]. The Pb-contaminated soil was obtained by adding a certain amount of Pb(NO<sub>3</sub>)<sub>2</sub> solution to soil with an acquired optimal moisture content of 19.5%, and the calculated Pb concentration was added in the simulated contaminated soil to acquire contaminated soil with a preset Pb concentration (5000 mg/kg). Then, 20% of P42.5 Portland cement, calculated by reference to the dry weight of the soil, was used to prepare the S/S-treated Pb-contaminated soil samples. Specimens for strength tests ( $\Phi$ 39.1 \* 80 mm) and permeability tests ( $\Phi$ 50 \* 50 mm) were prepared by static pressing with suitably sized molds. The prepared S/S samples were cured for 7 d under standard curing conditions ( $20 \pm 2$  °C, humidity 95%) before the conduction of the following tests. Ordinary Portland cement was purchased from the China Huaxin Cement Co., Ltd., and the reagents used in the research, namely, sodium hydroxide and acetic acid, were analytically pure, with contents of 99%, and purchased from the China Pharmaceutical Group Chemical Reagents Co., Ltd.

Table 1. Basic physical properties of the soil used in the tests.

Water Content	Natural Density	Specific Gravity	Void Ratio	Liquid Limit	Plastic Limit	Optimum Moisture Content	Grair Sand	-Size Distributi Silt	on/% Clay	Maximum Dry Density
20.78%	1.89 g/cm <sup>3</sup>	2.72	0.74	41.6%	21.8%	19.5%	3.45	62.27	34.28	$1.72 \text{ g/cm}^3$

## 2.2. Unconfined Compressive Strength (UCS) Test

To investigate the unconfined compressive strength of the S/S-treated Pb-contaminated soil under different conditions, a series of soaking solutions were prepared by adding different dosages of sodium hydroxide and acetic acid, the pH values for which were 2.65, 3.65, 5.00, 6.86 and 10.00. The samples were soaked in the above solutions for 1 d, 7 d, 15 d, 28 d, 60 d, 90 d, 360 d, 450 d, 720 d and 1080 d, and then the samples were taken for the conduction of UCS tests with a WDW-20 universal testing machine manufactured by the Jinan Zhongzheng Testing Machine Manufacturing Co., Ltd. The test rate was 5 mm/min, and each group was repeated three times and the results were averaged. Moreover, the soaking leachants, with different pHs, were completely replaced when the samples were taken for the conduction of the strength tests.

A model was established to describe the evolutionary process of UCS variation in the long-term curing environment. Consistent with the cement hydration-reaction process, it was assumed that the UCSs of samples would increase rapidly in the starting months and that the rates of increase in UCSs would decelerate in the following years, reducing to zero when the S/S products reached maximum strength. The growth-rate-decrease model (GRDM) model for UCS change as a function of time in the natural environment was established as follows:

$$U(t) = -C * e^{-At} + U_{max} \tag{1}$$

where *A* is the initial UCS growth rate of the S/S monolith in a specific environment; *C* is the maximum increment of samples, which equals  $(U_{max} - U_0)$ ; and  $U_{max}$  is the maximum UCS of the S/S product.

#### 2.3. Permeability Test

The permeability test was conducted consistently with the curing time of the UCS test. The samples were taken and pre-saturated with deionized water in a vacuum saturator for 24 h, then loaded into a flexible wall permeameter (PM 3230) for the permeability test. According to ASTM D 5084, the confining pressure of the permeability test was kept at 100 kPa and the permeability pressure of the sample was 80 kPa. The permeability test was carried out with distilled water. At the beginning of the permeation, the permeation was recorded every hour, and the permeability test was terminated when the recorded hydraulic conductivity was stable.

#### 2.4. Batch Leaching Test

The leachability tests for Pb in the S/S products were evaluated by the toxicity characteristic leaching procedure (TCLP) and availability tests (NEN 7371). The total amounts of potentially toxic elements in the soil and in the S/S-treated soil at different times were determined after microwave digestion. TCLP [32] and NEN 7371 [33] tests were carried out on polluted soil and S/S samples after curing for 28, 360, 720 and 1080 days. The NEN 7371 method was used to test the maximum amounts of inorganic components from building and solid-waste materials in the leaching process. The aim of this was to determine the leaching amounts of potentially toxic elements when the materials were exposed to the surrounding environment or extreme conditions (e.g., the materials disintegrated and acid-neutralization ability was completely lost). The TCLP tests were conducted based on Chinese leaching standards, and the acetic acid buffer solution used in the TCLP tests was prepared according to Chinese leaching toxicity standards [34]. Briefly, the tested samples (2 g) were mixed with acetic acid solution (40 mL, pH 2.64) at a liquid-to-solid ratio of 20 and then the mixture was agitated for 18 h in a shaker. The supernatants were filtered with a 0.45 µm membrane filter and collected to determine the Pb concentrations.

In order to compare the maximum leachability of potentially toxic elements between Pb-contaminated soil and the S/S-treated soils, the NEN 7371 leaching test was carried out on artificial-origin contaminated soil and S/S samples soaked in an ear-neutral solution (pH = 6.86) for 28 d, 360 d, 720 d and 1080 d, respectively. The NEN 7371 method, a two-step leaching test, was carried out based on the Dutch standard NEN 7371 [33]. Firstly, 5 g samples were leached with distilled water at a liquid-to-solid (L/S) ratio of 50, and the leaching solution pH was adjusted to remain at  $1.0 \pm 0.5$  for 3 h. Then, the residues separated in the first step were sent for the second step leaching, which was conducted with a pH of  $4.0 \pm 0.1$  for 3 h with an L/S ratio of 50. The leachates from step 1 and step 2 were filtrated and mixed to determine the concentrations of Pb. The concentrations of Pb for all the leachates were determined by ICP-MS at the end of the experiment with an inductively coupled plasma mass spectrometer (ICP-MS 7700) manufactured by Agilent Technologies, Inc.

The leaching percentage (P) of each test was calculated according to Equation (2):

$$P = \frac{c \times v}{M} \times 100\%$$
 (2)

where P is the leaching percentage of Pb leached by the TCLP or the NEN 7371 leaching test (%); *c* is the leaching concentration of Pb in the leachate; *V* is the total volume of leachate for each test; and *M* is the total amount of Pb in the sample. The TCLP leaching concentration of Pb from untreated contaminated soil was 97.32 mg/L, and the Pb concentration drastically decreased to 4.45 mg/L for the S/S sample after curing for 28 days. This indicated that the Pb leaching concentration of the S/S-treated soil was lower than the acceptance criteria for Chinese landfill (5 mg/L) [34,35], demonstrating that the cement S/S treatment was effective for the disposal of Pb-contaminated soil.

#### 2.5. Sequential Extraction Test

Chemical fractions of Pb in contaminated soil and S/S products were determined by a modified three-step BCR test proposed previously [36]. According to this method, the speciation of potentially toxic elements was classified into four fractions, namely, an acid-soluble fraction (F1), a reducible fraction (F2), an oxidizable fraction (F3) and a residual fraction (F4), which were determined by specific procedures presented in Table S1. The residues of the samples obtained from step 3 were digested by microwave-assisted digestion, following the standard procedures of Method 3052 of the U.S. Environmental Protection Agency (USEPA) to determine the residual fractions of samples. The samples chosen for the sequential extraction tests were consistent with those chosen for the batch leaching tests.

#### 2.6. Microstructural Analysis

X-ray diffraction (XRD) analyses were performed with a Brook D8 Advance X-ray diffractometer made in Germany. Before the tests, the contaminated soil samples and the S/S samples cured at different ages were prepared by drying, crushing, grinding and passing the samples through a 200-mesh sieve. During the experiment, the powder samples were scanned with Cu-K $\alpha$  radiation in the scanning range (2 $\theta$ ) of 2.5°~70° at ascanning speed of 2°/min. A Quanta 250 scanning electron microscope was used to conduct the microscopic morphological analysis. It should be noted that the inner part of the sample was taken from the cylindrical center of the sample and that the outer part of sample was taken from the outer ring of the sample.

#### 3. Results and Discussion

#### 3.1. Long-Term Leachability of the S/S Monolith

In order to investigate the leachability of Pb in the S/S products in natural field environmental conditions, S/S samples soaked in distilled water (pH 6.86) for different periods were chosen to conduct the TCLP and NEN 7371 leaching tests. Figure 1 shows the leaching concentration of Pb from S/S products as a function of curing age, as determined by the TCLP and NEN 7371 leaching tests, and the corresponding leaching percent ages for each leaching test were also calculated and presented. The leaching concentration of Pb from S/S samples decreased gradually from 4.45 mg/L to 0.68 mg/L with the increase in curing age over 2 years, while the leaching concentration of Pb slightly increased to 1.02 mg/L after three years. The decline in Pb concentration could have been due to the continuous cement hydration in the S/S matrix and the encapsulation and stabilization of Pb, with the hydration product mitigating the release of Pb from the S/S monolith [21,37]. Numerous studies have confirmed that the hydration of cement in S/S products will last for many years and that leaching concentrations of potentially toxic elements decrease continuously with curing time [12,23,31,38]. Wang and Al-Tabbaa [23] reported that cement hydration could last for more than 5 years, while potentially toxic-element leaching during hydration will continue to decrease. It is worth noting that the leaching concentration of Pb in the S/S sample increased from 0.68 mg/L to 1.02 mg/L after 1080 days' curing. The increased release of Pb could be attributed to the carbonization between hydration products and carbon dioxide reducing the acid-neutralization abilities of the sample matrixes, leading to increases in Pb leaching concentrations [12,39].

Figure 1b presents the Pb availability in the untreated contaminated soil and S/S samples after curing for different periods. The Pb concentration in the untreated soil, as determined by the NEN 7371 leaching test, was 0.792  $\mu$ g/L, suggesting that the availability or maximum leaching capacity of Pb in the soil was equal to 79.90 mg/kg. The total amount of Pb released in the NEN 7371 leaching test accounted for 1.83% of the total content of Pb in the soil, which was a lesser amount than that released in the TCLP test (44.64%). Based on the leaching concentration of Pb from the NEN 7371 test, the maximum leaching capacities of Pb in the S/S samples soaked in pH 6.86 conditions for 28 d, 360 d, 720 d and 1080 d were 328.3 mg/kg, 174.0 mg/kg, 76.30 mg/kg and 45.18 mg/kg, respectively, and accounted for 8.28%, 4.42%, 1.95% and 1.18% of the total Pb in the S/S samples, respectively. To make a comparison, the total Pb percentages released in the TCLP test by the samples cured for 28 d, 360 d, 720 d and 1080 d were 2.24%, 1.64%, 0.35% and 0.53%, respectively. It was found that the amounts of Pb extracted in the TCLP and NEN 7371 tests were almost of the same order of magnitude, and the results are consistent with those of [40]. The total amounts of Pb extracted in the NEN 7371 leaching test from the S/S products at different curing ages were about 2–4 times higher than that of TCLP test, which could be attributed to a higher buffer capacity of the leachant of the NEN 7371 leaching test. It should be noted that the availability of Pb in the S/S samples (328.3 mg/kg) was much higher than in the artificial contaminated soil (79.90 mg/kg). This unreasonable phenomenon was mainly caused by the NEN 7371 experimental method and procedure, which requires continuous acid addition during the first three hours of the test to maintain the neutrality

of the solution. The highly alkaline matrix of the S/S monolith consumed much more acid than the contaminated soil because of its high buffer capacity. As a result, much more Pb was released from the S/S samples, while smaller amounts of Pb leached from the contaminated soil during the NEN 7371 leaching procedure. A similar phenomenon was observed by Jing et al., who found that S/S treatment increased the availability of Pb [40].



**Figure 1.** Leaching concentration of Pb from samples cured for different periods: (**a**) TCLP; (**b**) NEN 7371 availability test.

### 3.2. Long-Term Chemical Fraction Change of Pb

The chemical fractions of Pb in the untreated contaminated soil and S/S products at different curing ages are presented in Figure 2. As shown in Figure 2a, the acid-soluble, reducible, oxidizable and residual fractions of Pb in the untreated contaminated soil were 70.32%, 23.04%, 4.02% and 1.36%, respectively. After S/S treatment and curing for 28 days, the percentage of acid-soluble, reducible, oxidizable and residual fractions of Pb changed to 18.70%, 69.24%, 4.09% and 1.89%, respectively. Acid-soluble Pb decreased from 70.32% to 18.70% after the S/S treatment, while the reducible fraction increased from 23.04% to 69.24%. It was found that Pb speciation in the contaminated soil transferred from the acid-soluble fraction to the reducible fraction, and both the mobility and leachability of Pb dramatically decreased after S/S treatment. After S/S treatment, the acid-soluble Pb may have been bound up in calcium silicate hydrate (C-S-H phase) or present in insoluble compounds or hydroxide precipitates, leading to the decrease in the acid-soluble fraction [41]. The increase in there ducible fraction of Pb could possibly be attributed to the formation of sulfate during the cement hydration process [42]. S/S treatment with cement could provide an alkaline environment with the excess hydroxide, which could promote the transformation of lead from carbonate minerals [40,43]. It is reasonable that the residual fraction reaches a stable level (2.0%) after S/S treatment, because potentially toxic elements in this form are present in the mineral crystal lattice, while it is practically impossible to stabilize Pb in a crystal lattice short-term in the cement treatment.

The chemical fractions of Pb in the S/S samples immersed in pH 6.86 distilled water for 28, 360, 720 and 1080 days are presented in Figure 2b. Different chemical fractions of Pb

behave differently overtime. The acid-soluble and residual fractions of Pb did not change noticeably over the soaking time, while the oxidizable and reducible fractions changed a lot. As soaking time increased from 28 days to 1080 days, the reducible fractions of Pb decreased from 74% to 72%, while oxidizable fractions increased from 4% to 6%. The variation in chemical fractions indicated that Pb gradually transformed from acid-soluble fractions to reducible fractions and oxidizable fractions as the immersion time increased, demonstrating that Pb in the S/S samples became more stable overtime. The hydration of cement would last for many years in S/S monoliths, which would enhance the stabilizing effectiveness and decrease the leachability of potentially toxic elements in S/S monoliths [12]. Previous studies have reported that Pb in contaminated soils is mainly stabilized/solidified by precipitation or adsorbed on the surface of cement hydration products [44,45]. Along with the continuous hydration of cement, the leachability and availability of Pb decreases because of long-term Pb–cement–soil interferences and chemical reactions [16].



**Figure 2.** Lead speciation in untreated soil and S/S monoliths cure for different ages: (**a**) potentially toxic-element speciation change, before and after S/S treatment (cured for 28 days); (**b**) metal speciation variation in S/S samples cured for different periods.

#### 3.3. Long-Term Permeability Variation of theS/S Monolith

The performance of S/S products, which is of great importance in the field to support contaminated-site remediation and control the release of toxic components, would be greatly affected by natural erosive environments, such as acid-rain conditions. Permeability is an important parameter to guarantee the effectiveness of S/S treatments [7].

Figure 3 shows the permeability coefficients of the S/S monolith in different pH environments. It was found that the environmental conditions significantly affected the permeability coefficients of the samples. Figure 3a presents the evolution of permeability coefficients under weakly acidic and alkaline environments (pH 5.00–10.00). The permeability coefficients of the S/S monolith gradually decreased with soaking time overthree years. The decrease in permeability coefficients along with curing time was significant after 90 days of immersion. During 90 to 1080 days of immersion, the permeability coefficients of the S/S products decreased slowly and tended to become stable. One possible reason is that the weakly acidic and alkaline environments had weak erosion effects on the S/S monolith, such that the microstructure of the S/S monolith was not significantly altered during the relatively long-term erosion. In strongly acidic environments (pH 2.65 and 3.65), the permeability coefficients exhibited quite different behavior, as can be seen in Figure 3b. In the environments with pHs of 2.65 and 3.65, the permeability coefficients reached the lowest values of  $1.89 \times 10^{-10}$  cm/s and  $4.13 \times 10^{-10}$  cm/s at 60 and 90 days, respectively. It is worth noting that there were large amounts of suspended solids floating in the leachates after 30 days' immersion, which blocked the pores of the specimens and thus reduced hydraulic conductivity. Thereafter, the permeability coefficients increased to  $6.70 \times 10^{-5}$  cm/s and  $9.37 \times 10^{-8}$  cm/s after 1080 days' immersion for the environments with pHs of 2.65 and 3.65, respectively. The acid could react with the hydration products and destroy the internal structure of the S/S monolith due to the dissolution of hydration products in the S/S monolith [9]. The dissolution of hydration products, such as Ca(OH)<sub>2</sub> and C-S-H, in the S/S monolith enhances the internal pore structure of the S/S monolith, thus increasing the permeability coefficient [9]. Although the hydration reactions and structural stability of the S/S monolith can be maintained for many years, once the erosion rate exceeds the hydration rate, the permeability coefficient increases.

In order to explore the relationship between the long-term permeability coefficients and curing age, a logistic model ( $y = A_2 + (A_1 - A_2)/(1 + (x/x_0)^p)$ ) was used to fit the test results. The fitting results are shown in Table 2 and Figure S1. The logistic model fitted well with the permeability coefficient data for the S/S monolith materials in different environments. The model reached a goodness-of-fit value higher than 0.99 for a pH of 5.00–10.00. The model had a lower performance in fitting the permeability coefficients under the acidic environment, with goodness-of-fit values of 0.60 and 0.96. It can be concluded that the logistic model can be used to predict the permeability coefficient variation of the S/S monolith in weakly acidic and alkaline environments, while many more experimental data and associated effective methods are still needed to model permeability coefficients in strongly acidic environments, which deficiencies will be addressed in future research.



**Figure 3.** Hydraulic conductivity variation over3 years of immersion: (**a**) weakly acidic and weakly alkaline environments; (**b**) strongly acidic environments.

pН	Fitting Equation	R <sup>2</sup>
2.65	$y = 5.55 \times 10^{-4} - 5.55 \times 10^{-4} / (1 + x / 1349)^{8.92}$	0.99997
3.65	$y = 7.11 \times 10^{-7} - 6.96 \times 10^{-7} / (1 + x/4004)^{1.58}$	0.60433
5.00	$y = 7.89 \times 10^{-10} + 4.21 \times 10^{-6} / (1 + x / 0.00459)^{0.86}$	0.99627
6.86	$y = 4.92 \times 10^{-10} + 3.90 \times 10^{-6} / (1 + x / 0.00563)^{0.86}$	0.99588
10.00	$y = 5.99 \times 10^{-10} + 3.13 \times 10^{-6} / (1 + x / 0.00951)^{0.47}$	0.99537

Table 2. Fitting results for hydraulic conductivity under different pH conditions.

#### 3.4. UCS Variation and Model

The UCS of an S/S monolith is one of the most important factors to ensure the effectiveness of S/S treatment. The UCSs of the S/S products soaked in simulated erosion conditions (pH 2.65–10.00) for different periods are presented in Figure 4. Similar to the change in permeability coefficients, the long-term UCS evolution over time was significantly affected by environmental pH. Similarly, the UCSs of the S/S monoliths increased gradually with the increase in immersion time under weakly acidic and weakly alkaline conditions. Meanwhile, the strength of samples increased rapidly during the first 90 days for the rapid hydration of cement and increased slightly and tended to become stable over 90 to 1080 days. After soaking in conditions with pHs of 5.00, 6.86 and 10.00 for 1 day to 1080 days, the UCSs of the S/S products increased from 6.8, 6.9 and 7.0 MPa to 17.0, 19.7 and 20.2 MPa, respectively. Previous work reported that the UCSs of S/S products would keep increasing for more than 5 years due to the continual hydration reactions of cementitious materials [12,46]. However, in strongly acidic environments with pHs of 2.65 and 3.65, the strengths of the samples reached their maximum valuesat60 days and 150 days, respectively. The drastic decrease in UCSs in the acidic environment were caused by the dissolution of  $Ca(OH)_2/C-S-H$  in the S/S products, which resulted in a losing the integrity in the S/S monoliths and their associated strengths [9]. The strengths of the S/S monolith materials gradually decreased to 0.2 and 10.9 MPa after three years of immersion. The reason for the UCS change is similar to that for the permeability coefficient variation, which could be attributed to the deterioration of the microstructure of the S/S monoliths caused by acid erosion. Consequently, acids and alkalis react with alkaline hydration products and destroy the internal integrated structure, thus reducing the strength and increasing the permeability coefficient [9].

It is of great importance to establish a model to describe and predict the UCS evolution of S/S monoliths in the field in order to support the engineering and long-term assessment of in-situ and ex-situ S/S treatments. In most scenarios in natural environments, the environmental pH values are in arrange between 5.00 and 10.00, namely, weakly acidic and weakly alkaline conditions. Based on the long-term test results and previous results [7,47], it is reasonable to conclude that the strength of S/S samples would reach a maximum value after several years' curing. In order to model the strength evolution of S/S monoliths under conventional environments (weakly acidic and weakly alkaline), a strength-variation model, the GRDM, was established based on the three-year performance change in weakly acidic and weakly alkaline environments.

In the simulated erosion scenarios, the UCS results for the samples cured for different ages (1 d, 7 d, 15 d, 28 d and 90 d) were substituted into the model. Numerical solutions were performed separately, and the detailed solver is described in the Supplementary Materials. The results for the parameters in different scenarios are listed as follows:

When pH = 5:  $A_1 = 0.03835$ ;  $C_1 = 9.940$ ;  $U_{max1} = 16.51$ ;

When pH = 6.86:  $A_2 = 0.02963$ ;  $C_2 = 11.98$ ;  $U_{max2} = 18.72$ ;

When pH = 10:  $A_3 = 0.03481$ ;  $C_3 = 11.65$ ;  $U_{max3} = 18.19$ .

The predicted values of the model and the specific values of the tests are shown in Figure 4b. The detailed error analysis for UCS prediction and the detailed solver for the model are listed in the Supplementary Material (Table S2). As shown in Figure 4b, the model can be used to simulate and predict long-term test data. Meanwhile, this model can predict

maximum long-term strength based on short-term test data, which is of great significance for the engineering design of S/S-treated heavy-metal-contaminated soil. The GRDM model can use at least three data points to fit and predict the maximum strength of an S/S monolith, which can be used to guide engineering design and long-term effectiveness assessments.



**Figure 4.** UCS variation as a function of time under different pH conditions: (**a**) experimental data for the S/S monoliths; (**b**) comparison data.

# 3.5. Mineralogical Analysis

Figure 5 presents the identified crystalline mineral composition of the contaminated soil and S/S products cured in different scenarios. The main crystalline minerals identified in the untreated contaminated soil were quartz, montmorillonite, albite, kaolinite/kaolin, muscovite and plagioclase. After cement S/S treatment, some crystals of hydration products, such as calcium hydroxide (CH) and ettringite (AFt), were formed. According to the hydration-product analysis for the S/S products at different ages, the main hydration products of cement under short-term curing were CH and AFt, which results were consistent with those of previous studies [48–50].

To explore the mineral change in the S/S materials under long-term erosion conditions, the internal and external parts of a cylindrical S/S product (sample soaked in pH 2.65 leachant for 1080 d) were sampled to conduct an XRD analysis (Figure 5b). It was found that, after 1080 days of leaching at pH 2.65, the main crystalline minerals in the S/S monolith external part were quartz, albite, alumina calcite, montmorillonite, kaolinite, muscovite, microcline and aluminosilicate. Compared with the sample cured at pH 6.86 for 1080 d, the CH and AFt phase had disappeared, indicating that these minerals were dissolved by acid due to long-term immersion under strongly acidic conditions. However,

aluminosilicate was formed in the external part of the S/S product because of the reaction between calcite and aluminum hydrate calcite. In conclusion, it was confirmed that acid erosion significantly affected the minerals in the S/S products, especially the dissolution of portlandite and ettringite, which greatly decreased the strength and effectiveness of the S/S treatments, even though some new substances (aluminosilicates) were formed.

Therefore, S/S treatment fails to stabilize/solidify potentially toxic-element-contaminated soil under long-term acid erosion because of the dissolution of hydration products. The degraded structure of the S/S monolith would no longer offer strength, permeability and leaching resistance for contaminated soil, which should be avoided in field conditions.



**Figure 5.** XRD analysis of the untreated soil and S/S samples cured in simulated scenarios for different periods: (a) untreated contaminated soil and samples soaked in pH 6.86 leachants for different periods; (b) interior and external parts of cylindrical S/S product soaked in pH 2.65 conditions.

#### 3.6. Microstructural Analysis of the S/S Monolith in Different Erosion Environments

The SEM results of representative samples are shown in Figure 6. The evolution of the structure and the mineral change of the samples as a function of curing age and pH are depicted. The S/S samples cured in pH 6.86 leachant for 28 d, 360 d and 1080 d are shown in Figure 6a–c, respectively. A large number of C-S-H short fibers and some CH crystals emerged between the pore interfaces of the soil particles inside the S/S monolith (Figure 6a). C-S-H short fibers, with lengths of 0.5–2  $\mu$ m, were one of the main products in the initial hydration-reaction stage. Furthermore, these could connect the pores and fissures between soil particles over a short curing time (within 28 days) and increase the cohesion between soil particles and the strength of the S/S monolith [47]. Moreover, with the increase in immersion time, the cohesion between hydration products and particles increased and

the density of the S/S products also increased at the same time. After 1080 days' curing, many hydration products were filled between the layers and pores of the solidified material (Figure 6c) and between the rod-like ettringite minerals which appeared in all directions and layers and increased the structural strength of the S/S monolith. Consequently, the internal structures of the samples had fewer communicating pores and tight interlayer structures, which were important factors that contributed to the increase in macro-strength and the decrease in the permeability coefficient of the S/S-treated soil.

SEM images of the S/S samples after 1080 days' immersion in different pH conditions are shown in Figure 6d–f. It was found that many hydration products of the samples were eroded after 1080 days of immersion in strongly acidic environments. In addition, there were some rod-like and reticulated grooves; the former may be dissolution traces of ettringite or C-S-H, while the reticulated structures were skeletons of C-S-H left after dissolution by the acid solutions. Similarly, there were no needle-like ettringite minerals in the 17-year-old S/S-treated soil, because the hydration process had been completed [12].

Due to the dissolution of hydration products, the cementation ability with respect to soil and binder particles was lost. Therefore, the strength of the S/S monolith decreased significantly after long-term acid erosion. However, under the conditions of pH 6.86 and 10.00, the S/S monolith materials still maintained integrity and good cohesiveness, with rich hydration products. In particular, the spherical products observed in alkaline environments were calcium carbonate produced by the reaction of alkaline products with carbon dioxide. Accordingly, carbonation reactions represent an important factor affecting the long-term properties of S/S treatment materials [12,39]. Long-term erosion caused by carbonization is an important and common factor affecting the performances of S/S monoliths, which should be paid much more attention in further studies.



**Figure 6.** SEM images of S/S samples in the simulated scenarios: (**a**) S/S product soaked in pH 6.86 leachant for 28 d; (**b**) S/S product soaked in pH 6.86 leachant for 360 d; (**c**) S/S product soaked in pH 6.86 leachant for 1080 d; (**d**) S/S product soaked in pH 2.65 leachant for 1080 d; (**e**) S/S product soaked in pH 6.86 leachant for 1080 d; (**f**) S/S product soaked in pH 10.00 leachant for 1080 d.

#### 4. Conclusions

The performance evolution of S/S products under simulated erosive-environmental conditions and the corresponding micro-mechanisms of the S/S treatment were investigated in this work. It was found that performance, including strength, permeability and leachability, can be significantly affected by environmental conditions. The following conclusions can be drawn:

- (1) S/S treatment can significantly reduce the leaching toxicities of potentially toxic elements in contaminated soils. The leachability of Pb in the S/S monolith, including leaching toxicity and availability, continued to decrease over three years in weakly acidic and alkaline environments with pHs ranging from 5.00 to 10.00.
- (2) The percentages of exchangeable and residual fractions of Pb in the S/S monolith remained stable over three years, while Pb was gradually transformed from acidsoluble fractions to reducible fractions and oxidizable fractions. The mobility of potentially toxic elements decreased with the continuous hydration of the cementitious materials.
- (3) During the three-year curing, the performances, including permeability and mechanical strength, of the S/S monolith samples in weakly acidic and alkaline environments continued to improve. The strongly acidic environment caused the dissolution of hydration products, destroyed the structure of the S/S monolith and reduced the strength. The GRDM model can be used to predict the evolution and maximum values of S/S monoliths in common natural environments.
- (4) After cement S/S treatment, the main cementitious substances in the S/S matrixes formed by hydration reactions were CH, AFt and C-S-H. Furthermore, over three years, there was no significant change in the main components of the S/S monolith samples in weakly acidic and weakly alkaline conditions. However, strongly acidic conditions resulted in the dissolution of mineral components, such as calcium hydroxide and ettringite.

Furthermore, environmental erosion is the direct reason for the microstructural change in S/S materials, which leads to deterioration in the performance of S/S monoliths and the secondary dissolution of potentially toxic elements which pollute the environment. In any case, more work should be conducted to explore the direct quantitative relationships between S/S performance and environmental factors to facilitate construction-lifecycle engineering and environmental-assessment methods for S/S treatments. At present, a large amount of research has focused on the performance evolution of S/S monoliths over twenty years and there is still a lack of research on the performance degradation and evolutionary modeling of S/S monoliths. Quantitative evaluation of the performance of S/S monoliths over longer time periods could provide more accurate results for the engineering design of potentially toxic-element-contaminated soil remediation.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3 390/w14203314/s1, **Figure S1**. Fitting curves of hydraulic conductivity in different scenarios; **Table S1**. Extraction media used in the modified BCR sequential extraction. **Table S2**. Model prediction Error Analysis.

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