Leaching characteristics and curing mechanism of magnesium phosphate cement solidified zinc-contaminated soil in an acid rain environment

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ABSTRACT

A semi-dynamic leaching test was used to simulate the erosion effect of acid rain on magnesium phosphate cement (MPC)-stabilized/solidified zinc-contaminated soil. The leaching characteristics and curing mechanism were studied with a combination of X-ray diffraction (XRD) and scanning electron microscopy (SEM). Influences of the initial pH value of the simulated acid rain, the ratio of the curing agent ($\text{MgO}/\text{KH}_2\text{PO}_4$, abbreviated M/P), and the mass of water glass on the leaching characteristics of Zn^{2+} and conductivity in the leachate of the sample were studied. It is shown that the curing effect of the cement component on Zn^{2+} is better for M/P = 6 when compared to M/P = 4 in a strong acid environment. While in a weak acid environment, it is observed that the curing effect is superior when M/P = 4. Also it is observed that 4% water glass content can effectively improve the cement curing effect of heavy metal Zn in an acid rain environment. These results indicate that water glass can be effectively applied to MPC solidified heavy metal Zn.

Keywords: Acid rain, Leaching characteristics, Solidified/stabilized, Water glass, Zinc contaminated soil

1. Introduction

In recent years, with the acceleration of urbanization, soil pollution has become increasingly severe, and soils in many countries and regions have been polluted by heavy metals to varying degrees [1-3]. Investigations have found that the zinc content accounted for a large proportion of the heavy in contaminated soil [4-6]. The heavy metal zinc poses a serious threat to groundwater bodies, human health, and the ecological environment [7], so it is necessary to treat and repair zinc-contaminated soil.

Solidification/stabilization (S/S) technology has been widely used to treat and repair heavy metal-contaminated soil due to its advantages, such as high efficiency, economy, and convenience [8-11]. Generally, the S/S method generally refers to the ordinary Portland cement S/S method.

Many scholars worldwide have conducted extensive research on the leaching characteristics of solidified heavy metal-contaminated soil [12-14]. Existing studies have shown that several

factors, such as the cement materials, cement components, and curing time, can affect the leaching characteristics of contaminated soil, and reasonable cement components and prolonged cement curing time can effectively reduce the leaching behavior of heavy metals in polluted soil [11, 15, 16]. However, when the solidified contaminated soil is affected by acid rain, it affects the dissolution of the heavy metals in the solidified contaminated soil. Fu found that the leaching infiltration of acid rain causes cement hydration products to dissolve and diffuse the heavy metals solidified therein and even exceed the limit instituted by the Ministry of Environmental Protection on the concentration of the leaching in heavy metals, causing secondary pollution to the surrounding environment [17]. Du found that when cement solidified heavy metal contaminated soil, a strongly acidic leaching solution (pH = 2.0) significantly changed the leaching behavior of the lead and calcium in the soil, but when the leaching agent was weakly acidic (pH = 4.0) and neutral (pH = 7.0), the difference in the soil leaching behavior was small [18]. Therefore, research on the solidification

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Received May 21, 2020 Accepted August 21, 2020

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mechanism and heavy metal leaching mechanism of solidified heavy metal-contaminated soil in an acid rain environment is of great scientific significance to improve the acid resistance of solidified contaminated soil.

There is also increasing research on the use of magnesium phosphate cement (MPC) for curing radioactive and hazardous wastes. Rao showed that magnesium phosphate cement is widely used to solidify contaminated soils because the solubility of heavy metals in phosphate is very low [19]. Bui used potassium magnesium phosphate cement (MKPC) to solidify contaminated soil and obtained improved curing results in acidic and neutral environments [20]. Li and Arora found that magnesium phosphate cement has a better curing effect on pollutants than that of ordinary cement, and the effect of reducing the solubility of pollutants in solidified contaminated soil is achieved by generating poorly soluble alkaline hydrates or solidifying them in the hydrate lattice [21-22]. Although much research has been carried out on the solidification of magnesium phosphate cement-contaminated soil, there is little research on the acid resistance of magnesium phosphate cement-contaminated soil under acid rain. Xu found that the total amount of leaching of zinc ions significantly increases when magnesium phosphate cement-cured zinc-contaminated soil is affected by acid rain [23]. Therefore, to effectively prevent the impact of the acid rain environment on solidified heavy metal-contaminated soil and improve the acid resistance of solidified contaminated soil, it is necessary to find suitable additives and evaluate whether the additives can effectively consolidate and stabilize heavy metals in acidic environments.

Most acid-resistant cements worldwide are prepared by adding water glass according to a certain proportion. Studies have shown that water glass has good acid resistance and high adhesion [24]. Microscopic analysis of the mechanism of water glass on MPCs found that the addition of water glass to MPCs can accelerate the early hydration of the MPC, which can decrease the size of the grains of hydrated products in the MPC hardened body, improve the structural compactness, and reduce the dissolution of the hydrated products [25-26]. However, whether the long-term properties and acid resistance of solidified heavy metal-contaminated soil can be maintained under the combined effects of acid rain and heavy metals needs further research.

In this paper, the effect of the initial pH value of simulated acid rain, ratio of the curing agent, and mass of water glass on the leaching characteristics of Zn^{2+} , such as the concentration, pH value, and conductivity in the sample leachate, are studied and analyzed through semi-dynamic leaching tests. X-ray diffraction (XRD) is used to study the effect of water glass content on the hydration process and hydration products of heavy metal Zn solidified by magnesium phosphate cement. Scanning electron microscopy (SEM) is used to qualitatively analyze the mineral phase and microstructure characteristics of the magnesium phosphate cement-cured zinc-contaminated soil under an acid rain erosion

environment. These results provide a reasonable basis for improving the selection of the solidifying agent and amount of water glass for treating soil pollution of heavy metal zinc in the future.

2. Sample Preparation and Test Methods

2.1. Experimental Materials

The soil used in the test was soft kaolin, which was produced by Lingshou County Zeshun Mineral Products Trading Co., Ltd. in Lingshou County, Hebei Province, China. The basic physical properties and mineral composition of kaolin are shown in Table 1.

The test used magnesium phosphate cement (MPC) as the curing agent. It was prepared in the laboratory by adding an appropriate amount of water according to a certain proportion from over-fired magnesium oxide (MgO, abbreviated M, with a specific surface area of $235 \text{ m}^2 / \text{kg}$), potassium dihydrogen phosphate (KH_2PO_4 , abbreviated K), borax ($Na_2B_4O_7 \cdot 10H_2O$, abbreviated B), and fly ash, for example. Among them, over-fired MgO was produced by the Yongxiang Mineral Powder Factory. KH_2PO_4 was analytically pure and produced by Hushen Chemical Reagent Co., Ltd. The borax retarder was analytically pure and produced by Taicang Meida Reagent Co., Ltd. For the preparation of the magnesium phosphate cement, the addition amount of the borax retarder was based on the mass of the over-fired MgO, and the addition amount was 5%. In this test, different components, namely, KH_2PO_4 and over-fired MgO, were used, and two ratios of magnesium phosphate cement were used, namely M: P = 4: 1 and M: P = 6: 1 (abbreviated as M4 or M6, respectively).

According to the current research of heavy metal polluted soil, zinc (Zn) was selected as the single heavy metal pollutant for research. The main anion in the acid rain was considered to be composed of SO_4^{2-} and NO_3^- , and the acid rain was formulated with concentrated sulfuric acid, concentrated nitric acid and de-ionized water by using the step dilution method. The concentration ratio of the concentrated sulfuric acid and concentrated nitric acid was 5:1, which was diluted with deionized water to a pH of 2, 4, and 7 to formulate the simulated acid rain. Because zinc nitrate has high solubility (high cationic activity) and ordinary cement hydration reactions are not as affected by the nitrate [27], the influence of different heavy metal salts on the strength of the cement does not have to be considered, so compounds with a purity grade of analytical purity (such as $Zn(NO_3)_2 \cdot 6H_2O$) were selected.

The water glass used in the test was sodium water glass ($Na_2SiO_3 \cdot 9H_2O$) provided by Shanghai Culture Chemical Pigment Co., Ltd. Studies have shown that sodium water glass has good flame resistance, strong acid resistance, environmental friendliness, non-toxicity, simple processing and a low cost. The disadvantages are low adhesion, poor water resistance, and high-temperature resistance [24].

Table 1. Basic Chemical Composition of Kaolin

Index	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO	K ₂ O	Na ₂ O	Loss on ignition
Content	47.86	38.26	0.06	0.19	0.08	0.13	0.04	0.05	13.65

2.2. Sample Preparation

First, the kaolin, cement and other dry materials were mixed in proportion (the cement was magnesium phosphate cement and $M = 4$ or 6). According to the soil design, a certain amount of deionized water was added, and a magnetic stirrer was used to fully dissolve the metal nitrate solution in the deionized water to obtain a metal nitrate solution (the heavy metal content was 0 and 0.5% relative to the dry soil weight). The nitrate solution and sodium water glass modifier were added to the dry material and mixed with a blender until uniform (the content of water glass modifier was 0, 2%, and 4% relative to the mass of the dry soil). Subsequently, a certain amount of soil sample was weighed (according to the debugging and the estimated mass of the concrete), and after mixing well, it was filled into a mold with a diameter of 39 mm and a height of 80 mm in 3 layers according to the requirements of the geotechnical test specification. After the sample was left for 1 h, it was demolded, weighed, and packed with plastic film to prevent any moisture loss. It was placed in a standard curing room for curing (temperature was $20 \pm 2^\circ\text{C}$ and relative humidity was $95 \pm 3\%$). The curing age was 28 days, and three parallel samples were made for each group.

The content of added heavy metals was based on the literature [28] that surveyed the pollution of industrial sites in Chinese cities. The average Zn concentration in the topsoil ranged from 1,189 to 16,478 mg/kg, and the moisture content of the samples was 20% (relative to the dry soil + cement content).

2.3. Test Methods

The test in this paper was based on ASTM C1308-08 [29]. The extractant was added to a simulated acid rain solution with pH = 2 and 4 based on the original standard (pH = 7). For different initial pH values, three parallel experiments were performed. The test used a soil sample surface area-to-extractant volume ratio of 1:9 (cm^2 / mL), which was 0.11 cm^{-1} , a single sample surface area of approximately 122 cm^2 , and an extractant volume of 1,100 mL.

The specific steps were as follows. First, a glass beaker was cleaned with acid, the impurities in the glass beaker were rinsed with deionized water, the prepared pH acid rain was poured into a beaker, and the initial extractant pH and temperature in the beaker were measured. After placing the standard contaminated zinc contaminated soil sample that was cured for 28 d on a pervious stone ($\Phi 80 \text{ mm}$) at the bottom of the beaker, the time was started, and the beaker was sealed to prevent the CO_2 of the air from acidifying the extractant. The extractant was renewed at intervals of 2 h, 5 h, 17 h, 24 h, 24 h, 24 h, 48 h, and 96 h, and the leachate was renewed 8 times for 10 days. After each sampling update, the pH, temperature, and conductivity of the filtrate were measured, and the sample was digested with nitric acid to make up the volume to measure the Zn^{2+} concentration. XRD and SEM were used to analyze the solidification mechanism of Zn-contaminated soil with magnesium phosphate cement and the leaching mechanism of the Zn^{2+} .

According to the Zn^{2+} concentration data measured at each leaching interval, the mass of Zn^{2+} dissolved on the surface of the sample was estimated by the following formula [30]:

$$C_{\text{Zn},i} = \frac{c_{\text{Zn},i} \cdot V_{\text{L},i}}{A_s} \quad (1)$$

In the formula, $C_{\text{Zn},i}$ represents the dissolution amount of Zn^{2+} on the sample surface after the i -th leaching (mg / cm^2); $c_{\text{Zn},i}$ represents the Zn^{2+} concentration (mg / L) in the leachate after the i -th leaching; $V_{\text{L},i}$ is the total volume (L) of leachate after the i -th leaching, calculated according to 1.1 L; and A_s is the contact area between the sample and the leachate (cm^2), and it is calculated to be 122 cm^2 . When the leaching is continuously updated, the total amount of Zn^{2+} dissolved can be calculated by superposing the mass of Zn^{2+} dissolved in each leachate at each stage:

$$C_{\text{Zn}} = \sum_{i=1}^N C_{\text{Zn},i} \quad (2)$$

3. Results and Analysis

3.1. Effect of Different Water Glass Contents on the Leaching Characteristics of Solidified Zinc-Contaminated Soil

The test abbreviated each component as $\text{MiZnj}(k)$ ($i = \text{M/P}$; j is heavy metal content; k is water glass content). According to the trend for the Zn^{2+} concentration with leaching time in the semi-dynamic leaching test shown in Fig. 1, during leaching at pH = 2, when the water glass content is 0%, the leaching solution from the M4Zn0.5 and M6Zn0.5 samples has a consistent trend for Zn^{2+} concentration over time, all of which decrease first, then increase, and then decrease significantly, but the Zn^{2+} concentration of the M4Zn0.5 sample at the initial stage of leaching (2 ~ 7 h) is much higher than that of M6Zn0.5. Upon comparing the leaching Zn^{2+} concentration of the M4Zn0.5 and M6Zn0.5 samples with different water glass contents, it is found that when the water glass content is 4%, the leaching Zn^{2+} concentration is the lowest herein. Comparing the M6Zn0.5 and M4Zn0.5 Zn^{2+} concentrations in the sample leaching solution with different water glass contents, it is found that M6Zn0.5 has a better zinc curing effect than M4Zn0.5.

At pH = 4,7 leaching, when the content of water glass is 0%, the dissolution of the Zn^{2+} concentration in the M4Zn0.5 sample is greater than that in the M6Zn0.5 sample, but the trend for the two after 96 h of leaching accumulation are basically the same, and the concentration difference is relatively small. Upon adding different doses of water glass to the M4Zn0.5 and M6Zn0.5 samples, it can be seen that when the content of the water glass is 4%, the concentration of Zn^{2+} leached from the sample is the lowest herein, indicating that the addition of water glass enhances the curing effect of cement on heavy metal Zn.

Fig. S1 shows a line chart of the leaching concentration of Ding [31] solidified zinc contaminated soil. Compared with this test, the difference is mainly in the difference of the test soil (this test uses kaolin, Ding uses standard sand), the type of curing agent and Is there any water glass added. By comparing the test results of the two, it is found that under the same leaching conditions, kaolin can better cure Zn^{2+} by MPC than standard sand; Comparing the leaching concentration of the solidified zinc contaminated soil under different experimental materials, it is found that the addition of water glass can reduce the Zn^{2+} leaching concentration of the

Fig. 1. Variation in Zn^{2+} concentration with leaching time during semi-dynamic leaching test. (a) Initial pH = 2, (b) Initial pH = 4, (c) Initial pH = 7.

solidified zinc contaminated soil of MPC. Comparing the leaching concentration of Zn^{2+} of solidified contaminated soil, it is found that MPC has better curing effect than ordinary Portland cement; Comparing the leaching concentration of the solidified zinc contaminated soil under different experimental materials, it is found that the addition of water glass can reduce the Zn^{2+} leaching concentration of the solidified zinc contaminated soil of MPC.

3.2. Effect of Different Water Glass Contents on the Total Leaching of Solidified Zinc-Contaminated Soil

The total amount of Zn^{2+} dissolved on the surface of the sample calculated by the above formula (2) is shown in Fig. 2. Comparing the total dissolution of heavy metal Zn^{2+} in the solidified zinc-contaminated soil at different pH values, it can be found that the total amount of Zn^{2+} dissolved on the surface of the sample when the initial pH = 2 during the semi-dynamic leaching test that simulates acid rain is generally higher than that when the pH = 4 and 7. The total amount of Zn^{2+} eluted from the surface of M4Zn0.5(0%) at pH = 2 is 14 times and 27.8 times that at pH = 4 and 7, respectively, and the total amount of Zn^{2+} dissolved on the sample surface of M6Zn0.5(0%) at pH = 2 is 9.9 times and 11.6 times that at pH = 4 and 7, respectively, indicating that a strong acid environment greatly disrupts the curing effect of magnesium phosphate cement on zinc contaminated soil.

When the initial pH of the simulated acid rain is 2, the total

amount of Zn^{2+} dissolved in the M4Zn0.5 and M6Zn0.5 samples at different water glass contents (0%, 2%, and 4%) is analyzed. When the content of water glass is 4%, the total amount of Zn^{2+} leached from the sample is the lowest among the water glass contents, indicating that the 4% water glass content has the best curing effect on the magnesium phosphate cement-cured zinc-contaminated soil.

The total amount of Zn^{2+} dissolved on the surface of the M4Zn0.5 sample compared with that on the surface of the M6Zn0.5 sample shows that when the content of the water glass is 0%, 2%, and 4%, the total amount of Zn^{2+} dissolved on the surface of the M4Zn0.5 sample is always higher than the total amount of Zn^{2+} dissolved on the surface of the M6Zn0.5 sample.

When the initial pH value of the simulated acid rain is 4, the total dissolved Zn^{2+} on the surface of the M4Zn0.5(0%) sample is 2.6 times and 3.4 times that of the M4Zn0.5(2%) and M4Zn0.5(4%) samples, respectively, and the total amount of Zn^{2+} dissolved on the surface of the M6Zn0.5(0%) sample is 1.46 times and 1.96 times that of the M6Zn0.5(2%) and M6Zn0.5(4%) samples, respectively. When the content of water glass is 0%, the total amount of Zn^{2+} dissolved on the surface of the M6Zn0.5 sample is less than that of the M4Zn0.5 sample. When the content of water glass is 2% and 4%, the total amount of Zn^{2+} dissolved on the surface of the M6Zn0.5 sample is greater than that of the M4Zn0.5 sample, indicating that when water glass is added in a weak acid environ-

Fig. 2. Total dissolved Zn^{2+} on the surface of the solidified zinc-contaminated soil sample. (a) Initial pH = 2, (b) Initial pH = 4, (c) Initial pH = 7.

ment, the curing effect of M4 on zinc is better than that of M6.

In a neutral environment with an initial pH = 7, the total amount of Zn^{2+} dissolved on the surface of the M4Zn0.5(0%) sample is 1.6 and 3 times that of the M4Zn0.5(2%) and M4Zn0.5(4%) samples, respectively, and the total amount of Zn^{2+} dissolved on the surface of the M6Zn0.5(0%) sample is 1.44 times and 1.67 times that of the M6Zn0.5(2%) and M6Zn0.5(4%) samples, respectively. The total amount of Zn^{2+} dissolved on the surface of the sample with $M = 4$ is always lower than that on the surface of the sample with $M = 6$.

Comparing the test results with the figure of total dissolution of Zn ions in Ding [31] solidified zinc contaminated soil in Fig. S2, it is found that kaolin can better cure Zn^{2+} of MPC than standard sand under the same leaching environment. This is because kaolin has a large specific surface area and good adsorption performance, and can play a certain role in adsorbing heavy metal ions; Compared with the total amount of Zn^{2+} leaching of the solidified contaminated soil, it is found that the total amount of Zn^{2+} leached by the ordinary Portland cement solidified zinc contaminated soil at the end of the leaching is greater than the total amount of Zn^{2+} leached by the MPC solidified zinc contaminated soil, indicating that MPC has better curing effect than ordinary Portland cement. The addition of water glass can reduce the total amount of Zn leaching of solidified zinc contaminated soil, especially 4% water glass greatly improves the curing effect of cement solidified soil on heavy metal zinc.

3.3. pH and Conductivity of the Leaching Supernatant of the Solidified Zinc-Contaminated Soil

Fig. 3 shows the change in the pH of the leaching supernatant with leaching time when the initial pH of the acid rain is 4. The study finds that the pH range of the leaching supernatant of the updated leaching group is 5.0 ~ 10.8 when the initial pH value of the simulated acid rain is 4. At the same time, when the initial pH of the simulated acid rain is 4, the excess OH⁻ in the solidification system is ionized, and H⁺ in the acid solution remains after neutralization so that the leaching solution becomes alkaline. It can also be seen from Fig. 3 that in each group of samples, the pH of the leaching solution of the solidified soil from the M6 group is generally higher than that of the M4 group. The abovementioned pH trend is basically consistent with the analysis results of the Zn^{2+} concentration law in the leaching solution and the Zn^{2+} diffusion mechanism. This is consistent with the results of the study by Wang on the change in the pH and leaching characteristics of Zn^{2+} , so the leaching characteristics of Zn^{2+} in the semi-dynamic leaching test can be confirmed again by the change in the pH of the leaching supernatant [32].

In this leaching test, the conductivity of the leaching solution of the sample in each updated leaching phase was tested, and the conductivity of the samples in the updated leaching group was cumulatively compared. As shown in Fig. 4, the conductivity of the leaching supernatant varies with the leaching time. The research finds that when the initial pH value of the simulated acid rain is 4, the conductivity trend is not much different. After the leaching accumulation time reaches 144 h, it is in a "dynamic equilibrium" state. The so-called "dynamic equilibrium" refers to the use of simulated acid rain to continuously replace the leachate

Fig. 3. Change in the pH of the leaching supernatant with leaching time.

Fig. 4. Changes in the conductivity of leaching supernatant with leaching time. (Initial pH = 4)

to extract heavy metals from the solidified soil in a semi-dynamic leaching experiment after a certain period of time. The total amount of ions in the leachate after leaching in the curing system reached a stable state, and the ionized ions are mainly OH⁻ ions; thus, the macroscopic performance of this state is that the conductivity of the leachate is stable after the cumulative leaching time reaches 144 h.

3.4. Reaction Mechanism of the MPC Cured Zinc Contaminated Soil

Fig. 5 and Fig. 6 show the XRD diffraction patterns of the M6Zn0.5(0%) samples and M6Zn0.5(4%) samples after semi-dynamic leaching, respectively, at the initial pH = 2, 4, and 7 of the simulated acid rain and after standard curing for 38 days. According to Fig. 5 and 6, it can be seen that the XRD patterns of the semi-dynamic leached sample M6Zn0.5(0%) and M6Zn0.5(4%) indicate the presence of $KMgPO_4 \cdot 6H_2O$ (MKP), $Mg_3(PO_4)_2 \cdot 22H_2O$, $Mg_3(PO_4)_2 \cdot 8H_2O$ and other major cement hydration products. This is because the reaction mechanism of magnesium phosphate cement is based on the acid-base reaction of sparingly soluble salts. After MPC powder is mixed with water, potassium

dihydrogen phosphate is dissolved and ionized to generate K^+ , H^+ and Mg^{2+} . After the magnesium oxide powder encounters water and H^+ , the surface of the particles is dissolved to form Mg^{2+} and OH^- , and H^+ reacts with OH^- to release a large amount of heat, and the acid-base neutralization reaction accelerates the dissolution of potassium dihydrogen phosphate and magnesium oxide. Free Mg^{2+} interacts with K^+ and H^+ to form hydrated gel $MgKPO_4 \cdot 6H_2O$ and other gel substances, among which $MgKPO_4 \cdot 6H_2O$ is the main reaction product. As the reaction progresses, white crystals precipitate on the surface of the test block, and the main components of the surface leaching process are $MgKPO_4 \cdot 6H_2O$ and a small amount of K_2HPO_4 crystals. [33-38]. The ionization equation during hydration includes the ionization process of KH_2PO_4 , the hydrolysis of magnesium oxide, and the formation of $MgKPO_4 \cdot 6H_2O$ [39-41].

Fig. 5. XRD pattern of the semi-dynamic leached M6Zn0.5(0%) samples.

Fig. 6. XRD pattern of semi-dynamic leached M6Zn0.5(4%) samples.

It can also be found on the spectrum that the strong diffraction peaks are mainly from SiO_2 , MKP formed by the reaction, and unreacted MgO and Al_2O_3 . In addition, $Zn_3(PO_4)_2 \cdot 4H_2O$ and $Zn(OH)_2$ are also detected in the M6Zn0.5(0%) and M6Zn0.5(4%) samples. Among them, $Zn(OH)_2$ is only detected in the sample with standard curing for 38 days, and $Zn_3(PO_4)_2 \cdot 4H_2O$ is detected in the environment with $pH = 2, 4$, and 7 and standard curing for 38 days. This is because Zn is an amphoteric metal that can generate phosphates (such as $Zn_3(PO_4)_2 \cdot 4H_2O$) with the acid ion ionized by KH_2PO_4 , and it can generate a $Zn(OH)_2$ amphoteric hydroxide with OH^- ions generated by the hydrolysis of MgO . $Zn_3(PO_4)_2 \cdot 4H_2O$ appears under simulated acid rain at $pH = 2, 4$, and 7 and the standard curing environment, while $Zn(OH)_2$ only appears in the sample after standard curing for 38 days, which is due to $Zn_3(PO_4)_2 \cdot 4H_2O$ being generated when the solution $pH = 3 \sim 7$. $Zn(OH)_2$ needs to be greater than 8 to generate, which is consistent with the microscopic research on magnesium phosphate cement solidified heavy metal zinc [20, 42]. Its chemical reaction equation is:

When simulating the effect of the initial pH of acid rain at $pH = 2, 4$, and 7 , the peak value of the MKP is lower than that after the 38 days standard curing, indicating that the amount of generated MKP is reduced, which can explain why many water and acidic environments can cause dissolution of MKP. The peak intensity corresponding to MKP is the lowest herein when the initial $pH = 2$. This is because a large amount of H^+ promotes the reverse reaction of MKP so that it dissolves into Mg^{2+} , K^+ , PO_4^{3-} . As the main product of the hydration reaction of MPC cement, MKP transforms into other more stable phases with changes in external water content and pH value, but under acidic conditions, MKP dissolves.

The main body of the sodium water glass adhesive is colloidal silicon dioxide, which is hydrolyzed into silicic acid in aqueous solution and interacts with carbon dioxide in the air. The silicic acid that is formed is gradually dried and solidified, finally forming a bonded network structure [24, 43]:

It can be found on the spectrum that the peak of $Mg_3(PO_4)_2 \cdot 22H_2O$ increases after adding water glass, which and it also promotes the generation of $Mg_3(PO_4)_2 \cdot 8H_2O$. This is because the addition of water glass can prevent MKP from dissolving again, and in a large amount of aqueous solution, MKP will tend to be converted into the more stable compound $Mg_3(PO_4)_2 \cdot 22H_2O$, which is a slower

conversion process, and then $\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$ turns into the most stable gel $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ under weak alkaline environment; After adding water glass, some of the SiO_2 peaks are higher after the standard curing for 38 days and in the acidic environment than in the weak acid environment, indicating that a certain acidic environment promotes the condensation of $\text{Si}(\text{OH})_4$ to form SiO_2 . The reason that $\text{Si}(\text{OH})_4$ is not detected in this test may be that, on the one hand, $\text{Si}(\text{OH})_4$ exists for a relatively short amount of time.

3.5. Microstructure Analysis of MPC Solidified Zinc Contaminated Soil

In this paper, a HITACHI S-4700 scanning electron microscope was used to scan the sample after the semi-dynamic leaching test. To determine the effect of the water glass content and heavy metal content on the effect of magnesium phosphate cement solidified zinc contaminated soil, the M6Zn0(0%), M6Zn0.5(0%), and M6Zn0.5(4%) samples were subjected to an environment of simulated acid rain at $\text{pH} = 4$. The microscopic image of MPC-cured zinc-contaminated soil is shown in Fig. 7.

Upon observing the microstructure of the sample with initial acid rain $\text{pH} = 4$, it can be seen that compared with the M6Zn0(0%) sample that did not contain heavy metals, the M6Zn0.5(0%) sample has a large number of coarse holes, broken crystals, and lack of water between the particles. The close connection of the gel product results in a decrease in overall compactness, which is caused by Zn^{2+} inhibiting the partial production of MKP. At the same time, the cementation between the soil particles and the gel is reduced, resulting in an increase in the structural dispersion of the solidified soil, decreasing the sample structure strength, and increasing the dissolution probability of Zn^{2+} . This is similar to the research results of Lai Z. Y and He Y. J, which show that heavy metal ions reduce the cementation between soil particles and gels, leading to an increase in the structural dispersion of the solidified soil and increasing the probability of the dissolution of heavy metal ions [44, 45].

Compared with the M6Zn0.5(0%) sample without water glass, the M6Zn0.5(4%) sample reduces the porosity between the particles and increases the compactness of the sample structure. This is consistent with the XRD analysis results for M6Zn0.5(4%) in Fig. 6, and the close connection of the hydrated gel products between the particles leads to an increase in the overall compactness and an increase in the strength of the macroscopic structure. This is due to the addition of water glass to form a bonded network structure, which increases the contact area and reaction time between MgO and phosphate and increases the possibility of generating hydrated gel structure products, thereby enhancing the compactness of the structure and alleviating the MKP dissolution tendency. At the same time, this behavior strengthens the cementation between the soil particles and gel, reducing the structural dispersion of the solidified soil, and reducing the dissolution probability of Zn^{2+} . This test result is similar to Yang [25] and Shi [26] microscopic analysis of the effect mechanism of water glass on MPC, indicating that under the joint action of acid rain and heavy metals, the addition of water glass can maintain the long-term properties and acid resistance of solidified heavy metal contaminated soil.

Fig. 7. SEM images of the semi-dynamic leached samples. (a) M6Zn0(0%), $\text{pH} = 4$ (2,000 times), (b) M6Zn0.5(0%), $\text{pH} = 4$ (2,000 times), (c) M6Zn0.5(4%), $\text{pH} = 4$ (2,000 times).

4. Conclusions

In this paper, laboratory studies were carried out for zinc-contaminated soil to investigate the MPC solidification mechanism, the erosion mechanism of acid rain and the acid resistance after adding water glass. The following conclusions can be drawn: In an acidic environment, the effect of M4 solidified zinc contaminated soil is more affected by acid than M6; The addition of water glass enhances the bonding between the soil particles and the gel body. Thus reductions in both the structural dispersion of the solidified soil and the dissolution probability of Zn^{2+} can be observed; Comparing different water glass content, it is found that 4% water glass content can effectively improve the cement curing effect of heavy metal Zn in an acid rain environment. Therefore, water glass can be used as a good admixture for the solidification of heavy metal Zn by MPC in acid rain environment, and maintain the long-term properties and acid resistance of solidified heavy metal contaminated soil.

Acknowledgment

This work was supported financially by the Provincial Fund-East China Institute Joint Fund / Key Project (LHZ19E090001) and National Natural Science Foundation of China (No.51778585). We thank Ding, Yaokun for his guidance on the test.

Author Contributions

Z.W. (Professor) provided the research ideas and thoughts. H.L.Z. (Ph.D. student) designed the experiment. And the experiment was mainly completed by H.J.Z. (ma.eng. student), X.H.W. (Ph.D. student), and B.P.W. (ma.eng. student). S.F.X. (Professor) summarized the experimental data and finished writing the experimental report.

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