

Cement-Based Solidification/Stabilization of Heavy Metal Contaminated Soils with the Objective of Achieving High Compressive Strength for the Final Matrix

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Abstract. *The Solidification/Stabilization (S/S) of heavy metal contaminated soils using Ordinary Portland Cement (OPC) is studied as a hazardous waste treatment technology. The soil-binder ratio of 8% by weight is selected for treatment by setting a justification constraint on the solidified matrix. In order to consider the physical and chemical characteristics of the solidified soil-cement mixtures, Compressive Strength, Toxicity Characteristic Leaching Procedure (TCLP), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) are the tests done during this research. The results indicate that despite an intensive decrease in the compressive strength of solidified soil at early curing ages, the justification constraint set on the preparation of specimens enhances hydration reactions; and the solidified matrix achieves high compressive strength after 7 curing days. The leaching metal concentration in leachates is decreased gradually by aging from 1 to 28 curing days, indicating more metal stabilization in the form of metal hydroxide precipitation, which presents itself in the developed crystalline phases of hydrated cement, as observed in XRD patterns or by absorption on CSH gel or crystals. Leaching metal concentration in leachates is lower than regulatory limits, so there is no strength concern for environmentally safe disposal. Heavy metal contamination diverts the cement hydration reactions toward production of more subsidiary products, that bear less compressive strength, instead of main hydration products. Therefore, the main crystalline phases develop irregularly and coat the aggregates poorly, as observed in SEM micrographs.*

Keywords: *Solidification/stabilization; Heavy metal contaminated soils; Portland cement; Leaching; XRD; SEM.*

INTRODUCTION

Solidification/Stabilization (S/S) is typically a process that involves mixing the waste with a binder to reduce the contaminant leachability by physical and chemical means, which convert the waste into an environmentally acceptable waste form for safe disposal or construction [1-4].

For the purpose of solidification, many organic and inorganic binders have been used, most of which have stabilizing characteristics. Ordinary Portland

Cement (OPC) is the most widely used binder due to its cost effectiveness, availability and compatibility with a variety of wastes [1-4].

The solidification and stabilization of heavy metal contaminated soils by Ordinary Portland Cement are studied in this research paper.

In much research, the final solidified wastes have achieved low compressive strength, in particular, wastes not containing lime, pozzolanic materials or high pollution level waste.

In this study, in addition to S/S treatment, a compressive strength achievement for the final matrix was considered so that it could be used as a construction material. Then, for this purpose, justification of the cement mortar is set as a constraint at the specimen preparation.

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MATERIALS AND METHODS

Materials

Ordinary Portland Cement type II supplied from the Abyek Ghazvin Cement Plant was used throughout this research.

The heavy metal contaminated soil (waste) was supplied from a mining factory. Due to moisture content, the clod soil is first crushed into small pieces and the air is dried for 24 hours under solar heat. Then, it is ground by a bar mill to particles of 100%, passing sieve number being 100 (150 μm) for the well micro encapsulation process.

Tables 1 and 2, respectively, indicate the chemical composition of the soil and soil pollution composition with the results of the untreated soil leaching test, following the Toxicity Characteristic Leaching Procedure (TCLP) [5]. Figure 1 shows a SEM micrograph of the soil structure and texture after physical changes and the passing sieve.

Double washed quarry sand was used as the aggregate material, controlled by ASTM C33-93 [6] for sieve analysis and ASTM C127-88 [7] for water absorption, which accounted for 2.02% of aggregate dry weight.

Table 1. Chemical composition of soil based on XRF (X-Ray Fluorescence) analysis.

Chemical Composition	Percent (%)
Silica, SiO ₂	28.4
Calcium oxide, CaO	4.8
Alumina, Al ₂ O ₃	10.1
Iron oxide, Fe ₂ O ₃	15.5
Manganese oxide, MnO	0.5
Sulfuric anhydride, SO ₃	6.0
Potassium oxide, K ₂ O	1.7
Titanium oxide, TiO ₂	0.5
Total heavy metals contamination	8.6
Loss on ignition (LOI)	23.9

Table 2. Soil pollution composition and results of untreated soil leaching test and TCLP limits.

Metal Concentration in Leachate (mg/l)			
Soil Pollution Composition (%)		Untreated Soil	TCLP Limits
Zn	7.7	2440	-
Pb	0.8-0.6	57.2	5
Cd	0.05	1.88	1
Ni	0.04	0.46	7
Co	0.01	0.51	-

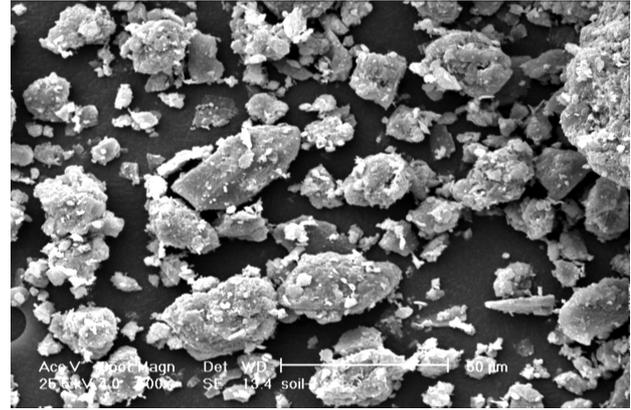


Figure 1. SEM micrograph of heavy metals contaminated soil after physical changes and passing sieve number 100 (magnification 200 \times).

Preparation of Specimens

The specimens were prepared according to ASTM C109-93 [8] with fixed water-binder and sand-binder ratios of 0.485 and 2.75, respectively.

Regarding the strength achievement objective, the final soil-binder (soil-cement) ratio for preparation of S/S specimens was selected by examining different soil-binder ratios and setting a justification constraint. Here, specimens with soil-binder ratios of 5, 10, 15 and 20% by weight were prepared. The justification constraint that was an observation or a visual control of the hardness achievement, excluded specimens with a related soil-binder ratio, which had not hardened for sound de-molding after 24 hours of casting. By slightly touching and pressing the top surface of the molded cement-soil mixtures, the hardness achievement control exerted itself during the justification constraint. Specimens with a higher soil-binder ratio had very soft surfaces and became deformed by touching or pressing.

Regarding the justification constraint, specimens with a soil-binder ratio of 5% by weight hardened fully and specimens with a soil-binder ratio of 10% by weight hardened appropriately, but specimens with soil-binder ratios of 15 and 20% by weight were rejected due to weak hardening characteristics.

In order to reach the final soil-binder ratio, further investigations were carried out by making more specimens with soil-binder ratios of 6, 7, 8 and 9% by weight. Additionally, during and after de-molding, the final cubic shape of the specimens were considered and the specimens with related soil-binder ratios that had deformed shapes or broken edges were omitted.

Following this justification, the soil-binder ratio of 8% by weight was finally selected for the solidification/stabilization treatment. Hereafter, all the main specimens made for studying the S/S treatment included a soil-cement ratio of 8% by weight and were considered at curing ages of 1,3,7,14 and 28 days.

In addition to main specimens, in order to compare the physical and chemical characteristics of the solidified soil-cement mixtures with an ordinary cement mixture at the same curing ages, control specimens that only included a cement mixture (not blended with contaminated soil) were prepared. When the specimens were de-molded, they had to be cured under lime-saturated water to prevent losing the heavy metal ions. The specimens were carried in air with $70 \pm 5\%$ R.H. and under 23°C conditions for the first 5 days and transferred to lime-saturated water for the rest of the curing process.

In this research, for each mixture combination, the specimens were prepared in triplicate, the average value of which represented the result.

Unconfined Compressive Strength Test

The compressive strength of the cement mortar in both solidified soils and with control specimens was tested in a conventional method according to the standard ASTM C109-93 test method, using 50 mm cubic molds. Regarding low compressive strength values, to measure the compressive strength of the main specimens cured for 1 and 3 days, a crew type machine for soil compressive strength testing was used. Compressive strengths of other main specimens and all control specimens were measured, using a hydraulic type machine for concrete testing with a loading rate of 1.0 k-N/s.

Leaching Test

The metal leaching was assessed by following the Toxicity Characteristic Leaching Procedure (TCLP) defined by U.S.EPA (Method 1311). The specimens tested in the compressive strength were crushed and the central core of each sample was further crushed to reduce the particle size to less than 9.5 mm; aggregates were discarded and then a 40 gr portion was sampled and transferred to the extraction vessel. The extract was acetic acid (pH 2.88), which was added at the solid-liquid ratio of 1:20 by weight. The vessel was agitated in an End-Over-End rotation at 30 ± 2 rpm for 16 hours using an agitation rotary apparatus or tumbler.

Due to agitation and neutralization reactions between the cement portion of the soil-cement mixture and the acidic extract, the turbid leachates included separated and suspended parts of the soil-cement mixture such as contaminated soil, cement and sand particles. At the end of a 16 hour leaching test, a short retention time was given to the extraction vessels for the settlement of suspended coarse solids; then, the leachate was filtered for the removal of fine suspended solids. To avoid metal precipitation from the dissolved liquid phase into the solid phase, which causes error in the accuracy of the metal concentration measurement,

the leachate pH was reduced to less than 2.0 by the addition of nitric acid before the metallic analysis, because metals remain dissolved in pH less than 2.0. Metal concentration was measured by flame Atomic Absorption Spectrometry (AAS).

X-Ray Diffraction (XRD)

The crystalline phases of cement hydrates and the probable compounds of stabilized metals were characterized using a Cu-K α XRD device. Here, some other parts of the crushed main specimens that were cured for 7 and 28 days were ground into powder and analyzed by the XRD device for the reflection angle (2θ) from 10° to 70° . To identify the crystalline phases, the results were compared with the Joint Committee on Powder Diffraction Standards (JCPDS).

Scanning Electron Microscopy (SEM)

A XL30 Philips SEM was used to consider the microstructure and phase development of the solidified soil. Flat surface pieces from previously crushed main and control specimens, which had been cured for 7 and 28 days, were selected and treated with acetone-alcohol solution to stop hydration reactions [9]. Gold was used as a conducting medium to coat the surface of samples under vacuum conditions in the Sputter Coater device.

RESULTS AND DISCUSSIONS

Compressive Strength Results

The compressive strength of the main and control specimens are shown in Figure 2.

The addition of heavy metal contaminated soil at the level of 8% by weight caused an intensive decrease in compressive strength from 123 kg/cm^2 in the control

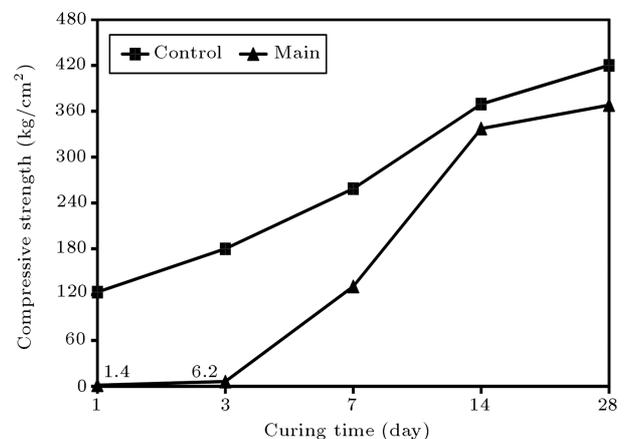


Figure 2. Compressive strength of specimens as function of curing time (day).

specimens to 1.4 kg/cm² in the main specimens, at a one day curing age.

The intensive decrease in the compressive strength of main specimens has both chemical and physical reasons. The chemical reason, which is the main cause of an intensive decrease in compressive strength at the early curing ages of 1 and 3 days, is attributed to heavy metal contamination [9-17]. Heavy metal oxides such as zinc, lead, chromium and iron cause the retardation of cement paste and prevent the formation of main cement hydration products such as Calcium Silicate Hydrates (CSH) and portlandite (Ca(OH)₂) crystals, which bear the mechanical forces [9] such as compressive forces in a solidified cement matrix.

Physical reasons include the presence of fine particles of soil with high specific surface areas, which might effectively reduce the amount of cement available for binding the fine and coarse aggregates required to provide adequate strength [18]. In addition, soil might cover the surface of aggregates and prevent the adhesion of the cement paste and the aggregates [19].

Compared to specimens cured for one day, the compressive strength of main specimens cured for 3 days has increased, but negative effects, especially chemical effects, on cement hydration limited this increment strongly.

Extending the curing period of solidified soil, especially after 3 days, the hydration reactions of the cement started and resulted in the formation of main products, which bear high compressive strength. As shown in Figure 2, even after an improvement in the compressive strength achievement of the main specimens including contaminated soil, the compressive strength was still less than the control specimens' at all curing ages. In fact, the presence of heavy metal contamination has a secondary chemical effect on the formation of cement hydration products, in addition to its primary retarding and disordering effects. Heavy metals diverted the cement hydration reactions toward production of more subsidiary products that bear less compressive strength, instead of main hydration products. This effect is studied in detail in the analysis of XRD patterns.

Therefore, the secondary chemical effect of heavy metal contamination on hydration reactions and the physical effects of soil together, caused a permanent difference between the compressive strength of main and control specimens, even after 7 curing days, when the cement hydration reactions and strength achievement in the main specimens started. This difference also lasts during all curing ages, as shown in Figure 2.

A comparison between the compressive strength of main specimens cured for 3 days and EPA regulatory limits for safe land disposal, equal to 3.5 kg/cm² [1], indicates that there is no strength concern for environ-

mentally safe disposal. Another comparison between compressive strengths of main specimens cured for long curing ages, especially 7 and 14 days, and ACI 299R-99 [20] shows that the final matrix (solidified soil) could be considered as Controlled Low Strength Materials (CLSM) for limited constructions. However, the compressive strength of the 28-day cured main specimens is close to that of the control specimens which are known as concrete, but before any application, the leaching results of the solidified soil should satisfy the environmental limits.

It is necessary to emphasize that if the solidified soil is considered for a specific construction application, besides environmentally safe disposal tests and leaching tests, it must undergo other related standards and acceptable test methods for the desired characteristics and properties.

In fact, in this section, the compressive strength achievement procedure was studied tentatively and no construction application was exactly considered or offered. Furthermore, any application of the final matrix must be limited to environmentally disposable actions at or near the waste location such as polluted sites, landfills or tailing dams and so on, which are severely protected from public accessibility in order to avoid any possible health problems in the future.

Leaching Results

Figures 3 to 7 show Zn, Pb, Co, Cd and Ni concentrations in leachates in TCLP leaching tests, respectively.

It is generally observable that extending the curing age of solidified soil decreases the metal concentration in leachates. For example, lead concentration is decreased gradually from 0.155 mg/l in one day cured solidified soil leachate to 0.08 mg/l in 28-day cured solidified soil leachate.

This indicates that the treatment has been en-

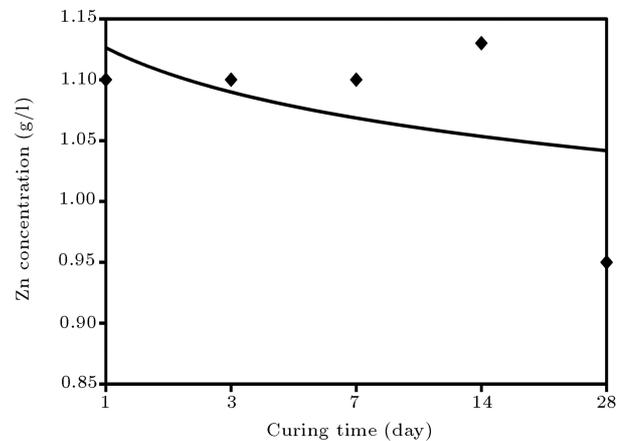


Figure 3. Zn ion concentration leached from cement-based solidified soil (main specimens).

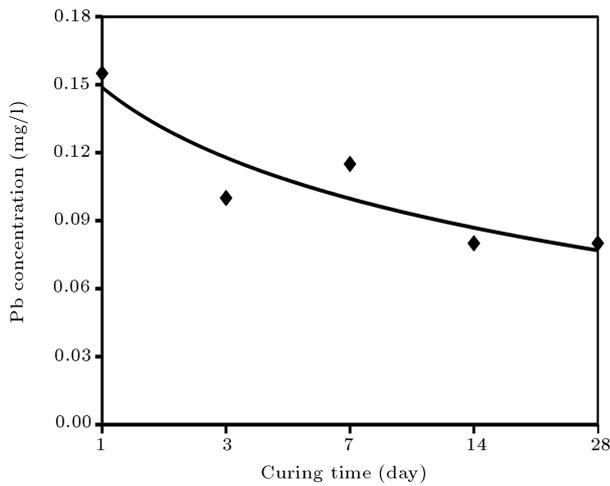


Figure 4. Pb ion concentration leached from cement-based solidified soil (main specimens).

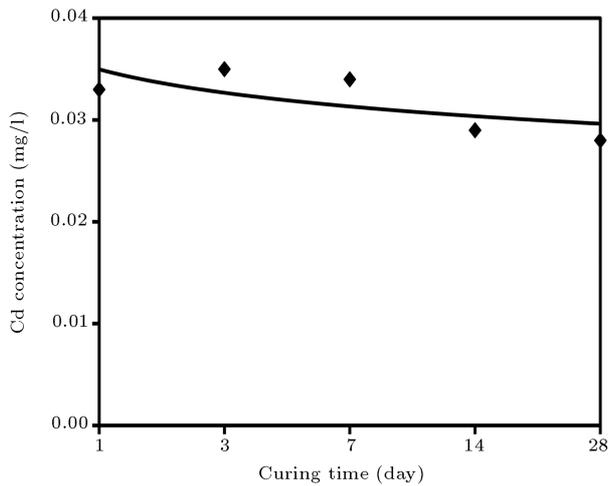


Figure 5. Cd ion concentration leached from cement-based solidified soil (main specimens).

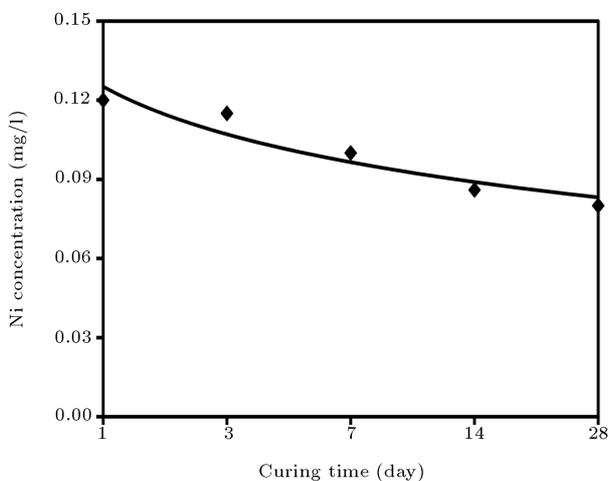


Figure 6. Ni ion concentration leached from cement-based solidified soil (main specimens).

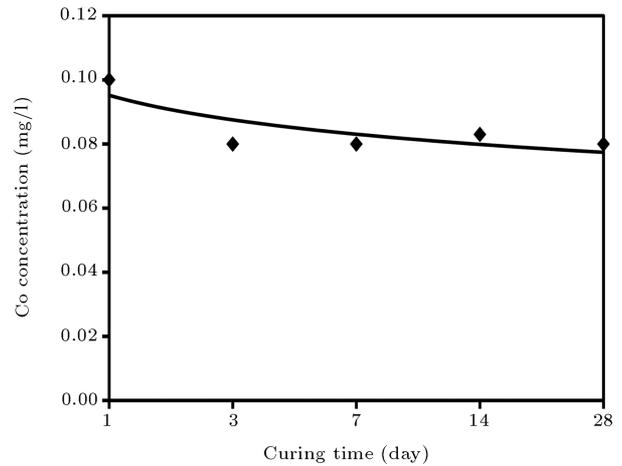


Figure 7. Co ion concentration leached from cement-based solidified soil (main specimens).

hanced [15] by the hardness achievement and formation of main crystalline phases, which increased the acid neutralization capacity of the matrix and prevented metal solution in acidic leachants [21,22].

Additionally, due to aging, more hydration reactions took place and, as a result, more metals stabilized in the form of metal hydroxide precipitations, which presented themselves in the developing crystalline phases of hydrated cement or were absorbed into the CSH gel or crystals.

As a significant result, the leaching concentrations of all metals at any curing age were considerably lower than TCLP regulatory limits according to Table 1.

At the end of the leaching test (TCLP), after 16 hours of contact between the extract and 40 gr crushed particles of the main specimens selected for TCLP test, the leachate pH increased from the initial values of 2.88 to 11.56, 11.68, 11.10, 11.24 and 10.89, which relate to specimens cured for 1, 3, 7, 14 and 28 days, respectively.

As mentioned in compressive strength results, at the early curing ages of 1 and 3 days, cement-soil mixtures contained little amounts of cement hydration products, especially main products. Thus, during leaching tests, acid neutralization was mostly due to the direct solution of the unhydrated cement portion of the cement-soil mixtures.

After cement retardation, since the hydration reactions started in the soil-cement mixture, main hydration products developed and increased in the hydrating mixture; also compared to early curing ages, the amount of unhydrated cement decreased in the main specimens that were cured for longer times. Main products such as $\text{Ca}(\text{OH})_2$ and CSH crystalline are more resistant to acidic conditions than unhydrated cement. So, acid neutralization in greatly cured specimens results from the dissolution of $\text{Ca}(\text{OH})_2$ and the CSH crystalline and decalcification reaction

of the solidified mixture. Therefore, compared to specimens cured for 1 and 3 days, the leachate pH of specimens cured for 14 and 28 days decreased generally, as mentioned above in the pH results.

XRD Results

Figures 8a and 8b show the XRD patterns of cement-based solidified soil hydrated for 7 and 28 days, respectively. Results show that due to the presence of ground aggregates in the powdered sample one sharp and some thin peaks of Quartz were observed in both patterns.

As observed in Figure 8a, pontlandite, one of two main cement hydration products, was detected in the related XRD pattern of a soil-cement mixture cured for 7 days. This crystalline phase was also detected in the XRD pattern of the soil-cement mixture cured for 28 days with a little sharper peak, especially about the reflection angle (2θ) of 18.5. This indicates that despite retardation and other negative impacts at early curing ages, the hydration reactions have continued.

The presence of Ettringite (subsidiary hydration product) and some unhydrated di- and tricalcium

silicates (cement clinker constituents) indicate that the hydration reactions have been diverted toward the production of subsidiary products. Typically, it is defined that the heavy metals pollution enhances Ettringite production in hydrating cement pastes [22,23]. In both patterns, especially in Figure 8b, zinc and lead were found in stabilized forms of $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ [9-11,24,25] and $\text{Ca}_2\text{Pb}_2\text{O}_5(\text{OH})_2$, respectively.

In fact, these metals are stabilized in pontlandite crystals, based on J. Conner's S/S mechanisms, as shown in Figure 9 [24].

According to Conner's mechanisms, the major mechanism for lead stabilization is to be absorbed on CSH crystal surfaces; however, results showed that Pb could also be stabilized as the detected compound in Figure 8.

SEM Results

The microstructure of 7-day hydrated cement in control specimens is shown in Figure 10a, which includes normally developed forms of main crystalline phases (CSH and $\text{Ca}(\text{OH})_2$) and Ettringite. Blending the contaminated soil with cement paste decreased the

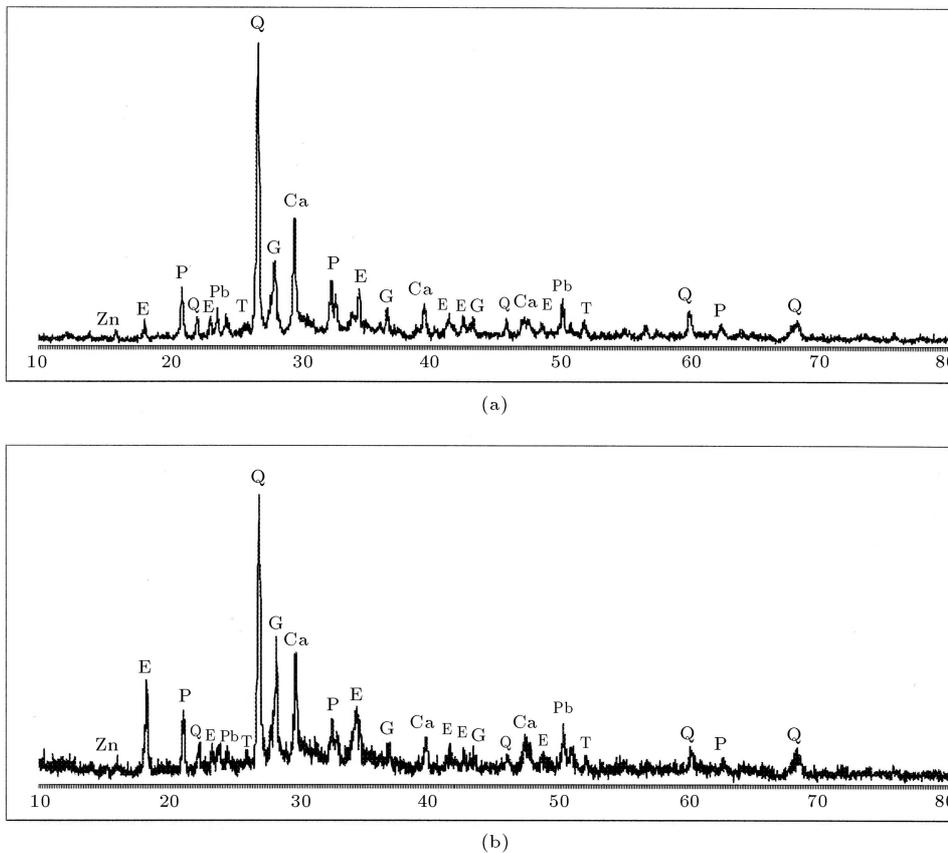


Figure 8. XRD patterns: (a) 7-day cured main specimens and (b) 28-day cured main specimens. P = pontlandite; Q = quartz; E = Ettringite; T = di and tri calcium silicates; Ca = CaCO_3 ; G = gypsum; Zn = $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$; Pb = $\text{Ca}_2\text{Pb}_2\text{O}_5(\text{OH})_2$.

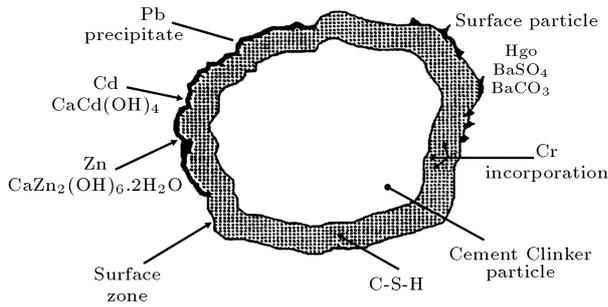


Figure 9. Solidification and stabilization of heavy metals by hydrates of Portland cement [15,24].

production and development of the main crystals and caused the hydration products to coat the aggregates poorly, as shown in Figure 10b.

Figures 10c and 10d show the microstructure of the control and main specimens cured for 28 days. As shown in Figure 10c, due to aging and continuous hydration reactions, the crystalline phases in the 28-day cured control specimens were more developed than in the 7-day cured control specimens (Figure 10b); but, in Figure 10d, the crystalline phases in the 28-day cured solidified soil were developed irregularly. Then, as a result, the porosity of the matrix increased.

Figures 11a and 11b show large amounts of Ettringite with a needle shape structure that grew in the solidified matrix microstructure.

CONCLUSION

This research was carried out to investigate solidification and stabilization of heavy metal contaminated soil as a hazardous waste treatment technology and also to consider the high compressive strength achievement for the final solidified matrix by setting a justification constraint on the treatment.

This research has shown that, despite an intensive decrease in the compressive strength of the solidified soil at early curing ages, the justification constraint set on the preparation of specimens enhanced hydration reactions and the solidified matrix achieved a high compressive strength after 7 curing days.

Besides blending cement (binder) with contaminated soil (waste) in S/S treatment, the justification constraint significantly decreased metal leaching concentrations to the TCLP regulatory limits that are required for environmentally safe land disposal of any waste treatment such as solidification and stabilization.

Heavy metal contamination and soil presence in treatment mixtures had negative effects on cement hydration reactions and retarded them at early curing ages. As a result, the solidified soil-cement mixtures achieved low compressive strength.

According to low compressive strength achievement and the final leachate pH of the solidified soil specimens, waste treatment included metal stabilization and acid neutralization at early curing ages of

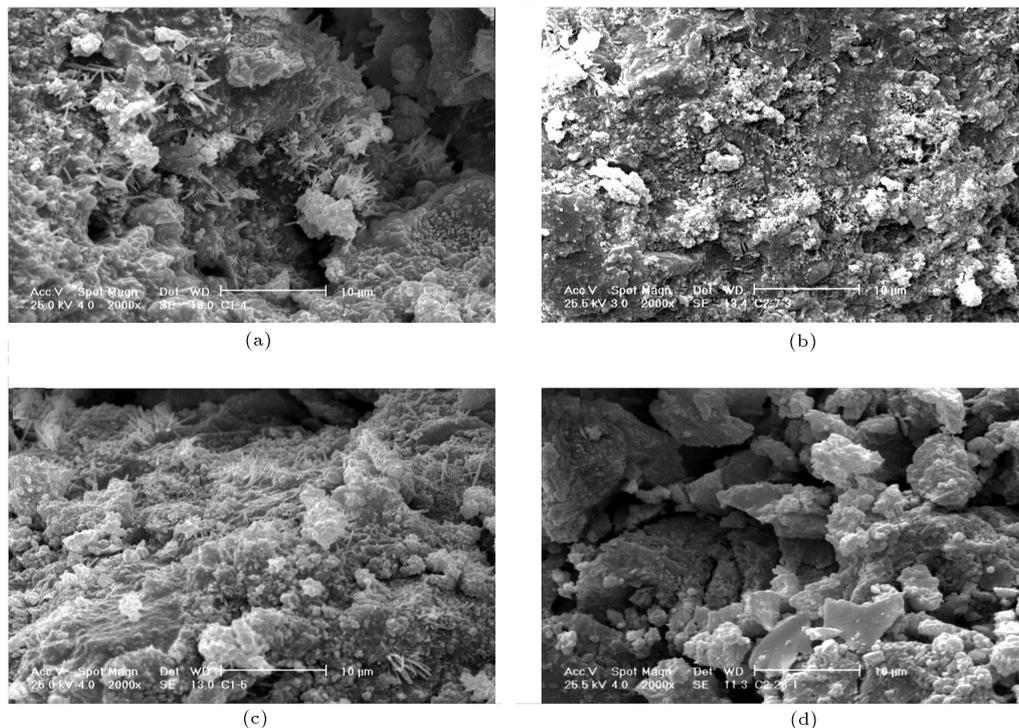


Figure 10. SEM micrographs of 7- and 28- day cured main (solidified soil) and control specimens at magnitude of 2000×: (a) 7-day cured control; (b) 7-day cured solidified soil; (c) 28-day cured control; and (d) 28-day cured solidified soil.

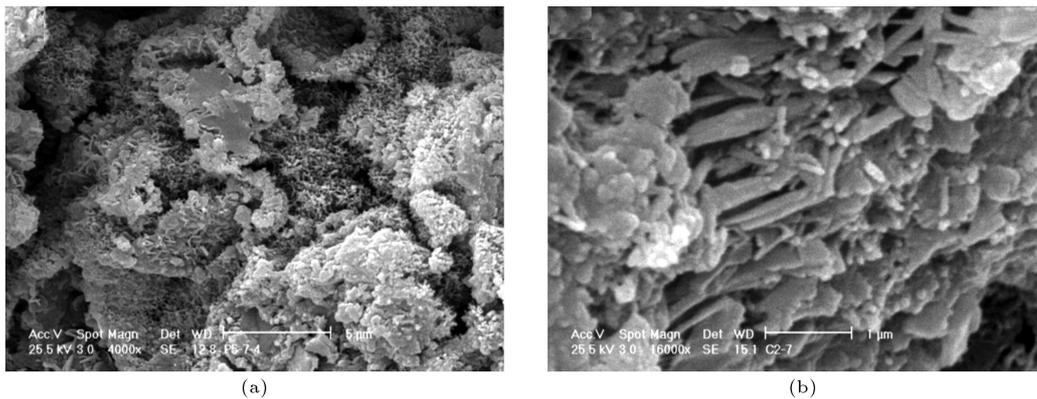


Figure 11. SEM micrographs of Ettringite produced in solidified soil: (a) at magnitude of 4000 \times ; and (b) at magnitude of 16000 \times .

1 and 3 days. After the cement hydration reactions resumed, waste treatment included solidification and more stabilization in portlandite crystals based on J. Conner's S/S mechanisms.

An analysis of XRD patterns showed that heavy metals contamination diverted hydration reactions toward the production of subsidiary low strength products instead of major high strength products. Therefore, the main crystalline phases developed irregularly and coated the aggregates poorly, as observed in SEM micrographs.

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