

Microstructural Evaluation of Stabilization and Solidification of Heavy Metals by Cement at the Presence of Nano Montmorillonite

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ABSTRACT: Stabilization/Solidification (S/S) is an attractive technology which helps to reduce the toxicity and facilitate the disposal of sediments containing heavy metals, industrial wastes, and contaminated soils. The efficiency of the S/S technology can be enhanced by the use of clay nanoparticles. The S/S process incorporating montmorillonite nanoparticles can be employed to prevent the dissemination of heavy metals effectively. Although many studies have addressed the stabilization of contaminant by the use of cement, the microstructural interactions between montmorillonite nanoparticles, heavy-metal contaminants, and cement in different time intervals have been discussed rarely. In addition, there are not enough researches on the impact of montmorillonite nanoparticles in the efficiency of the solidification process. Therefore, this study aims to investigate the interactions between montmorillonite nanoparticles, heavy metals, and cement in different time intervals from the microstructural point of view and to determine the impact of clay nanoparticles on toxicity leaching from solidified/stabilized contaminants. To achieve the above-mentioned objectives, different concentrations of heavy metal (zinc) and different percentages of Portland cement were added to nano-montmorillonite. The contaminant retention mechanism was then experimentally analyzed through monitoring the changes in pH, evaluating microstructural changes (using X-Ray Diffraction), and toxicity characteristic leaching procedure (TCLP) measurement. The results indicated the role of clay nanoparticles in retaining the heavy-metal contaminant and the lack of linear relationship between the quantity of cement content of the specimen and the contaminant retention efficiency.

Review History:

Received: 6/25/2018

Revised: 8/4/2018

Accepted: 8/5/2018

Available Online: 8/25/2018

Keywords:

Stabilization and solidification

Heavy metal

Nano montmorillonite

Microstructure

XRD

1. INTRODUCTION

An increase in dissemination of heavy metal contaminants in recent years highlights the importance of effective methods for engineering disposal of industrial wastes. The most important challenge ahead of this endeavor is perhaps the determination of the right framework and mechanism of action. The precise mechanism of the mobility of contaminants can be grasped by gaining an accurate and comprehensive understanding of system behavior and evaluating it from the nano- and micro-structure perspectives [1-3]. Nano clay particles can be used effectively as adsorbents of many contaminants (e.g. heavy metal ions and organic compounds) in sewage and water [2]. High specific surface area (SSA), mechanical and chemical stability, layered structure, and good cation exchange capacity (CEC) of clay soils have made them a good choice for a wide range of industrial processes and particularly for adsorption of heavy metal contaminants [2]. Solidification and stabilization (S/S) process are methods for reducing the leaching of hazardous waste into the environment. This process isolates heavy metal pollutants and

contaminants of the waste in macroscopic and microscopic scales by turning them into more stable and controllable compounds [4-5]. S/S process can be carried out with different materials, but low cost, wide availability and environmentally friendly nature of the cement-based systems make them a good choice in this regard [6].

While there have been extensive researches on cement-based stabilization of contaminants, various aspects (appearance) of cement-based solidification have remained neglected. Also, microstructural aspects of nano clay-zinc-cement interactions and process of formation of a pozzolanic compound have received marginal attention. The main objective of this study is therefore to examine the time-evolution of nano clay-zinc-cement interactions from a microstructural perspective and to determine the extent of formation of calcium-silicate-hydrate (C-S-H) nanostructures. This paper also studies, from a microstructural perspective, the mechanism of adsorption and immobilization of heavy metals in the hydrated cement matrix with a focus on adsorption, chemical precipitation and incorporation of hydration products in the presence of nano clay during solidification and stabilization process.

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2. MATERIALS AND METHODS

In this study, the behavioral tests were conducted on nanomaterials with the "Cloisite®Na+" trademark, a soil sample obtained from the "South America Clay" Production Company. The purpose behind the selection of hydrated cement was its easy mass production and usage. Cement samples used in the study were provided by Hegmatan Cement Company.

The majority of experiments of this study were conducted based on ASTM standards and geotechnical-environmental test guidelines of McGill University (Canada) [7-8]. Density and pH of clay samples were determined in accordance with ASTM, D854 and ASTM, D4972 standards [7]. Soil carbon content was determined by titration. Specific surface area (SSA) of the soil was measured using the EGME solution. The cation exchange capacity (CEC) of the soil was determined using 0.1 M Barium chloride solution [9]. To do this, 1 in 10 suspensions of barium chloride (4g of dry soil mixed with 40g of barium chloride) was mixed using a laboratory vibrator. After 72 hours, liquid and solid phases were separated by a centrifuge running at 3000 rpm. Cations of sodium, calcium, potassium and magnesium in the liquid phase were measured with an atomic absorption spectrometer (AAS-model GBC 932 AB Plus) at the geotechnics and soil mechanics laboratory of Bu Ali Sina University, Iran. The CEC was then calculated through the method described in [9] by summation of the cation values measured in the liquid phase with the help of GBC-Avenal (Ver. 1.33) software.

To prepare X-ray diffraction (XRD) samples, a scale with 0.001g accuracy was used to take 1g of dry soil from each soil sample. Each of these small samples was then inserted into 50 ml centrifuge tube and was mixed with 50ml of electrolyte (distilled water). The suspension was shaken for three hours with a laboratory shaker and was then retained for 24 hours to ensure equilibrium conditions. Afterward, the suspension was stirred for another three hours and was again retained, but this time for 120 hours, to ensure full homogeneity. The samples were then again stirred for 60 minutes. In the end, 5 to 7 drops of resulting suspension were spread on a glass slide, and once dried, was tested with an X-ray diffractometer (Siemens-Diffractometer D8 Advance). Table (1) shows some of the geotechnical and geo-environmental characteristics of samples of natural clay soil.

The interaction of the clay-metal system with cement was studied with equilibrium tests. These laboratory tests were conducted on saturated soil suspension with different concentrations of heavy metal contaminant to determine metal retention capability of samples. In these tests, first, aqueous zinc nitrate solutions ($Zn(NO_3)_2 \cdot 6(H_2O)$) in concentrations of 0.001 to 0.05 molar were prepared. 1g of dried clay sample (weighted using a scale with 0.001g accuracy) was inserted into 50 ml centrifuge tube and was then mixed with 50 ml of electrolyte (containing zinc nitrate in concentrations of 0, 5, 10, 25, 50, 100 and 250 cmol/kg-soil). The suspension was then mixed for three hours with a laboratory shaker, retained for 24 hours to reach equilibrium conditions, and was then shaken again for three hours. This process was repeated for 7 days to ensure full cation exchange and allow soil- electrolyte system to reach equilibrium. After 7 days, the clay-contaminant suspension

Table 1. Geotechnical and geoenvironmental characteristics of Nano Montmorillonite

Geoenvironmental properties of Cloisite® Na ⁺	Quantity measured
pH (1:10 ; soil : water)	10.03
Carbonate content (%)	0
Organic content (%)	6
Organic Modifier	-
Modifier Concentration	-
Surface area (m ² / kg*10 ⁻³)	525 ± 5
CEC (cmol/kg-soil) Na ⁺	47.02
Ca ⁺²	2.68
Mg ⁺²	0.58
K ⁺	0.88
Total:	51.16
X Ray Results: d ₀₀₁	11.7 Å°
Color	White
G _s	2.86
Classification	CH
Mineral composition	Montmorillonite
in decreasing abundance	-

was mixed with cement at the weight ratios of 4%, 6%, 8% and 10%. Resulting samples were retained for 14 days to allow the hydration processes to be completed and let soil-electrolyte-cement system reach equilibrium.

3. RESULTS AND DISCUSSION

3.1. Contaminant adsorption-retention characteristics obtained with the cement-based S/S process

Absorption characteristics and retention of Cloisite®Na⁺ nano clay samples and modified samples with different percentages of cement in interaction with zinc heavy metal contaminants have been presented in Figure 1. Based on the curves presented in Figure 1, nano-montmorillonite (Cloisite®Na⁺) at concentrations of 25 cmol/kg-soil has the ability to retain more than 94% of zinc heavy metal contaminants. At a concentration of 50 cmol/kg-soil, zinc heavy metal contaminants also retain about 43 cmol/kg-soil contaminants. Furthermore, nano-montmorillonite at concentrations of 100 cmol/kg-soil of zinc heavy metal contaminants has the ability to retain more than 50% concentration of zinc heavy metals. It is worth noting that at concentrations of 250 cmol/kg-soil of zinc heavy metal contaminants, about 55 cmol/kg-soil of contaminants are retained by the sample. The adsorption-retention process of this sample has been influenced by two factors of specific surface area (SSA) and cation exchange capacity (CEC).

Based on the contaminant retention capacity curve presented in Figure 1, in a nano-montmorillonite sample modified with 6% cement at concentrations of 100 cmol/kg-soil of heavy metal contaminant, 72.7% of zinc heavy metal contaminant has been retained by the sample. On the other hand, in the same sample, at concentration of 250 cmol/kg-soil, more than 38% of the contaminant was retained by a sample containing cement. It is worth noting

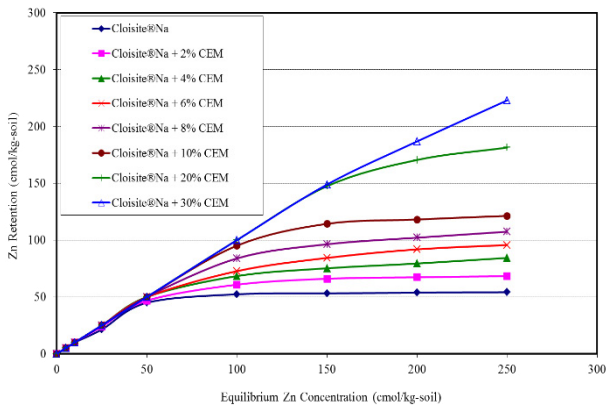


Fig. 1. Zinc retention characteristics of untreated samples and samples treated with different concentrations of cement (after 14 days of storage)

that by increasing the cement content by 10%, the amount of contaminant retention capacity at a concentration of 250 cmol/kg-soil was increased more than 123% compared with the unmodified soil sample. Based on the results presented in Figure 1, in a sample modified with 20% cement, the ability to retain zinc heavy metal contamination at a concentration of 100 cmol/kg-soil reached to 100% and at 250 cmol/kg-soil, about 181.40 cmol/kg-soil of the contaminant retention by the sample. The results show that an increase of 20% of the cement resulted in an increase in retention capacity at a concentration of 250 cmol/kg-soil 250 in comparison to the unmodified sample and the sample modified with 10% cement by 235% and 69%, respectively. Modification of nano- montmorillonite with 30% of the cement modifier has increased retention capacity at a concentration of 250 cmol/kg-soil to about 222 cmol/kg-soil. Accordingly, it seems that during the formation of cement hydration products, a part of heavy metal contaminant precipitates into crystalline hydrates (formation of CSH nanostructure) and forms the hydrated metallic silicates, and becomes fixed and non-movable.

In general, it can be stated that: 1) the ability to maintain a significant portion of the heavy metal contaminant by a Cloisite®Na⁺ nano clay sample due to the high CEC of clay nanoparticles (51.16 cmol/kg-soil) [2]; 2) stabilization and adsorption of zinc contaminant on the surface of the C-S-H and C-A-H nanostructures (high specific surface area of C-S-H nanostructure improves the adsorption characteristics); 3) pozzolanic reactions and lime released in the cement hydration process and, consequently, precipitation of zinc heavy metal contaminant and 4) zinc heavy metal solidification in the hydrated cement matrix by the formation of a CSH nanostructure, play a major role in the retention of the contaminant.

2.2. Microstructural study of the role of nano-montmorillonite in the process of stabilization and solidification

The interactions between clay, contaminant, and treatment substance affect the forces between flakes and components forming the new compounds and thereby

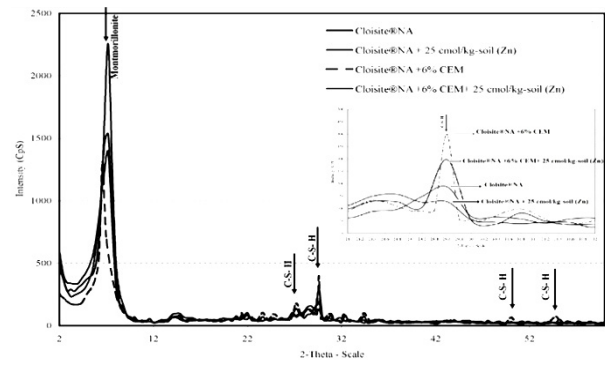


Fig. 2. X-ray diffraction plots of the uncontaminated untreated sample, the uncontaminated sample treated with 6% cement, and the sample containing 25 cmol/kg-soil of Zinc contaminant and treated with 6% cement

change the microstructure of the clay and the rate and extent of formation of new compounds. To study the effects of heavy metal contaminant on the microstructure of clay samples, a group of samples was subjected to an X-ray diffraction test. Figure 2 shows the X-ray diffraction results for uncontaminated untreated sample, the uncontaminated sample treated with 6% cement, the untreated sample containing 25 cmol/kg-soil of Zinc contaminant, and the sample containing 25 cmol/kg-soil of Zinc contaminant and treated with 6% cement. According to the results of Figure 2, with an increase in zinc concentration, the peak intensity of the major reflection line of montmorillonite has dropped from 2200 cps to 1400 cps. Based on the results presented in Fig. 1, one of the main causes of heavy metal contaminant retention in cement-modified samples is the formation of a C-S-H nanostructure and the capture of heavy metals contaminations in these crystals (solidification). Based on the results presented in Figure 2, the presence of the cement modifier compound results in the formation of new compounds and the C-S-H nanostructure ($d_{001} = 3.02 \text{ \AA}$). Based on the results presented in Figure 2, the intensity of the major peak of C-S-H crystals ($d_{001} = 3.02 \text{ \AA}$) reached about 400 cps in the Cloisite®Na⁺ nano clay sample modified with 6% cement (in the absence of contaminant). On the other hand, nano-montmorillonite (Cloisite®Na⁺) contaminated with 25 cmol/kg-soil of zinc heavy metal contamination and modified with 6% cement, the intensity of the major peak of C-S-H structure, reached about 180 cps. In fact, it can be concluded that the formation of the C-S-H nanostructure increases the retention capacity of the contaminant. On the other hand, the presence of heavy metal contamination reduces the formation of the C-S-H compounds. Moreover, the results of X-ray diffraction over time show that the presence of heavy metal contaminants has delayed the hydration process and formation of the C-S-H nanostructure.

In a nano-montmorillonite (Cloisite®Na⁺) sample modified with 6% cement at concentrations of 100 cmol/kg-soil and 250 cmol/kg-soil, no zinc heavy metal contamination was

observed on CSH nanostructured crystals. Moreover, in the Closite®Na⁺ nano clay modified with 6% cement, the peak intensity has decreased due to increased pH and solubility of montmorillonite. The similar pattern was observed for the main peak of montmorillonite. It seems that in the sample of Closite®Na⁺ nano clay modified with 6% cement, the distance between clay plates (displacement of the main peak) has increased, due to the presence of calcium ions released from the cement hydration process, which has been located between clay plate layers.

4. CONCLUSIONS

According to laboratory results obtained in this study, the following conclusions can be derived:

1) Nano-montmorillonite (Closite®Na⁺) has considerable potential for retention of contaminant due to having a higher SSA and high CEC so that at concentrations of 100 cmol/kg-soil of zinc heavy metal contaminant this soil sample can retain more than 50% of zinc heavy metal contaminant.

2) According to the results of X-ray diffraction analysis, the presence of heavy metal contaminants undermines the formation of calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H) nanostructures. For example, the result showed that the presence of zinc contaminant with a concentration of 25 cmol/kg-soil reduced the peak intensity of C-S-H nanostructure by about 1400 cps.

3) At high concentrations of contaminants, due to considerable SSA and high CEC of clay nanoparticles, on the one hand, clay nanoparticles prevent the interference of the hydration process of the binding material with the full absorption of heavy metal contaminants, and on the one hand, the change in the structure of the nanoparticles facilitates the solidification process.

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HOW TO CITE THIS ARTICLE

V.R. Ouhadi, M. Amiri, *Microstructural Evaluation of Stabilization and Solidification of Heavy Metals by Cement at the Presence of Nano Montmorillonite*, *Amirkabir J. Civil Eng.*, 52(1) (2020) 27-30.

DOI: 10.22060/ceej.2018.14654.5707

