

Cement-Based Solidification/Stabilization of Soil Contaminated by Polycyclic Aromatic Hydrocarbons Using Organophilic Clay

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Abstract

The solidification/stabilization (S/S) method is the most widely used to remediate all types of inorganic pollutants, which has not been developed for organic matters. In this research, the application of cement and organophilic clay (OC) was investigated for the S/S of contaminated soil by polycyclic aromatic hydrocarbons (PAHs). Pyrene, Acenaphthene, Benzo[a]Pyrene, and Benz[a]Anthracene were spiked in a soil specimen. X-ray diffraction analysis (XRD) indicated that OC has a considerable ability to absorb PAHs in its inter-laminar molecular spaces, unlike ordinary bentonite. Toxicity characteristic leaching procedure (TCLP) results showed that application of OC increased PAHs' removal efficiency from contaminated soil up to 80% on average compared to the use of cement only. Samples containing 30% cement and 30% OC with a 14-day curing time had the best removal efficiency. Also, the removal efficiency of heavier PAHs was lower than the lighter ones. Additionally, unconfined compressive strength (UCS) showed a linear descending by increasing OC's proportion. Scanning electron microscopy (SEM) analysis indicated that two reasons have effectively increased the PAHs' removal efficiency of solid samples: a) increasing the amount of OC that increases the PAHs absorption capacity, b) reducing the size of pores in the matrix reduces the pollutant leaching.

1. Introduction

Remediation of the contaminated soils is one of the major concerns of environmental researchers. Due to the development of oil production and its related activities, soil pollution with organic compounds such as polycyclic aromatic hydrocarbons (PAHs) is increasing globally. PAHs are highly toxic materials and have carcinogenic effects on humans. Over the past decades, petroleum processing plants have caused environmental concerns, especially the groundwater and soil contamination by oily wastes containing significant amounts of PAHs (Ma et al., 2018). Therefore, contamination control/remediation in these areas is essential. There are several methods, including bioremediation, S/S, chemical oxidation, and incineration, to remediate contaminated soil by organic materials; however sustainable methods have become more popular today (Hou and Al-Tabbaa, 2014). S/S process is one of the sustainable procedures that require low energy with less atmospheric emissions.

Furthermore, the S/S method has been successfully used in many sites contaminated by organic materials (Ma et al., 2018). In this method, a binder is applied to trap the contaminant in a solidified matrix with or without additives. Cement is one of the most popular binders. Considering the adverse effects of organic matter on cement's hydration process, finding additives to overcome such a problem is necessary (Jebeli et al., 2019). Ordinary and organophilic clays activated carbon, and synthetic compounds (e.g., fly ash and organic polymers) can use as additives to increase the efficiency of the cement hydration process (Heidarzadeh et al., 2017). Additionally, successful application of organophilic clay as a solidification adsorbent in inorganic waste containing organic content was reported (Montgomery et al., 1988).

There are several studies related to organics remediation in soil by the S/S process. Lo (1996) examined the effect of organophilic clay (OC) on removing the phenolic compounds by cement on nine solidified samples. He applied the Toxicity Characteristic Leaching Procedure (TCLP) to evaluate the pollutants leaching behavior, and the amount of cement for all samples was fixed (equal to 8%). The results indicated that adding OC increases the performance compared to pure cement. Moreover, by adding 10% OC, more than 90% of the phenolic compounds can be stabilized depending on the amount of contaminants concentration in the soil. Gitipour et al. (1997) investigated the removal efficiency of the BTEX using OC in the S/S process. This study reported that OC is 51% more efficient than ordinary bentonite in removing BTEX. Furthermore, the solidified samples by cement and OC increased the BTEX stabilization efficiency by about 55%. Cioffi et al. (2001) investigated the effect of OC on the stabilization of chloride organic matter (2-chlorophenol and 1-chloronaphthalene) in a matrix containing cement and fly ash. This research was carried out to overcome the negative effects of organics on cement hydration to improve the efficiency of the S/S process. The study results indicated that the addition of the OC significantly increases the removal efficiency and reduces 1-chlorophenol leaching more than 2-chloronaphthalene. Amini (2006) was implemented S/S on the wastes of the Qazvin Shahid Rajaee power plant in two different matrixes, including cement/waste and cement/waste/sand. In this study, no additive was used to improve the performance of stabilized samples. The results indicated that the optimal waste to cement ratio is 0.2 and 0.25 for cement/waste and cement/waste/sandy matrixes, respectively. Malviya and Chaudhary (2006) investigated the affective factors in the S/S process of hazardous wastes. This study has mainly focused on the use of cement for the S/S of the heavy metals, and it has been shown that various binders and wastes can reduce or increase the unconfined compressive strength (UCS) of the solidified sample. Al-Ansary and Al-Tabb (2007) conducted a study on the S/S of petroleum drill cuttings using Portland cement, blast-furnace slag, micro silica, hydrated lime, and manganese oxide with fly ash. The results of this study indicated that unlike the usual trend of the negative effects of organic matter on the hydration process, the petroleum waste did not have much effect on the curing characteristics of the binders. Karamalidis and Voudrias (2007) investigated on leaching behavior of the polycyclic aromatic hydrocarbons (PAHs) (16 compounds) and alkanes during the S/S of the oil refineries sludge. In this research, two types of cement, type I (Portland) and II (without any additive), were used as binders. The results indicated that adding cement can even increase the leaching of some organic pollutants, especially alkanes. Moreover, increasing the cement content does not necessarily improve process efficiency. It was also indicated that the cement type I has better performance than type II in the stabilization of some PAHs, including Anthracene, Benz(a)Anthracene, Benzo(a)Fluoranthene, Benzo(k)Fluoranthene, Benzo(a)Pyrene, and Dibenz(e,h)Anthracene. While Type II cement had a good performance for five other PAHs, including Naphthalene, Anthracene, Benzo(B)Fluoranthene, Benzo(a)Pyridine, and Dibenz(e,h)Anthracene. Mohebbi et al. (2013) solidified a soil contaminated by cresol using cement and OC. TCLP test showed the increase in OC and cement reduces cresol leaching and enhances the performance by up to 70%. Heidarzadeh et al. (2017) studied a cement-based S/S process of phenol-contaminated soil. They applied ordinary bentonite and OC as additives to reduce the negative effect of phenol on the white cement hydration process. The results revealed that the UCS is reduced by increasing the amount of clays while the leaching is declined by

increasing both clays. However, in the samples containing OC, the leaching was less than ordinary bentonite ones. Finally, a sample containing 30% white cement and 13.3% MC with a phenol removal percentage of 80 was introduced as the optimal combination. Ma et al. (2018) proposed a new method for S/S of PAHs-contaminated soil with Portland cement and activated carbon. In this method, adding 0.02% of sulfonated oil to the S/S of PAHs-contaminated soil increases the UCS to 2.3 times and decreases leaching of benzo(a)pyrene from 14–25%. Kujlu et al. (2020) studied seven large-scale oil-contaminated soil sites by three different S/S methods. In this study, Portland cement, sodium silicate, diatomaceous earth, and their combination used as binders, as well as consumed time for treatment and TPH leaching were evaluated. Their results indicated that oil-contaminated soil sites treated by the combination of Portland cement sodium silicate-diatomaceous earth had lower TPH leaching than others. Meanwhile, increasing the number of binders led to an increase in time treatment. Tayebi Jebeli and Heidarzadeh (2021) investigated the S/S method efficiency of contaminated soil by TPH in the waste of a used oil treatment plant using quick lime (binder) and OC (additive). Their results showed that quick lime could not increase the UCS of S/S wastes more than 350 kPa, but a combination of quick lime and OC fulfilled the minimum UCS required for S/S waste disposal in landfills and decreased TPH leaching by about zero.

The general purpose of the present study is to investigate the effect of using cement and OC on the efficiency of the S/S method for remediation of soil contaminated by PAHs. For this purpose, an artificially PAH-contaminated soil was prepared by spiking these hydrocarbons into clean soil. Organophilic and ordinary bentonite were used as additives to improve the efficiency of the process. After conducting the X-Ray Diffraction (XRD), the OC was selected as the best additive. Then, several samples were prepared with different proportions of cement and OC. Finally, TCLP, UCS, and scanning electron microscope (SEM) were performed for two different curing-times.

2. Materials And Methods

2.1. Materials used and samples preparation

The physical characteristics of uncontaminated soil are shown in Table 1. Uncontaminated soil was a fine-grained silty-clay soil without any PAHs. Materials used in this study were Portland cement type I, ordinary bentonite, and OC. The used OC was a product of Southern Clay Products Company, known as CLAYTONE® 40 (Southern Clay Products Inc, 2007). The physical characteristics of bentonite and OC are also presented in Table 1. As shown in Table 1, the main difference between the ordinary and OC is the moisture content and the two compounds' specific density. The OC has a lower density due to its higher organic content. The selected PAHs for soil contamination include Acenaphthene (AC), Pyrene (PY), Benz[a]anthracene (B[a]A) and Benzo[a]pyrene (B[a]P). Moreover, the two heavier PAHs (i.e., B[a]A and B[a]P) have higher adverse effects on human health than lighter ones. All solvents and chemicals were prepared by Merck Company, except Benz [a] anthracene (Aldrich Company) and Benzo [a] pyrene (FLUKA Company).

Table 1. Physical characteristics of uncontaminated soil, ordinary bentonite, and OC

Characteristic	Uncontaminated soil	
Wet density (g/cm ³)	1.9	
Dry density (g/cm ³)	1.6	
Liquid limit (%)	31.7	
Plasticity index (PI)	11.8	
Permeability (cm/s)	7.410 ⁻⁸	
Porosity (n)	0.42	
Natural soil moisture (%)	20.8	
Solid particles density (G _S) (g/cm ³)	2.7	
pH ^a	7.6	
Cation Exchange Capacity (meq/100gr)	26.8	
	Ordinary bentonite	Organophilic clay
Viscosity (cP)	7.5	Low in water, High in organic matter
Color	Light cream	Light cream
Density (g/cm ³)	2.4-2.7	1.7
CEC (meq/100gr)	95-105	95
Moisture content (%)	10	2
Loss on Ignition in 1000 °C	8.8	38.5

^a Water/Soil = 1/2.5

To prepare the PAH-contaminated soil samples, 20 mg/kg of the solid form of each compound (AC, PY, B[a]A, and B[a]P) was added to the uncontaminated soil. Thus, total PAH concentrations were equal to 80 mg/kg. Then, the contaminated soil was solidified by different ratios of cement and OC, as shown in Table 2. For this purpose, the contaminated soil samples were first mixed by OC with the ratios of 8, 15, 30 wt.% and were kept for 20 minutes at room temperature to complete stabilization (Gitipour, 1985). After that, cement was added to the mixture by 20 and 30 wt.%. Two control samples were also made without using OC and with 20 and 30 wt.% of cement. The amount of water used for making solidified samples was fixed as 33 wt.% of total solids (solid to water ratio 3:1). All samples were kept for curing times of 14 and 28 days to complete the cement hydration process,

TCLP test was conducted for all samples. Furthermore, UCS and SEM tests were only performed for the samples with 28 days curing time (Onitsuka et al., 2001; Markgraf and Horn. 2007). The samples used for the UCS test had a height to diameter ratio of 1.15 based on the ASTM D1632-17 testing procedure (U.S.EPA, 1989; Barth et al., 1989). For the XRD test, clay samples were directly inserted into the sample holder after injecting the necessary fluids and mixing them.

Table 2. Specification of samples for uncontaminated soil of S/S process with PAHs using cement and organophilic clay

Sample Name ^a	PAHs-Contaminated Soil	Organophilic clay		Cement		Water		Total Sample Dry Weight (g)
	Weight (g)	Clay to Soil ratio	Weight (g)	Cement to Soil-Clay ratio	Weight (g)	Water to Solid ratio	Weight (g)	
C20	40	0	0	0.2	8.0	0.33	15.8	48.0
C20M8	40	0.08	3.2	0.2	8.6	0.33	17.1	51.8
C20M15	40	0.15	6	0.2	9.2	0.33	18.2	55.2
C20M30	40	0.3	12	0.2	10.4	0.33	20.6	62.4
C30	40	0	0	0.3	12.0	0.33	17.2	52.0
C30M8	40	0.08	3.2	0.3	13.0	0.33	18.5	56.2
C30M15	40	0.15	6	0.3	13.8	0.33	19.7	59.8
C30M30	40	0.3	12	0.3	15.6	0.33	22.3	67.6

^a C: cement, M: organophilic clay

2.2. Experiment procedures

PAHs were analyzed based on the U.S.EPA Method 8100 (U.S.EPA, 1986) using High-Performance Liquid Chromatography (HPLC) equipment with the specifications as follows: HP 1100 series, Agilent (Agilent Technologies, Palo Alto, CA, USA) Equipped with two UV and FLD detectors, column specifications: 150 mm x 4.6 mm i.d., 5µm particle, Zorbx C8 capillary column with 20 µl sample injection rate.

To calibrate the HPLC equipment, standard solutions containing four PAHs (AC, PY, B[a]A and B[a]P) with three different concentrations (5, 10, and 50 mg/L) were injected into the device.

X-ray diffraction test was used to determine the basal interlaminar spacing of both clays after contacting them with water and organic contaminants. X-ray machine AXS D8 conducted these experiments with $\lambda = 1.54 \text{ \AA}$, Cu-Ka. The values for analyzes were from 2 to 32 degrees.

The TCLP leach test was carried out based on the U.S.EPA Method 1311 (U.S.EPA,1992), except that instead of rotary turning, a shaker was used at a rate of 30 ± 2 rpm for 18 ± 2 hours.

For the solidified samples for the UCS test, a UCS device was applied which had a maximum force of 50 kN and seven adjustable power sensitivity states. The test was conducted on the solidified samples by 0.94 mm/min power speed with a curing time of 28 days.

The SEM device used in this study was an electron microscope scan XL30 model made by Phillips Company, and Switzerland Bal-Tec company made the gold coating device. For SEM tests, the solidified samples should have dimensions of about $5 \times 5 \times 5$ mm to be connected to the base of the sample holder. The tests were also performed on the solidified samples cured for 28 days.

3. Results And Discussion

3.1. XRD analysis

The XRD analysis evaluates the basal interlaminar spacing changes of the clays. For this analysis, ordinary bentonite and pure OC were exposed to water and PAHs. The XRD results showed that the primary thickness of ordinary bentonite and OC were 12.1 angstroms and 28.6 angstroms, respectively. Ordinary bentonite thickness and OC thickness changed 76% (21.3 angstroms) and 4.5% (29.9 angstroms) in contact with water. OC thickness revealed a notable rise by 20.3% (34.4 angstroms) interacted with PAHs, while Ordinary bentonite had a slight increase in thickness by 2.5% (29.9 angstroms). Two main points can be achieved by XRD analysis. First, OC did not tend to absorb water, unlike the ordinary bentonite. In other words, there is no significant increase in the OC interlaminar spacing after its exposure to water. While the thickness increasing of OC samples exposed to PAHs was 20.3% rather than 2.5% in ordinary bentonite. This relies on the ability of the OC to absorb PAHs and to replace it in the interlaminar spacing of this clay. Thus, to improve the conditions for the absorption of PAHs, OC can be a better option than the ordinary bentonite in the S/S process.

3.2. PAHs leaching behavior of the solidified samples

The TCLP test is one of the most critical tests to determine the performance of the S/S process. The concentrations of pollutants leached out from solidified samples and a comparison of the efficiency of the stabilization process by adding different ratios of OC in two curing times of 14-day and 28-day are presented in Fig. 1. In this figure, the comparison basis was the leaching rates of OC free samples (C20 and C30 contained only cement). In other words, the leaching of the OC free samples was considered 100%. Thus, if the number was closer to zero, it indicated less leaching and then better performance.

The efficiency of the S/S process in the TCLP test can be investigated from two aspects: The first one is the leached concentration of the pollutants and the second one is the leaching difference in the solidified samples with and without OC. In all samples, the addition of OC reduces the PAHs' leaching. The leach percentage of PAHs in the OC samples ranged from 0.4% (28-day C20M30 sample for PY) to 84.1% (14-day C30M8 sample for B[a]P). The total average of the PAHs leaching percentage in the samples

containing the OC in 14-day and 28-day was about 45% and 51.5%. The removal efficiency (remove PAHs from contaminated soil) of heavier PAHs (B[a]A and B[a]P) was lower than the lighter PAHs removal efficiency (AC and PY). Among different samples, considering the total average of PAHs leaching percentage, samples of C20M15 (14-day), C30M30 (14-day), C20M30 (28-day), and C30M30 (28-day) had the best removal efficiency, with an average leaching percentage of 10.6%, 8.4%, 8.7%, and 11.7% respectively; and among the four samples mentioned, the C30M30 (14-days) sample had the lowest total PAHs leaching percentage. Additionally, the leached concentration of Anthracene and B[a]P was highest and lowest in all cases, respectively. Besides, reducing the leached concentration from lighter to heavier compounds can be observed. The reason for this is probably related to the structure of these compounds and the number and arrangement of their rings. By a simple calculation, according to Fig. 2, it can be observed that increasing the OC can logarithmically reduce the leached concentration of all types of PAHs. The logarithmic reducing pattern indicated that significant removal efficiency could be expected by adding a small amount of the OC.

3.3. Curing time effect on the contaminants leaching

As illustrated in Fig. 3 (A and B), the leached concentration changes in different curing times were investigated for all PAHs with different cement ratios (20% and 30%).

Regarding Fig. 3 (A and B), in most cases, increasing the curing time from 14 days to 28 days increases the efficiency and reduces the contaminants leaching except PY and B[a]A, which were combined with OC-free samples. In other words, OC free samples of these compounds have shown an increasing leached concentration trend by increasing the curing time. Therefore, in such samples and for these pollutants, it could not be expected that curing time increasing can improve the removal efficiency. However, in OC included samples, an increase in the curing time reduces the leached concentration.

3.4. UCS test

The UCS values of S/S samples are a major geotechnical property for its end-use. The US EPA guidelines, France and the Netherlands, UK and Canada standards suggested a minimum UCS of 350kPa, 1000 kPa, 700 kPa, and 3500 kPa at 28 days for material disposals, respectively (Interstate Technology & Regulatory Council, solidification/stabilization team, 2011; Perera et al., 2005; Spence and Shi, 2004). Fig. 4 represents the UCS changes of different samples with a curing time of 28 days with different ratios of the OC and its comparison by the minimum allowable limits suggested by different countries. As illustrated in Fig. 4, the UCS of the samples decreased by increasing the amount of OC, and a linear function can explain this reduction with determination coefficients of 90 to 92%. Moreover, all samples fulfilled the minimum allowable limits of the S/S final product according to France, the Netherlands, the United Kingdom and, the United States standards (Malviya and Chaudhary, 2006, Spence and Shi, 2004). The only exception is the Canadian standard, which has been suggested to use the final S/S products for the structural subbases rather than landfilling (Spence and Shi, 2004).

3.5. SEM analysis

The SEM images of all samples with 28 days curing time were illustrated in Fig. 5. As shown in Fig. 5, the microscopic structure of the samples is not significantly different. There are three different materials in the matrix of all samples, including contaminated soil, cement, and OC. Because of the precedence of certain phases in the images, it is not easy to distinguish them. Moreover, there are no large cracks in any samples. It means that the added OC does not have an adverse effect on the solidified matrix integrity. In some cases, like the C20, micro-cracks along several pores can be observed that there are not important. Moreover, the main cement hydration products are visible among all samples and form a dominant superimposed phase. It means that the hydration process products have not been affected by the OC or pollutants. On the other hand, the presence of cement hydration products, especially ettringite in all samples (the needle-like shapes in the images), indicates a complete hydration process, and it also shows the amount of water used to prepare the samples is appropriate.

One of the most important differences between the sample images was the presence of micro-pores in their matrix. Micro-pores can affect the leaching ability and the extracted fluid flow in the solidified matrix and its contact with the contaminants. As shown in Fig. 5, among 20% cement samples, the C20 sample had a denser structure due to the lack of OC. Among the samples containing 30% of the cement, by increasing the amount of OC, micropores increase, and then the matrix becomes looser. For example, there are almost no holes in the C30, while C30M8, C30M15, and C30M30 have many pores. The results of UCS tests mentioned before also confirm this finding.

Moreover, it seems that by increasing the amount of OC, the size of the matrix flocculation becomes gradually more extensive, and their internal linkage becomes weaker. Thereby, the presence of micro-cracks in the matrix can be expected. Thus, it can obtain an easier situation for the pore water contact with the surface of the flocculation and then dissolve the absorbed contaminants. Hence, if the solidification process is the only effective mechanism to reduce the contaminants leaching, the C30M30 sample should have more leaks than all compounds. However, the TCLP results show its lower leaching behavior. Thereby, the stabilization mechanism of contaminants created by the OC in the matrix seems to be more effective than the solidification mechanism in this case. In other words, if the effect of the stabilization mechanism is not considered, according to images of samples containing 30% cement, the rank of reduction in the leached concentration is expected to be $C30M30 > C30M15 > C30M8 > C30$. In comparison, there is no such evidence in the TCLP tests mentioned before. The leach rate of the C30 sample is more than the other samples in this group. In the C30 sample, there is no effect of the stabilization mechanism due to the lack of OC, which is a stronger mechanism. Such a conclusion could be drawn for the samples containing 20% cement due to the similarity of the pore arrangements and TCLP test results. Moreover, between two OC free samples (i.e., C20 and C30), C30 has a denser structure with fewer pores. In this case, solidification is the only predominant mechanism on the leaching behavior of the contaminants. Hence, it is expected that the C30 will have lesser contaminants leaching, which confirms the TCLP test results.

4. Discussion

The results of the XRD test indicated that the OC (organophilic clay) is more efficient than ordinary bentonite in absorbing the four desired PAHs. The efficiency of this clay for lighter aromatics is better than heavier ones. Therefore, using OC as an additive is more reasonable due to its considerable ability to stabilize PAHs in the S/S process.

TCLP test indicated that the addition of OC decreases all samples' leaching. It averagely increases the PAHs leaching efficiency up to about 80% compared to pure cement. This increase in efficiency was consistent with the increase in the percentage of OC in many cases. Meanwhile, samples containing 30% cement with 30% OC (C30M30) (at 14 days) had the best efficiency. Moreover, the removal efficiency (remove PAHs from contaminated soil) of the heavier PAHs is lower than the lighter ones for almost all OC included samples. This finding could be due to the OC type and its efficiency in absorbing various organic compounds, as well as the structure of these PAHs and the number of rings and their arrangement. In other words, more complex aromatic hydrocarbons have less leaching probably.

In most cases, increasing the curing time from 14 days to 28 days increases the removal efficiency exceptions related to PY and B[a]A in combination with OC free samples. In these cases, increasing the curing time does not necessarily reduce the PAHs leaching.

Comparing the SEM results and the TCLP test indicated that two reasons can be effective in increasing the PAHs' removal efficiency: 1) stabilization mechanism, which is the effective factor for OC included samples, and 2) solidification mechanism, which is due to applying cement for all samples. Moreover, the results of the SEM analysis confirm the UCS trends of the samples. The looser samples (i.e., OC included samples) have a lower UCS. Furthermore, the results of the UCS test indicated that increasing the amount of OC (up to 30%) will not reduce the compressive strength to an unacceptable level. Consequently, it can be concluded that the use of OC positively affects the stabilization of PAHs and improves the efficiency of the solidification process.

4.1. Future scope

It is recommended to continue further researches to answer other questions that are not considered in the present research:

1. The removal efficiency (remove PAHs from contaminated soil) of the S/S process for PAHs using other types of OCs modified by different quaternary ammonium salts (such as Hexadecyl trimethyl ammonium chloride and Trimethyl phenyl ammonium chloride) to achieve appropriate compounds.
2. As the relatively low concentration of the PAHs has been studied in the present research, research with higher contamination levels may be helpful to expand the findings.
3. The variables such as pH, temperature, and water-to-solids ratio were not studied, which can be considered in future research.
4. It is recommended that after completing the S/S study on the PAHs removal using OC, other tests were studied to evaluate the performance of this process, such as freeze/thaw, durability, and wet/dry tests.

Declarations

Competing interests

There is no conflict of interest in this paper.

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Figures

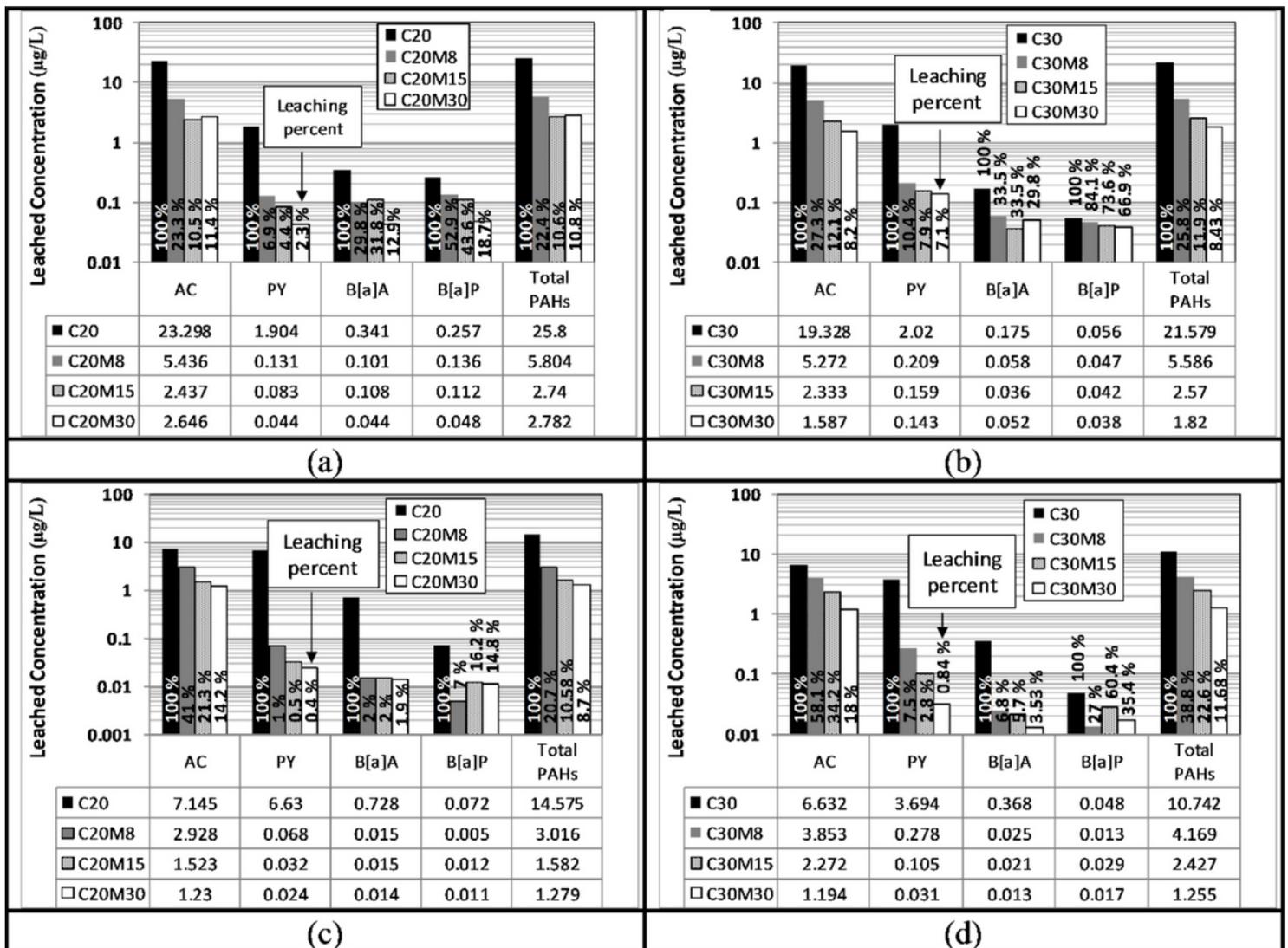


Figure 1

Comparison of PAHs leach in different samples: (a): cement=20%, curing time: 14 days; (b): cement=30%, curing time: 14 days; (c): cement=20%, curing time: 28 days; (d): cement=30%, curing time: 28 days

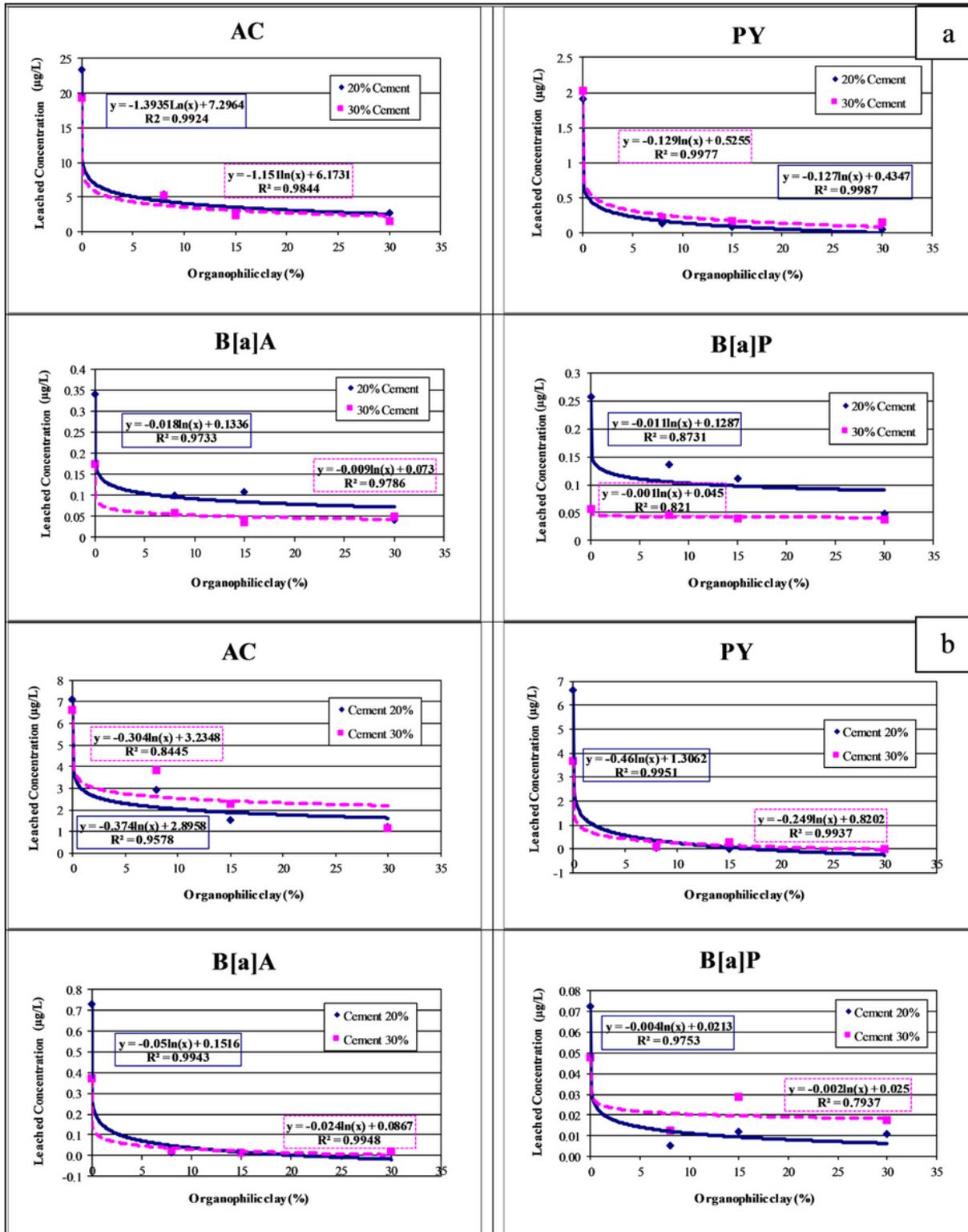


Figure 2

Mathematical equation of the PAHs leaching; a: 14-day; b: 28-day

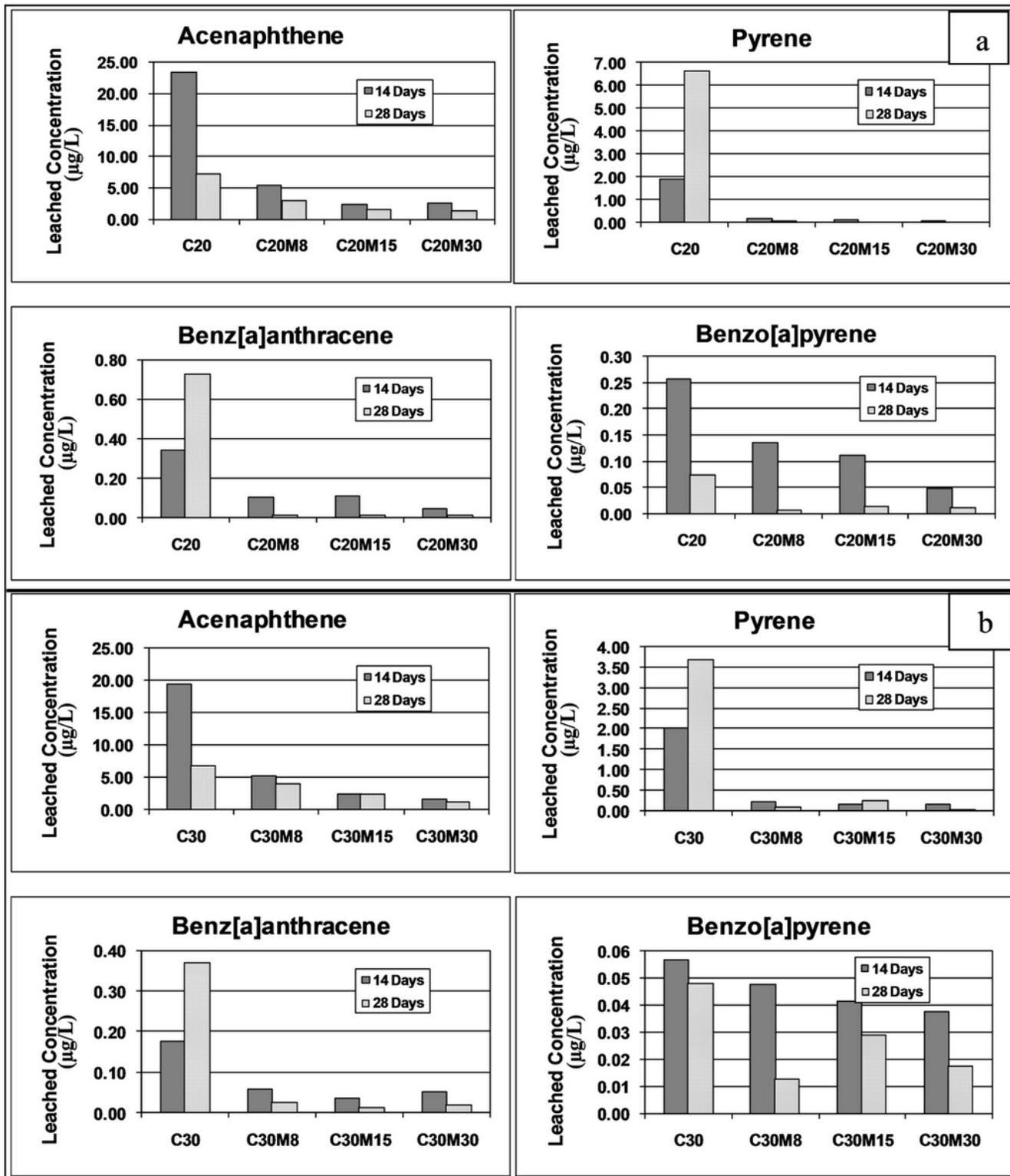


Figure 3

Comparison of the leaching of PAHs in different curing time; a: 20% cement, b; 30% cement

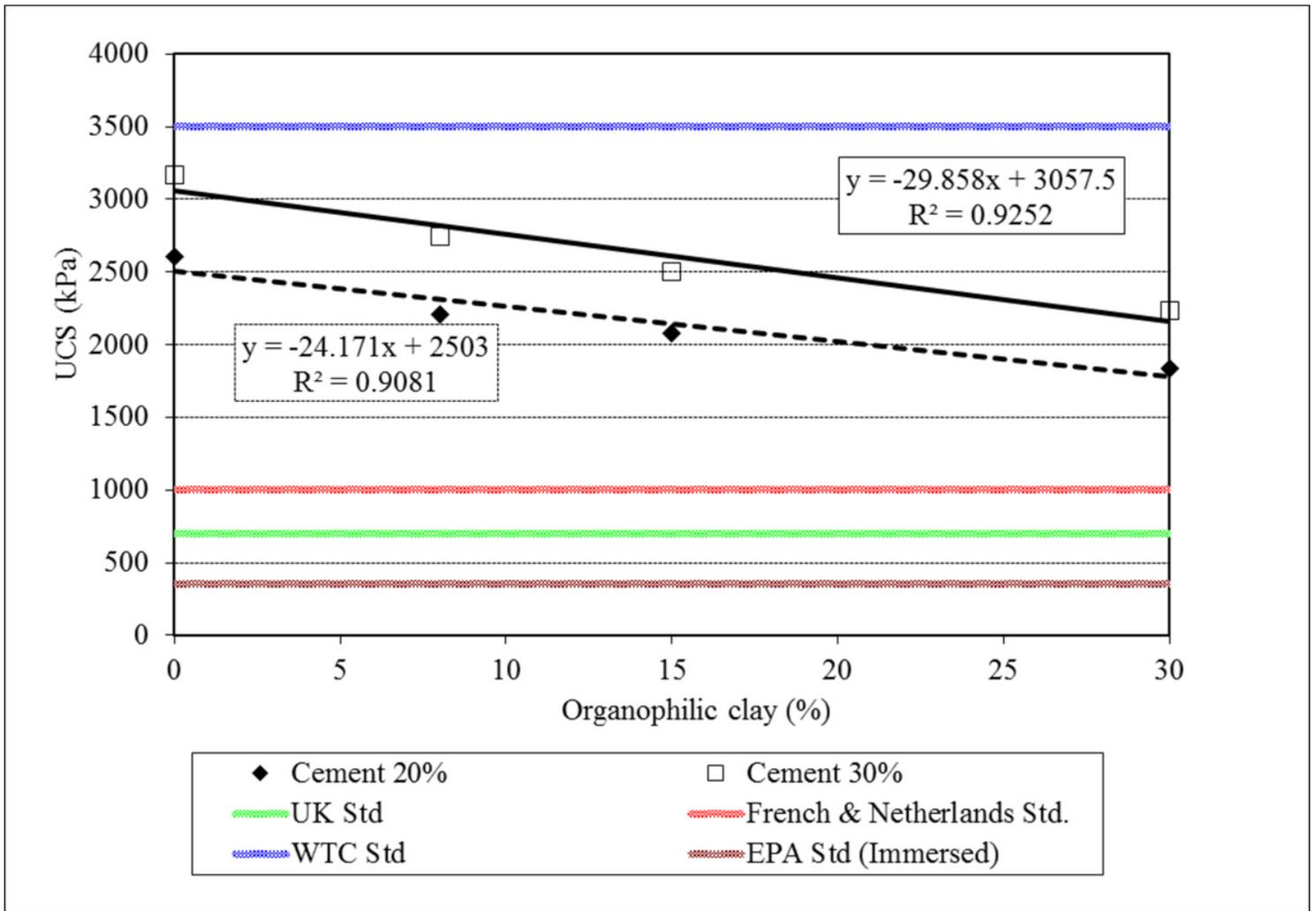


Figure 4

UCS variations with different proportions of OC (28-day curing time)

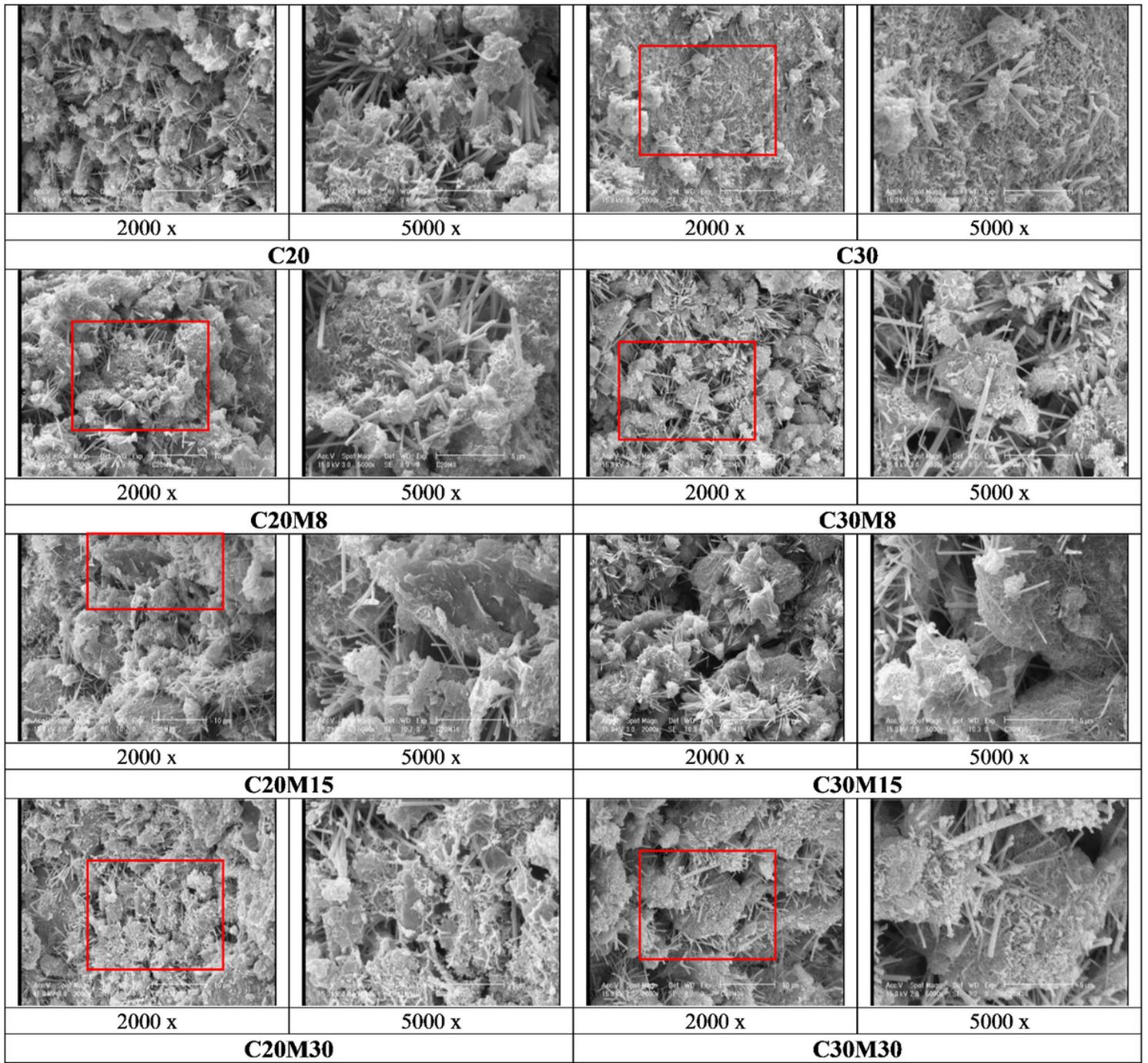


Figure 5

SEM images of the solidified samples with 28-day curing time