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Microsilica-Cement Stabilization of Organic Contaminated Soil: Leaching Behaviour of Polycyclic Aromatic Hydrocarbons

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ABSTRACT

In this study, Polycyclic Aromatic hydrocarbons (PAHs) contaminated soil were collected from Ray Petrochemical industry and treated by Solidification/Stabilization (S/S) which is an effective technique for reducing the leachability of contaminants in soils. Since organic compounds interfere with cement hydration process, S/S technology will have difficulties while trying to immobilize organic contaminants. The treatment process was conducted using Portland Cement (PC) as the main binder and Microsilica (MS) as an additive to improve the effect of PC in immobilization of organic contaminants. Specimens were divided in two groups with constant cement percentage of 25% and 35%. Each group were again divided to three subgroups with 0%, 4% and 8% of MS. The efficiency of using MS in leaching behaviour of S/S samples was assessed by toxicity characteristic leaching procedure (TCLP). Lowest leach percentage of 14.66% for total PAHs in the paste contained 25% of cement and 8% of MS were obtained. The results indicated that the presence of MS in cement pastes had positive effect on reduction in concentration of contaminant in leachate.

Key words: Sotabilisation, Solidification, TCLP, Microsilica, PAHs, Portland Cement.

INTRUDUCTION

Soil pollution is an ordinary side-effect of several industries. The oil industries is mainly responsible for soil contamination due to actions related to crude oil extraction, refineries and transfer, underground crude oil storage tanks and the wastewaters[1].

Polycyclic aromatic hydrocarbons (PAHs) are one of such above mentioned contaminants. They are hydrocarbons-organic compounds containing only carbon and hydrogen, consist of two or more benzene rings[2]. United States Environmental Protection Agency (USEPA) named 16 different compounds of PAHs as priority pollutants according to their carcinogenicity and mutagenicity at very low concentrations[3, 4].

Stabilization/Solidification (S/S) method has been widely used for treatment of heavy metals[5] and other contaminants in hazardous wastes, industrial sludges, power plant residues, municipal ashes, nuclear wastes, and contaminated soils and debris before final disposal since 20 years ago[5]. USEPA documented S/S method as the Best Demonstrated Available Technology (BDAT) for the land disposal of the majority toxic and hazardous substance [6-8]. Furthermore, it is one of the most regular remediation processes used at Superfund sites in the U.S. (about 24% of the sites applied this method between 1982 and 2002)[8, 9], and it has been known as one of the most cost effective techniques[10, 11].The stabilization stands for a process that is convert contaminants into forms that are much less mobile, soluble, and toxic[8, 11]. Additionally, solidification encapsulated the contaminants within a monolithic solid with high structural integrity[8, 11].

Since organic compounds interfere with cement hydration process, S/S technology could be run into difficulties when trying to immobilize organic contaminants[12, 13]. A possible process for improving the efficiency of S/S for organic contaminants is using binders as an additive like fly ash, modified clay, activated carbon[14]. Microsilica (MS) is a by-product of the smelting process of silicon metal and ferrosilicon alloy production[15]. It's amorphous structure, high SiO_2 content, and large surface area makes it reactive with calcium hydroxide produced by cement hydration[15-17].

The aim of this research was to analyse the effect of adding MS on leaching behaviour of high oily PAHs contaminated soil solidified and stabilized by Portland cement.

MATERIALS AND METHODS

Sampling and preparation

Soil sampling was carried out from different parts of petrochemical industry (Rey Petrochemical Industry) located in the South-East of Tehran, Iran (Figure 1).

Following collection of the samples, they were dried at room temperature for 24 hours. Subsequently soil samples moved into 1000 ml glass jars and then placed in fridge (with the temperature of 4 °C). American Society for Testing and Materials (ASTM) methods were performed to characterize the properties of soil samples[18](Table 1).

Binders

PC is most frequently used and widely studied binder. S/S with cement is widely understood and simple, is easily available and results in a stable product[19]. The PC applied in this study was obtained from Tehran Cement Factory. Other binders (activated carbon, fly ash, MS, modified clay, lime, etc.) can be partially added to PC, which can enhance or negatively affect the properties of cement in S/S[19-21].

The properties of MS are determined by the procedures it has been undergone during the manufacturing, also based on this its colour could vary from light to dark gray. The surface area of MS varies between 15,000 to 35,000 m^2/kg and its average diameter is smaller than 1 ìm and it can come in different forms of slurry, powder and condensed[22, 23]. Numerous researchers have been conducted during past years to evaluate the properties of concrete by adding MS to the cement[24-26]. Table 2 contains the Comparative Physical properties and chemical compositions of MS and PC which have been used in this study.

Its effects are related to the strength, ductility, air void content, freeze-thaw durability, permeability, shrinkage, creep rate, specific heat, abrasion resistance, coefficient of thermal expansion

Fig. 1: PAHs contaminated soil sample collected from Rey Petrochemical Industry

(CTE), chemical attack resistance, bonding strength with reinforcing steel, defect dynamics, thermal conductivity, and degree of fibre dispersion in mixes containing short microfibers[26-29].

Preparation of specimens

The various mixes and their designations in presence, absence and different ratios of MS used in this study are shown in Table 3. Specimens were divided in two groups:

- C25 with constant Portland cement percent of 25
- C35 with constant Portland cement percent of 35

Samples were transferred into the molds which have been made due to ASTM D 1633:00 method A with the Height to diameter ratio equals 1.15[18].

Testing method

The United States Environmental Protection Agency (USEPA) developed toxicity characteristic leaching procedure (TCLP) to simulate the worst possible situation for disposal of municipal solid waste and hazardous waste in a landfill and has been widely applied as a regulatory test to evaluate contamination levels[30, 31]. During last decade, the TCLP has been used extensively to test the leachability of contaminations in soils to evaluate the efficiency of contaminant immobilization[32, 33].

For conducting leaching of the crushed wastes, Method 1311 of SW-846 of the USEPA (1992) Toxicity Characteristics Leaching Procedure was used[34, 35]. Cylinders samples were crushed to less than 9.5 mm in size After 28 days of curing. Acetic acid-water solution with the pH of 2.88was used as a extraction fluid and the liquid-to-solid ratio of it was 20:1. it was added to the crushed specimens at room temperature and were rolled thoroughly for 18 hr in extraction bottles made of stainless-steel at 28 to 30 rpm. A 0.45 ìm membrane filter was used to remove suspended solid from the leachate and finally gas chromatograph with flame-ionization detector (GC-FID) and split/splitless injector were used to analyse the PAHs[35].

Table 1: Characteristics of soil samples in Ray Petrochemical Industry

Soil Properties	Value
Gravel	4.30%
Sand	69.50%
Silt & Clay	26.20%
Moisture Content	38%
pH	6.21

Table 2: Compared chemical compositions and physical properties of PC and MS

Compound	PC(%)	MS(%)
SiO_2	22.57	87.6
Al_2O_3	5.31	1.35
Fe_2O_3	3.25	0.9
SO_3	0.59	0.13
Specific Surface (m^2/Kg)	312	23500

Table 3: Mixing Ratio

Mixing code	PC/ Soil	MS/ Contaminates Soil	Contaminated Soil (gr)	W/C
$C_{25}MS_0$	0.25	0	55	0.35
$C_{25}MS_4$	0.25	0.04	55	0.35
$C_{25}MS_8$	0.25	0.08	55	0.35
$C_{35}MS_0$	0.35	0	55	0.35
$C_{35}MS_4$	0.35	0.04	55	0.35
$C_{35}MS_8$	0.35	0.08	55	0.35

RESULTS AD DISCUSSION

Leaching Behaviour

PAHs Concentrations in TCLP leachate were evaluated by GC apparatus. For analyzing the efficiency MS in S/S process, a control sample of contaminated soil without any added MS was used, and the contaminants' concentrations in leachates of solidified samples were compared to that of control samples as an index (100%). Wherever this amount is closer to zero indicates the higher solidification and stabilization prohibiting performance. Two factors of the S/S process effectiveness were investigated: (1) concentration of contaminants; and (2) effect of using MS in leachate behaviour. Table 4 and Table 5 show the results of leachate concentrations and percentages. These observations indicated that addition of MS played a significant role in decreasing the amount of leachate in S/S specimens compared to the untreated contaminated soil.

In group C25 with 4 percent MS (C25MS4), B[a]P with 22.47% was the specimen with the least leachate percentage. Whilst, in C25 specimens with the 8% MS, the least leaching percent belonged to B[a]A with amount of 6.06%. results showed that with increasing the MS content to 8% a reduction of almost 50% in average leachate percentage would be observed. Confirming the above mentioned results the 36.54 percent TPAH leachate in C25MS4 decreased to 14.66 in C25MS8.

Data from group C35 showed differences to of group C25. Although 4 percent content of MS resulted in decrease in amount of leaching, with increasing MS to 8 percent not only no improvements were observed but also there was a noticeable increase in leaching percent. This occurrence probably caused due to the fact that using MS increases the water demand of samples for hydration and using more MS defected the cement hydration process in samples[24, 36].

The relation between the contaminant's release and the MS proportion was found to have a logarithmic pattern, which is shown for different

Table 4: Relative concentration of PAHs leaching in S/S samples

Cement Percent	MS Percent	Concentration (ppm) Nap[1]	Chry[2]	B[a]A[3]	B[a]P[4]	TPH[5]
25	0	302.703	886.647	569.22	258.878	2017.448
	4	118.919	377.225	182.89	58.163	737.198
	8	58.108	175.087	34.495	28.061	295.751
35	0	286.486	852.601	536.101	232.755	1907.94
	4	52.838	143.064	53.761	22.398	282.061
	8	94.596	252.139	112.661	41.276	500.669

1. Naphtaline, 2. Chrysene, 3. Benzo[a]Anthracene, 4. Benzo[a]Pyrene,5. Total Polyaromatic Hydrocarbon

Table 5: Relative Leaching percentage of PAHs

Cement Percent	Micro silica Percent	Leachate Percentage NAP	Cry	B[a]A	B[a]P	TPH
25	0	100	100	100	100	100
	4	39.29	42.55	32.13	22.47	36.54
	8	19.2	19.75	6.06	10.84	14.66
35	0	100	100	100	100	100
	4	21.93	16.78	10.03	9.62	14.78
	8	33.02	29.57	21.01	17.73	26.24

cement mixes in Figures 2 and 3. High correlation coefficients (r2 > 0.94) indicate that a slight increase of the Micro Silica significantly reduces the concentration contaminants in leaching.

In addition, equations extracted from Figure 2and 3illustrated that increasing in cement percent in S/S samples enhanced the efficiency of removal. However, Ln coefficients in the equations demonstrated that this improvement could be considered insignificant compared to the effect of MS in leaching behaviour of solidified and stabilized samples.

CONCLUSION

All together it seems that stabilization/ solidification is a useful method for decreasing leaching from contaminated sites. S/S offers technological advantages over the alternative remedial options for contaminated soils and sediments. This method offers reduction and prevention of further movements and mobility of hazardous wastes and contaminants in the environment by physical means. While the solidification contains the pollutant in a limited space, stabilization converts the toxic compound into a less

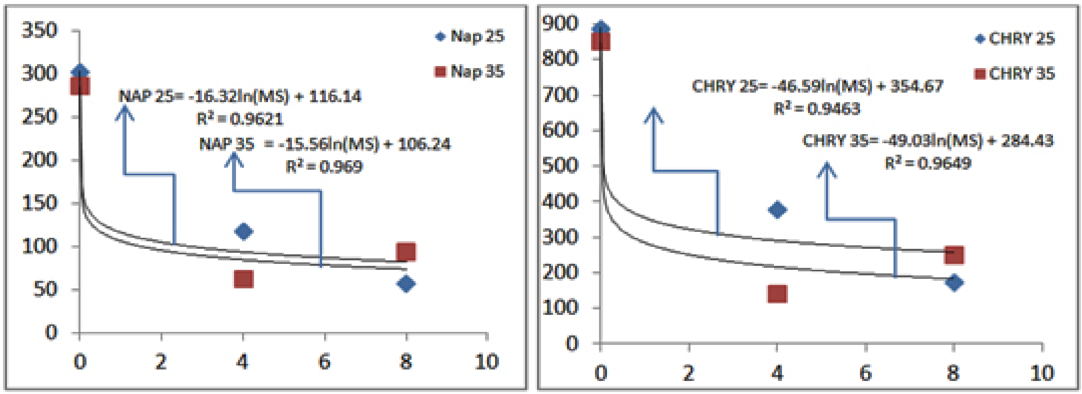

Fig. 2: logarithmic relationship between leachate and percent of Micro Silica for Naphtalin and chrysen

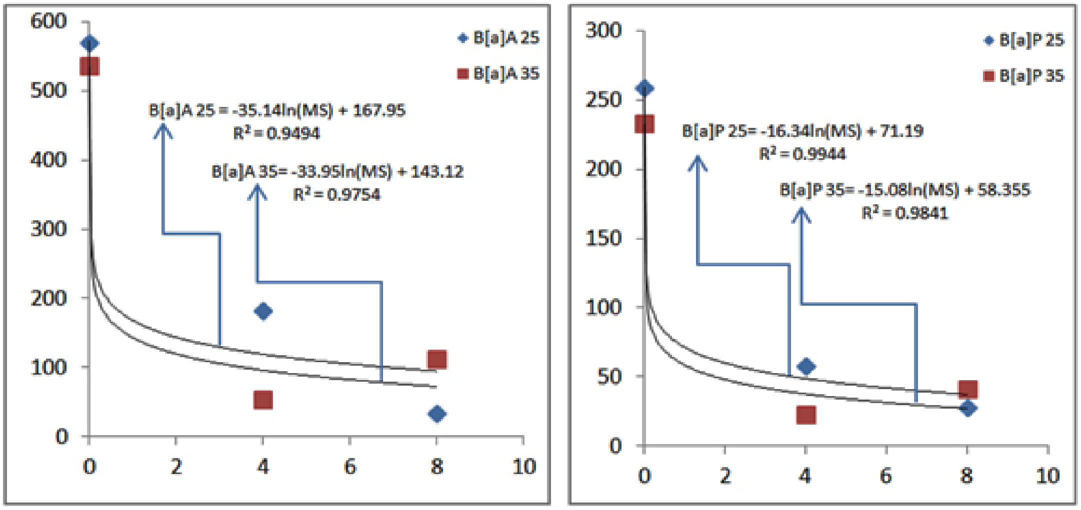

Fig. 3: relationship between leachate and percent of Micro Silica for Benzo[a]Anthracene and Benzo[a]Pyrene

toxic one. Conclusions of this study are highlighted below:

- The least contaminated leachate was related to B[a]A paste S/S by 25% cement and 8% of MS with the 6.06%
- In group C 25 increasing in MS percentage from 4% to 8% resulted in almost 50% reduction in contaminant leachability of contaminated soil.
- The TPAH leachate of the specimens S/S by 25% cement and 8% MS were lower than all of other S/S combinations
- In group C35 adding more MS posed adverse effect on leachability of contaminants in S/S samples
- Analysis of diagrams extracted from leaching data illustrated that soil S/S by 35% cement and different portions of MS had better results in immobilization of PAHs
- Equations extracted from results suggested that adding MS had more influence in S/S of the contaminated soil compared to the cement itself.

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