

Treatment of Petroleum Drill Cuttings Using Stabilization/Solidification Method by Cement and Modified Clay Mixes

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Received: 11 Dec. 2016, Revised: 31 Jan. 2017, Accepted: 14 Jan. 2017

ABSTRACT

High organic content in petroleum drill cuttings is a substantial obstacle which hinders cement hydration and subsequently decreases the clean-up efficiency of the stabilization/solidification (S/S) process. In this study, a modified clayey soil (montmorillonite with low to moderate polarity) was used as an additive to cement. Because of its high adsorption capacity, the clay is capable of mitigating the destructive role of organic materials and preventing their interference with the hydration process. Mixes containing different ratios of cement, waste and modified clay were prepared and tested for their mechanical and chemical characteristics. Total petroleum hydrocarbons (TPH) and Pb content of the samples were analyzed as well. For this purpose, the mixes were subjected to unconfined compressive strength (UCS) and toxicity characteristic leaching procedure (TCLP) tests. The results indicated that the specimens with 28-day curing time at a cement/waste ratio of 25% or higher (w/w) and 10% modified clay (w/w) met the Environmental Protection Agency (EPA) criterion for compressive strength. Moreover, a reduction of 94% in the leaching of TPH was observed with the specimens undergoing the TCLP with a cement/waste ratio of 30% (w/w) and a clay/waste ratio of 30% (w/w). Finally, the specimens with 30% cement/waste and 10% clay/waste ratios showed the least concentration (6.14%) of leached Pb.

Keywords: Drill cuttings, Stabilization/solidification, Cement, Modified clay, Lead, Organic matter

LIST of ABBREVIATIONS

S/S: Stabilization/solidification

TPH: Total petroleum hydrocarbons

UCS: Unconfined compressive strength

TCLP: Toxicity characteristic leaching procedure

EPA: Environmental Protection Agency

API: American Petroleum Institute

BDAT: Best demonstrated available technology

RCRA: Resource Conservation and Recovery Act

PC: Portland cement

GC-MS: Gas chromatography mass spectrometry

ICP-MS: Inductively coupled plasma mass spectrometry

AAS: Atomic absorption spectrophotometry

NISOC: National Iranian South Oilfields Company

ASTM: American Society for Testing and Materials

INTRODUCTION

Extensive use of natural resources has led to severe environmental pollution. During last few decades natural self-purification capacity of the environment has not been sufficient to cope with contamination problems. Fossil fuels (mainly oil) are huge resources of energy for industries. During oil exploration and extraction, a massive volume of waste or drill cutting is generated. According to a survey performed by the American Petroleum Institute (API) in 1995 (the

most recent year for which data are accessible), the accumulated volume of waste generated from crude oil and natural gas exploration and production was estimated to be approximately 140 million barrels [1]. Various methods and techniques are employed to manage drill cuttings.

One of the best known techniques to cope with the risks of hazardous waste is the stabilization/solidification (S/S) process [2], which is usually carried out prior to the conduction of other treatment

methods. This approach has been widely used since the early 1970s [3]. The Environmental Protection Agency (EPA) endorses S/S as a method by which the physical and chemical characteristics of waste and its handling are improved and the mobility, solubility, and toxicity of contaminants are mitigated [4]. The EPA has also reported that the S/S method was used in the treatment of 22% of Superfund sites from 1982 through 2005 [5]. Lack of related studies and high volume of such wastes necessitated an experimental research to investigate the feasibility of S/S process and results.

In addition, this method has been identified by the EPA as the best demonstrated available technology (BDAT) to clean up 57 types of Resource Conservation and Recovery Act (RCRA) listed hazardous waste [6]. The technique has also been employed to remediate soil contaminated with heavy metals and to immobilize organic pollutants in soil, sediment and waste [7,8].

S/S involves the use of various inorganic binders, including cement, lime, clay, fly ash, silica fume, and other pozzolanic materials [9]. The method may also use organic materials such as bitumen products, epoxy, and resins [10]. It was reported that 94% of Superfund sites were treated using inorganic binders [5].

Cement has been approved to be the most applicable binder for conventional S/S treatments owing to its low cost and huge availability [11,12]. Cement has also been the most studied material for the S/S of heavy metals and many experimental and modeling studies have been performed to assess its efficacy [4,7,13].

However, the process of cement hydration has been reported to be hindered mainly by high organic content in waste mass and this consequently decreases the clean-up efficiency of S/S [14,15]. To cope with the problem, S/S can be employed in combination with such techniques as bioaugmentation, washing and oxidation [8,16,17]. Alternatively, the method may be optimized by using additives with high absorbability to organic matter [18]. Various additives have been studied and reported to improve cement-based S/S [15]. In a study by Wang *et al.*, conventional and novel binders were compared from physical and chemical perspectives after 1.5-year of service. Ground granulated blast furnace slag, Portland cement (PC) and pulverized fuel ash strikingly improved strength development and immobility of heavy metals as well as total organics [18]. Because of their high absorbability to organic substances [12], clayey materials are also proposed as an alternative to boost the S/S of high-organic waste [19].

After the S/S process, the end product needs to pass tests such as leaching, wet/dry, freezing/thawing, and strength tests to make certain that the requirements are met [10].

Numerous studies have evaluated the parameters effective in the S/S of waste containing heavy metals and organic substances. Cioffi *et al.* investigated the cement-based S/S treatment of chloro-organics using bentonite in cement-blast furnace slag matrices. They found that although the strength of bentonite-containing specimens did not improve, it was in an acceptable range [20]. Katsioti *et al.* employed bentonite/cement mortar for the S/S of high-organic sludge and confirmed the feasibility of using clay as a viable additive because of its high capacity to adsorb organic substances [15]. In 2006, Malviya and Chaudhary reviewed factors affecting the S/S treatment and came up with unconfined compressive strength (UCS), hydration, carbonation, and pore structure as the most prominent parameters. Focusing on UCS, they concluded that cement content and curing time are the key factors contributing to strength development [4].

The present study was conducted with the dual aim of investigating the potential use of modified clay as an additive to PC and also exploring the compatibility between PC and clay in the S/S treatment of drill cuttings. The objective necessitated varying the mix design (PC/clay, water/binder ratios, etc.), assessing leachability based on the toxicity characteristic leaching procedure (TCLP), and analyzing leachate contaminants using gas chromatography mass spectrometry (GC-MS), inductively coupled plasma mass spectrometry (ICP-MS), and atomic absorption spectrophotometry (AAS). Additionally, the UCS of specimens was tested to assess compliance of mechanical properties with the EPA requirements. In addition, lead poisoning has been identified as one of the most prominent hazards. Whether inhaled or swallowed, lead entails serious risks to human beings and animals. It badly damages brain and the nervous system even at low exposure levels. Renal function is also affected by lead [7,21,22]. Because of the serious environmental and health hazards caused by lead poisoning, the present study observed lead before and after the S/S process and measured lead and petroleum hydrocarbon so as to evaluate the effectiveness of the process.

MATERIALS AND METHODS

Characterization of the waste

The waste used in the study was supplied by the National Iranian South Oilfields Company (NISOC), extracted from a depth of 3525 m, well No. 463 under oil rig No. 84 (Meraj) in Ahvaz, Khuzestan

Province. The drilling fluid was oil-based. The waste samples were then prepared for measuring initial concentrations of TPH and metals. Concentrations of heavy metals and organic compounds in waste mass are presented in Tables 1 and 2, respectively. Data for

Table 1: Concentrations of heavy metals in waste mass and TCLP regulatory levels

Element	Concentration (mg/l)	Regulatory Level ^a (mg/l)	Element	Concentration (mg/l)	Regulatory Level ^a (mg/l)
Silver	2.5	5.0	Sodium	157000	-
Aluminum	505	-	Molybdenum	1.8	-
Arsenic	6.5	5	Lithium	2.7	-
Barium	340	100	Manganese	90	-
Beryllium	<0.5	-	Lead	310	5
Cadmium	<0.5	1	Selenium	<1	1
Cobalt	0.6	-	Strontium	330	-
Magnesium	3700	-	Titanium	505	-
Chromium	6	5	Zinc	85	-
Copper	120	-	Vanadium	2.5	-
Iron	7760	-	Yttrium	0.68	-
Potassium	405	-			

a) Reference: [23].

As can be seen in Table 2, the organic compounds were mostly petroleum hydrocarbons, and evaluation of the characteristics of their leachates after the S/S process can be used in the assessment of the efficacy of the process. The GC-MS results revealed the high initial content of petroleum hydrocarbons in the waste mass (150,000 mg/kg). Considering the high concentration of organic hydrocarbons, a potential solution was to recover these materials, but it was not economical to do so.

Table 2: Mean percentages of organic compounds in drill cuttings (wet mud)

Organic compound	Percentage w/w	(%)
Decane	1.9	
Undecane	4.6	
Dodecane	6.9	
7-methyl-tridecane	3.0	
Tridecane	8.5	
2,6,10,14-tetramethyl-hexadecane	2.0	
Tetradecane	8.4	
Pentadecane	8.7	
2,6-dimethyl-naphthalene	2.7	
Hexadecane	9.7	
Trimethylnaphthalene	1.1	
Heptadecane	7.2	
Octadecane	5.8	
Nonadecane	5.6	
2,6-dimethyl-heptadecane	3.3	
Eicosane	4.1	

Binders used in the study

Ordinary Portland cement (OPC Type I 42,5) and modified clay were used as binders in the S/S application. The clay (Claytone® 40) was modified montmorillonite with a low to moderate polarity and was procured to be used in aliphatic systems where the solution is aromatic or aromatic-aliphatic. The

heavy metals and organic compounds were obtained via ICP-MS and GC-MS.

According to metal concentrations and regulatory levels in Table 1, lead and barium posed the most critical risk.

physical properties of this traditional organoclay are provided in Table 3.

There has been an increase in the use of clay minerals because of their high cation exchange capacity, swelling capacity, high specific surface area which causes strong adsorption capacity [19,24,25].

Table 3: Physical properties of the modified clay used in the study

Property	Value
Viscosity	Very low (in water) Very high (in organic matter)
Color	Cream
Specific gravity (gr/cm ³)	1.7
Cation-exchange capacity (meq+/100g)	95
Moisture content (%)	2

Preparation of specimens

Optimum mixture ratios were determined in order to achieve desirable strength, absorption of contaminants in waste, and economical efficacy. The samples with cement/waste ratios of 20, 25, and 30% and also the clay/waste ratios of 10, 20, and 30% were tested. All mixes were prepared by combining waste and binders in the amounts and ratios listed in Table 4. The water/solid ratio was constant (0.2) in all the pastes and was based on observations of various pastes, their compressibility and absence of free water.

Once they were completely mixed using a high-speed stirrer for 5 to 10 minutes, the pastes were allowed to be consolidated for 15 to 20 minutes and were then transferred into the molds. Afterwards, they were cured for 28 days in 100% moisture. The samples were prepared according to American Society for Testing and Materials (ASTM) D1633, method A [26].

Table 4:- Nomenclature and components of the specimens

Specimen	Waste (gr)	M-clay (gr)	Cement (gr)	Water (gr)	Clay/cement	Waste/binder	Water/cement	Water/binder
C20	140	0	28	33.6	0	5	1.2	1.2
C25	135	0	33.75	33.75	0	4	1	1
C30	130	0	39	33.8	0	3.33	0.87	0.87
C20-M10	140	14	28	36.4	0.5	3.33	1.3	0.87
C20-M20	130	26	26	36.4	1	2.5	1.4	0.7
C20-M30	110	33	22	33	1.5	2	1.5	0.6
C25-M10	110	11	27.5	29.7	0.4	2.86	1.08	0.77
C25-M20	110	22	27.5	31.9	0.8	2.22	1.16	0.64
C25-M30	100	30	25	31	1.2	1.82	1.24	0.56
C30-M30	90	9	27	25.2	0.33	2.5	0.93	0.7
C30-M30	90	18	27	27	0.67	2	1	0.6
C30-M30	80	24	24	25.6	1	1.67	1.07	0.53

Assessment methods

Unconfined compressive strength

The TCLP was performed on solidified/stabilized samples in compliance with the EPA method 1311 [27]. The output liquids of the TCLP on 25 specimens (24 stabilized specimens and one control specimen) were used to measure TPH and lead contents

The gas chromatography-mass spectrometry (GC-MS) analysis has been conducted as a reliable tool to measure TPHs [28]. The analysis was carried out on 25 samples (24 stabilized specimens and one control specimen). Moreover, ICP-MS analysis was performed to measure lead in non-stabilized samples. Also atomic absorption spectrophotometry analysis was carried out on liquid samples extracted from stabilized specimens to present lead content in the samples.

RESULTS AND DISCUSSION

Unconfined compressive strength test results

Organic matter causes delayed hydration of cement. To encounter this destructive effect, clayey materials were used in this study as adsorbents following the proposition in the literature [29,30]. Fig. 1 demonstrates the compressive strength of stabilized/solidified mixes after 28 days. It can be seen that adding cement to the paste improves strength. Moreover, at a given amount of cement, modified clay exhibited an appropriate improving effect. The corresponding values for pastes C20-M30, C25-M30 and C30-M30 were 39.87, 75.1 and 156.58 psi, respectively. Hence, adding 5% cement in the presence of 30% modified clay outstandingly doubles compressive strength.

For stabilized/solidified waste samples, the EPA minimum of 28-day compressive strength is 50 psi [31]. As can be observed in Fig. 1, pastes with 25% cement which contain at least 10% modified clay fulfilled the EPA criterion. Furthermore, higher

cement content caused higher strength in all the cases and clay showed a striking positive effect, particularly in the presence of 30% cement. The figure also demonstrates that for all the samples, the strength of modified clay/waste mixes after solidification increased in the order of 30%>25%>20%, respectively.

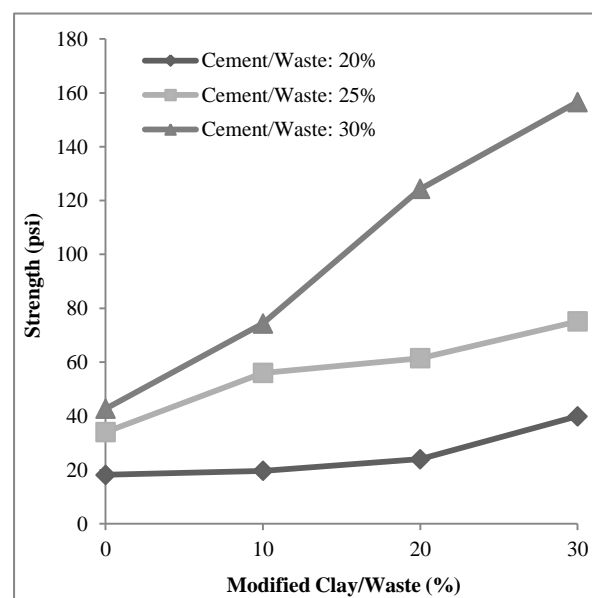


Fig. 1: The 28-day compressive strength of stabilized/solidified mixes

Results of leachate assessments

As explained in Materials and Methods, the GC-MS analysis was designed to measure TPH in 25 specimens (24 stabilized specimens and one control specimen). The GC-MS results revealed concentrations of hydrocarbons in the extracted leachate. This amount was assumed 100% and other stabilized/solidified specimens were compared to it. For other samples, their concentrations were

compared accordingly to obtain leached hydrocarbons in the non-stabilized condition. Lastly, the hydrocarbon concentration of each specimen was divided by the concentration in the non-stabilized condition in order to calculate the relative percentage of leached hydrocarbons which is shown in Fig. 2

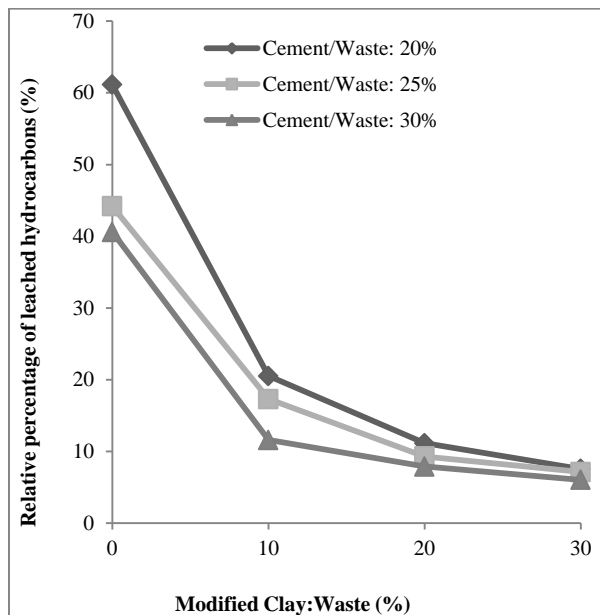


Fig. 2: Relative percentage of leached hydrocarbons for stabilized/solidified specimens

The AAS results presented lead concentration in the leached liquid. As it was calculated for hydrocarbons, concentration of each specimen was compared to the concentration in the non-stabilized condition and the relative percentage of leached lead was achieved. The percentages are compared in Fig. 3.

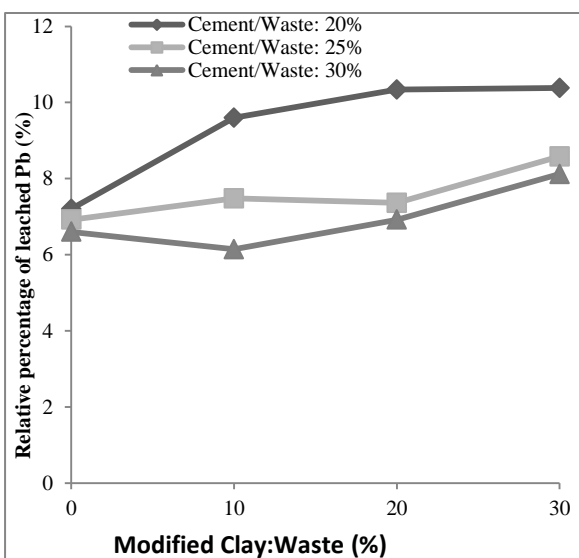


Fig.3: Relative percentage of leached Pb for stabilized/solidified specimens

CONCLUSION

This study investigated the clean-up efficiency of S/S technique while modified clay is used to mitigate the destructive role of organic materials and prevent their interference with the hydration process. Mixes containing different ratios of cement, waste and modified clay were prepared. Mechanical and chemical characteristics of the specimens were assessed. Based on the results from UCS tests, mixes with 25% cement and 10% (and higher) modified clay satisfied the EPA criterion for 28-day cured samples. Moreover, higher cement content caused higher strength. Additionally, adding modified clay in the presence of 30% cement showed a striking positive effect. The results can be ascribed to the high adsorption capacity of modified clay. Its capability to adsorb organic matter results in improved cement hydration and consequently increased sample strength [15]. Waste mixes with 25% cement and 10% clay proved to be the most economical samples in the research and also met the requirements set by the USEPA.

The leaching rate of control specimens (zero cement and clay content) was regarded as the control leaching rate, with which stabilized/solidified specimens were compared. Higher content of modified clay caused a lower rate of leaching. Comparing all results from leachate behavior tests indicated that specimens with 30% cement and 30% clay showed an impressive performance (with 94% reduction in TPH content). Accordingly, landfilling of the stabilized/solidified waste poses much lower risks to the environment.

In addition, the lead content of leached samples was measured in the stabilized/solidified specimens and was compared with control specimens (i.e., those without cement and clay). The results showed that at a given content of clay, more cement content lowers the leaching rate. Conversely, adding clay to a given amount of cement does not necessarily reduce the rate of leaching. Specimens with 30% cement and 10% clay showed the largest decrease (93.86%) in the concentration of the leached Pb. All of the stabilized/solidified specimens met the Pb regulatory level.

ETHICAL ISSUES

Ethical issues have been observed by the authors.

CONFLICT OF INTEREST

The authors have declared no conflict of interest.

AUTHORS' CONTRIBUTION

Conception or design of the work and data collection was done by Hamed Hedayati. Drafting the article and critical revision was implemented by Soroush Ghasemi. Gitipour's comments in all stages, specifically on design of the work and also final approval of the paper, were highly helpful.

FUNDING/ SUPPORTS

The project was funded by the authors.

ACKNOWLEDGEMENT

The authors would like to appreciate the priceless suggestions of the reviewers.

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