Journal of Engineering and Sustainable Development
Vol. 21, No. 6, November 2017
ISSN 2520-0917
www.jeasd.org

THE STRENGH AND LEACHING BEHAVIOUR OF SCRAP METAL CONTAMINATED SOILS USING CEMENTITIOUS MATERIALS

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Abstract: Solidification / stabilization is one of the most efficient technologies to restrict the leaching of heavy metals. Two stabilizers had been used as solidifying / stabilizing cementitious materials. Cement adjusted by clinker kiln dust were used as cementitious materials. The contaminated soil has been collected on a scrap site located in a residential area located 15 km south of Baghdad. Depending on the structure of metal analysis indicated that the highest metals existing in the soil were aluminium (6865 mg/kg), iron (30120 mg/kg), copper (175 mg/kg), zinc (560 mg/kg), lead (320 mg/kg). The unconfined compressive strength, Toxicity Characteristic Leaching Procedure (TCLP) and Scanning Electron Microscopy (SEM) were applied to estimate the efficiency of the treatment process. The results of the treatment were compared with the criteria for the admission of solidified waste, that were created on the basis of the regulatory limit on the disposal of waste at a disposal site in the United Kingdom, and the maximum concentration of toxicity contaminants, which is characteristic of Solid waste from the US Environmental Protection Agency(USEPA). The results showed that high alkalies in clinker kiln dust increase cement setting and hydration and increased compressive strength of cement. Therefore, dust high alkali altered cement reduces the discharge of heavy metals and increases the compressive strength of the waste form by the solidification / stabilization process.

Keywords: *Solidification, stabilization, leaching, contamination, OPC, TCLP, Heavy metals*

سلوك المقاومة والرشح للترب الملوثة بمعادن السكراب باستعمال مواد سمنتية

الخلاصة : التصلب / الاستقرار هي واحدة من التقنيات الأكثر فعالية لشل حركة الغسل للمعادن الثقيلة.تم استخدام اثنين من الموادالسمنتية. وهي الأسمنت البورتلاندي العادي (OPC) وغبار الافران المعدل. تم جمع التربة الملوثة من ساحة الخردة في منطقة سكنية تقع في 15 كم الى الجنوب من بغداد. وأشار تحليل التركيبة المعدنية الى المعادن الرئيسية الموجودة في التربة وهي الألمنيوم (6865 ملغ / كلغ)، الحديد (30120 ملغ / كلغ)، والنحاس (175 ملغ / كلغ) والزنك (560 ملغ / كلغ) والرصاص (320 ملغ / كلغ). تم تقييم فعالية العلاج عن طريق أداء قوة الضغط غير المحصورة (UCSواجراء الترشيح (TCLP) فحص المجهر الالكتروني (SEM). وتمت مقارنة نتائج العلاج للمعايير قبول النفايات المتصلبة التي تم تجميعها على أساس حدود التخلص من النفايات التنظيمي في موقع التخلص منها في المملكة المتحدة والحد الأقصى للتركيز الملوثات للخاصية سمية النفايات الصلبة من وكالة حماية البيئة في الولايات المتحدة. وأشارت النتائج إلى أن القلوية العالية في غبار افران الكلنكر تؤدي الى تسارع تعجيل عملية اماهة السمنت وزيادة قوة الضغط.لذلك نستنتج ان القلوية العالية للسمنت المعدل بغبار الكلنكر يؤدي الى تقليل نسبة غسل المعادن الثقيلة وزيادة مقاومة الانضغاط للتربة الملوثة من خلال عملية التصلب والتثبيت.

1. Introduction

The existence of contaminated soils is a concern in many countries. Thus, a disposal of chemical contamination has become one of the major problems currently faced by most of these countries. This has consequently led to increasing pressures on governments to urgently enact new legislation for the control and disposal of such waste [9].

The United Nations of Environmental Program at July 2004, received a plan to "support environmental governance in Iraq through environmental valuation and capability building". This mission has been reinforced by the UN Trust Fund for Iraq through funds made available by the Government of Japan. One of the most important elements of the project was to be able to assess the elimination of contaminated sites in Iraq, in cooperation with the Ministry of the Environment of Iraq (Moen).

This ministry selects five sites for priority assessment. The sites were mostly in the industrial area around Baghdad. This has been deteriorate, due to looting or in an ecological condition, fire, conflict or poor operating practices. These sites have been selected as a case study for the present research; it was scrapped Ouireej military grounds.

Ouireej is a scheduled residential area located 15 km south of Baghdad, in 2003 was awarded as one of the highest dumping and processing sites of military waste. So, this site contains a multiplicity of scrap metal, like a structural bar of steel, and metal structures of branch vehicles. It is also to be noted that these areas are uncovered, so it be exposed to the open channels of air. Accordingly, the contamination of vertical rainwater through metal poles and soil generalized contamination of groundwater [21].

Hence, various techniques, in situ and ex situ, have been used which aimed to reduce the impact of these metals on the soil. Furthermore, the main objective of these processes was either to modify the path from the source or to inhibit negative effects in the future [14, 17, and 18]. Disposal methods that are currently available as well as on-going research include spreading, dehydration and disposal in landfills; encapsulation and burial; in addition to stabilization and disposal on land or in landfills [6].

With regards to excavation, replacing contaminated soil with high quality soil imposed significant costs on construction projects. In addition, this may involve only the excavation and relocation the contaminants from one site to another but the trace of elements cannot be destroyed. Therefore, it is not always possible, in many cases, especially with the huge areas of contamination due to its high costs.

Hence, stabilization/solidification, as an alternative and convenient technique that is less environmentally hazardous, has been applied. It is one of the obvious advantages of choosing stabilization/solidification compared to other soil remediation techniques are its cost effectiveness means, relatively quickly and the ability to use this technology through in-situ and ex-situ. This method includes the use of chemicals and emulsions as auxiliary soil compactors as binders and water-repellents that modify soil behaviour and are more appropriate and efficient [6 and 4]. This technique allows to quickly find applications in contaminated soil remediation because of its economically effective way to reduce the leaching of hazardous components of waste landfilled [2].

However, Chemical stabilization of S / S treatment is generally distinct as a reduced chemical mobility modification technique so that the solubility of the contaminants present in the waste or soil to translate these waste or single layers form a chemically inert.. Thus, and due to these chemical stabilization treatments, the contaminated soil can produce a high-strength end product that can be reused as building constituents.

Ordinary Portland cement is the greatest commonly utilized as a stabilizer in stabilization technique. Many preparations have been created for the process S / S, depending on the variation of waste, heavy metals, etc. Therefore, Portland cement can be altered for this process using appropriate ash, lime, slag, solid silicates, clay, etc. [7].

It should be noted that the chemical alterations that occur as a result of the interaction between the components of the binder waste and solidification play an important role in monitoring the quality of solidified cement-based waste. Numerous studies have determined that obstruction and in some cases hindrance of cement hydration reactions have been derived from the addition of stabilized waste comprising heavy metals [5].

In resent search, O.P.C and another kind of OPC improved by C.K.D enclosing high alkali sulfate salts were used for S/S process. The development of contaminant strength and metal soluble properties has been studied to assess the quality of solidified wastes.

Leaching analysis was also applied in this study to monitor the mobility of heavy metals from cured contaminated soil samples into the surrounding environment by observing changes in heavy metal concentrations over time. This was specifically done to evaluate the effectiveness of both cement and clinker kiln dust binders on heavy metal stabilization. Leaching assays provide sufficient data on time dependent stabilizer effects that successfully prevent contaminant release to the environment. Different factors such as pH, environment, heavy metal adsorption, surface area, and heavy metal solubility all affect the utility of stabilizers.

All specimens have been dried in air, which was done to carefully simulate the situations of scrap metal zone. Physico-mechanical characteristics of the modified materials have been studied. In addition, the realization of S / S cementitious process materials, heavy metals leaching tests and the development of the compression strength of the waste have also been calculated.

2. Materials and methods

2.1. *Materials*

The contaminated soil was selected from the scrap metal yard located at 15 km south of Baghdad. For cement materials used in this study, as indicated above, OPC cement and CKD modified they were used. The chemical compositions of the OPC and CKD are specified in Table 1.The C.K.D indications extremely altitude alkali contents, 10.1 wt.% K_2O and 0.68 wt.% Na_2O, and high Sulfate content, 7.1 wt.%. The alkalies be as alkali sulfates, for example K_2SO_4 and Na_2SO_4.

Table 1: Chemical compositions of the two cementitious materials

The cementitious	Al_2O_3	SiO_2	Fe_2O_3	MgO	CaO	SO_3	Na_2O	K_2O
Ordinary Portland Cement(%)	5.6	22.1	3.4	3.1	60.8	1.8	0.16	0.6
Clinker Kiln Dust(%)	4.8	11.2	2.6	1.8	40.1	7.1	0.68	10.1

2.2. *Characterization of contaminated soil*

Table (2) presents the physical properties, it can be noted that the properties such as particle density, moisture content, soil pH, and granulomere distribution satisfied according to ASTM. The soil has been absorbed with acid by the 3050.b method preceding to the induction-induced plasma chemical analysis of OPTIMA 3000 optical emission spectrometry (ICP-OES) Perkin-Elmer induced

Table 2: The physical properties of contaminated soil(ASTM)

Item	*Value*
G.S	2.37
L.L	34.8
P.L	17.6
P.I	17.2
MDD	1.64
OMC	16.4
Clay%	27.2
Silt%	42.7
Sand%	30.1
Classified	CI

The result of the heavy metal analysis can be summarized at table 3 below

Table 3: The chemical properties of soil(the results of heavy metals concentration)

The heavy metals	*The concentration (mg/kg)*
Fe	30120
Al	6865
Zn	560
Cu	175
Pb	320

It should be noted that the high of iron concentration is due to the existence of. steel bars of construction that were the major type of scrap kept at the site.

2.3. *Sampling of contaminated soil*

All of laboratory equipment and sampling are pre-soaked in a solution of nitric acid at 5% which be followed with "distilled water" for a day before sampling to exclude concentrations of metals trace.

Contaminated samples of soil. They were taken to a depth of 20 cm from the surface with a stainless spatula and kept in cylindrical plastic containers. Based on the visual assessment, the color of soil was dark, and comprises variation of fragmented metal pieces. Plant residues and metal pieces.

They were thrown manually from samples of contaminated soil. Firstly, triturate the soil into small pieces then dried for 24 hours under solar heat air. Then, It was milled using a rod mill with a sieve of 2 mm for the microencapsulation process well. Substrate sludge digested with concentrated nitric acid, and then, heavy metals concentrations were analyzed by plasma atomic emission spectrometry (ICPAES).

The cement was added with. the contaminated soil was dissected in the. mixer and standardized for 15 minutes before adding water. It is necessary to ensure that the addition of water. cement and soil were able to create a combination with a flow rate of 10% using a K-slump tester according to ASTM C 1362-97. Waste sampling for testing. the compressive and leaching test was converted into a 5 × 5 × 5cm mold and treated at 20 ± 38 ° C. with 70% RH.

In this study, the leaching test was achieved following a procedure which was slightly adapted from TCLP method. Deionized water (pH= 6.8) was used as a leachate. The cured samples that were tested in the compressive strength test were ground and the core of each sample was ground to reduce the particle size to less than 9.5 mm.. Then 40 g was sampled and mixed with the leachate, which was added at the solid liquid ratio of 1:8 by weight, and then transferred to the batch mixer equipment on (Six-Unit Synch Auto Rise and Full Mechanical Stirrer) for 24 hr. and filtered. filter paper No. 5. IR spectroscopy was used to measure heavy metals in a filtered solution. Clinker kiln dust and conventional Portland cement were used as cement components in the study, as hown in Table 4.

Table 4: The mixture ratios of the Cementitious materials*

Criteria	*Acceptance Levels*
Compressive Strength at 28 days (N/mm^2)	0.34
"Leachability"	Cd:1
	Cr :5
	Pb : 5
	Cu : 10
	Zn : 10

2.4. *Acceptance Criteria of Solidified Materials*

Acceptance standards for hardened wastes were used to assess the effectiveness of stabilization / solidification. These standards were collected and applied to assess chemical stabilization. because of the inadequacy of soil and groundwater principles. as well as standard standards for cleaning solidified waste in most countries. Unconfined compressive strength and leaching capacity were two characteristic characteristics for the evaluation of treated soils. This is due to their key metrics measured for the success of S / S treatment in the United States, as shown in Table 5 [19].

It should be noted that the stages of UCS control and washing. have been removed from two bases; waste disposal. the limitation of the burial site in the United Kingdom [11] and the maximum concentration of pollutants for toxic properties. solid waste from the United States. Security agency [20].

It should be noted that acceptable levels of polishing of iron and aluminum are not listed because metals are perceived by authorities to be relatively less toxic than those listed.

Table 5: The acceptance criteria of solidified materials

Specimens	*Ordinary Portland Cement(O.P.C)*	*Clinker Kiln Dust (C.K.D)*
S1	100	0
S2	90	10
S3	80	20
S4	70	30

3. Results and Discussions

3.1. *Strength Development*

The unconfined compressive strength of cementitious materials is shown in Figure 1. As shown in this figure, it can notice the compressive strength development of sample S3 (70% OPC + 30% CKD) shows higher strength than that of controlled S1, and others samples especially at the late curing time. While, it shows lower strength at the early age compared with that of the controlled cement samples.

However, the higher strength at the late age was due to the presence of 30% of clinker kiln dust which encompasses high "alkali sulfates" (K_2SO_4 and Na_2SO_4). Thus, alkali metal sulphates accelerate the hydration of cement, leading to rapid installation and quick vulcanization of cement materials. These results were consistent with [8]. In addition, Singh et al. The 1995 report also found that "the addition of alkaline bypass dust has increased. Hydration, reduced porosity in the cured structure and better compression strength for OPC cement and sealed blade cement".

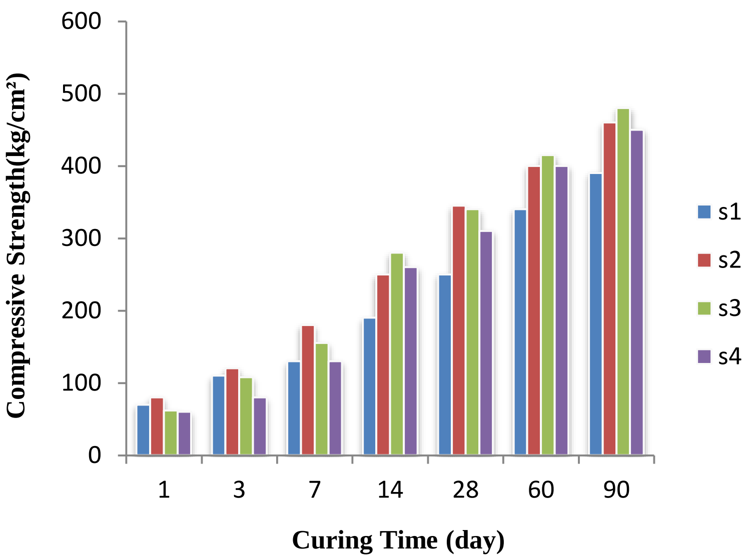

Fig. 1 The development of cementitious materials for unconfined compressive strength

3.2. *Microstructural Properties*

SEM micrographs of the two cementitious materials are shown in Fig.(2). As can be noticed, Figure (2a) shows the morphology of S1 (100% OPC + 0% CKD) at 1 days. While, Figure (2b,c,d) related to the morphology of S2,S3, and S4 respectively with the presence of clinker kiln dust at 1 day also. In Figure 2, it can detect the ettringite phase due to producing $4CaO.3Al_2O_3.SO_3$ and $CaSO_4$ causing in the formation and progress of ettringite at primary time of hydration. For S2, S3, and S4 and since they encompass high alkalies from clinker kiln dust enhanced the hydration of tricalcium silicate at initial Hydration time, calcium Silicate hydrate (C-S-H) and portlandite $Ca(OH)_2$ were molded much more than O.P.C at S1[16].

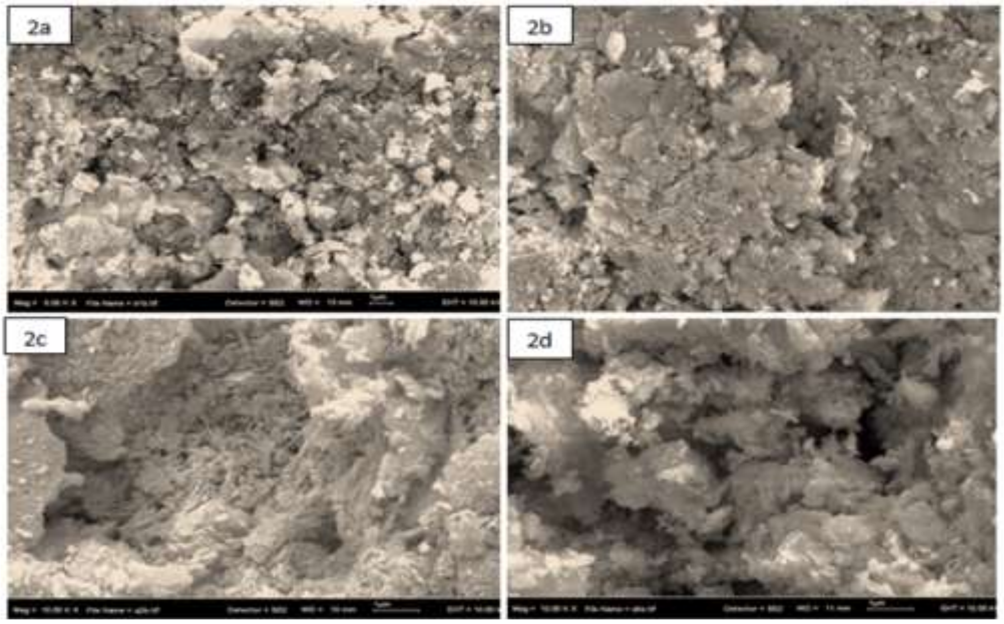

Fig. 2 Scanning Electron Microscope (SEM) of two cementitious materials for the S1, S2, S3, and S4 at 1 days

3.3. *Leaching Development*

Regarding to the leaching outcomes of T.C.L.P of the heavy metals (Al, Fe, Cu, Pb, and Zn beside to the two cementitious). It can be seen that the filtered metal ions have decreased with the polymerization time as shown (FIGS. 3-7). For the concentrations of the heavy metals for (Al, Fe, Cu and Pb) spilled from solidified samples were lower than O.P.C for all curing time.

These results are due to the existence of clinker dust, the large absorption surface of heavy and high-alkaline metals that accelerate hydration ions, leading to the creation of the amount of hydration product, high solfumed high specific calcium hydrate CSH surface, Heavy metal ions and chemical stabilization [3].

For Zn S / S, as shown in the figure, the concentration of Zn was not measured because the samples were cured 1 day. Various researchers have studied the effects of heavy metals on the hydration of cement [12, 15, 22, and 13]. The cement hydration is delayed in the existence of Zn, Pb and Cu as stated by Tashiro [17]. The inhibitory effect of Zn, Pb and Cu on the hydration of cement was associated with the formation of double salts that are formed between these heavy metals and calcined calcium ions [9].

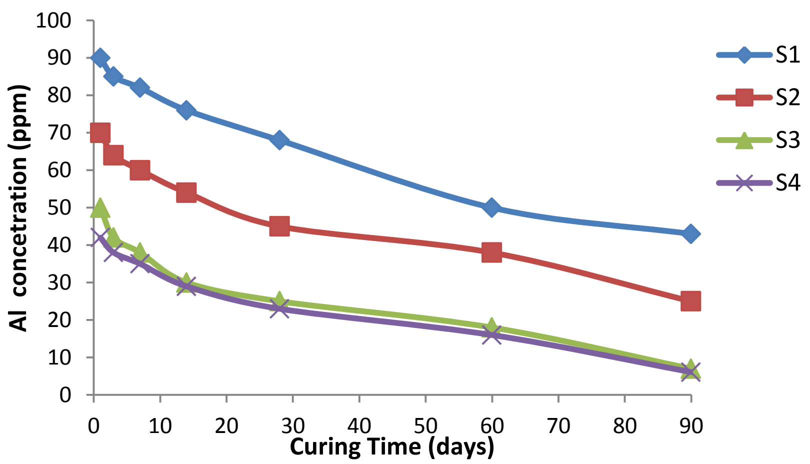

Fig. 3 The samples of two cementitious materials as a function of curing time for (Al) ion concentration leached

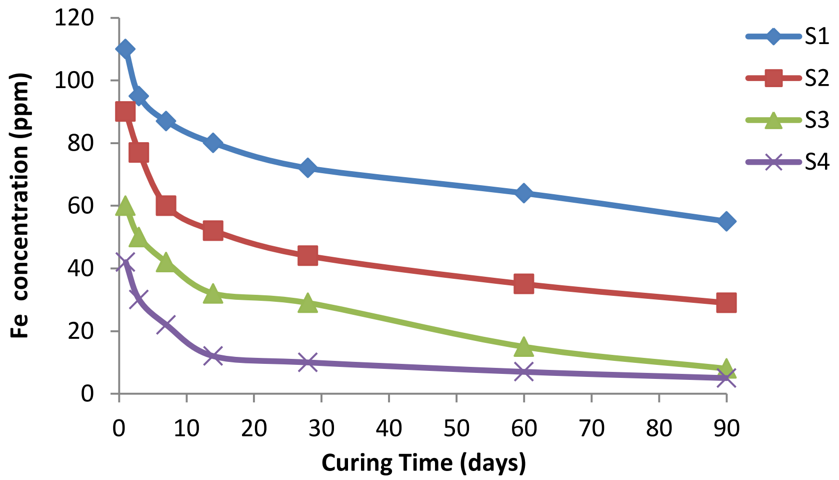

Fig 4. The samples of two cementitious materials as a function of curing time for (Fe) concentration leached

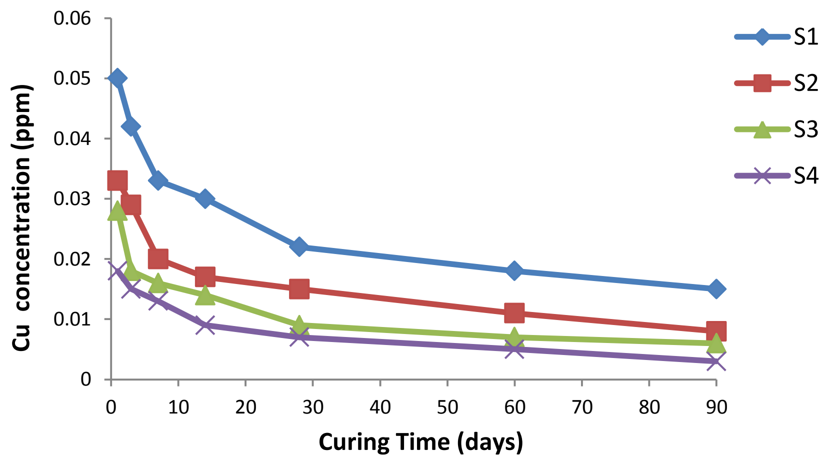

Fig. 5 The samples of the two cementitious as a function of curing time for (Cu) concentration leached

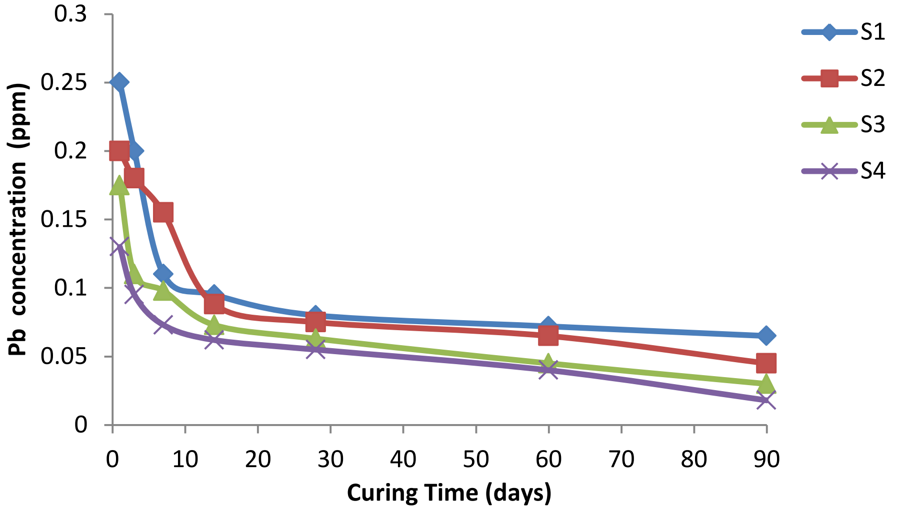

Fig .6 The samples of the two cementitious as a function of curing time for (Pb) concentration leached

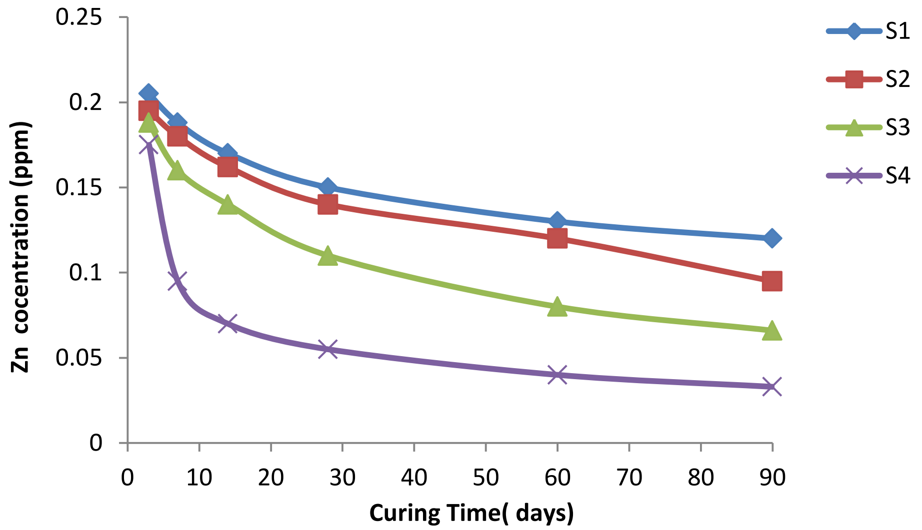

Fig. 7 The samples of the two cementitious as a function of curing time for (Zn) concentration leached

4. Concolusions

The addition of clinker kiln dust with different percentages (10% , 20% and 30%) to OPC have investigated the hydration and S/S effects of adjusted cementitious materials, and then conclusions can be achieved.

1. The high alkali for the presence of Clinker Oven (CKD) powder has led to accelerating hydration of cement to early hydration, which has the effect of quickly creating and strengthening waste. The material modified by the cement of the "CKD" had a high resistance up to 90 days without interruption during healing in air and showed a high surface area on the OPC. Cement-modified cementitious materials generated ettringite and Ca (OH) $_2$ as the main hydrates at the beginning of the hydration and $C_3A.CaCO_312H_2O$ after 7 days of curing. Q.S.A also increased to

primary hydration and formed a very well-crystallized ettringite. Heavy metal ions that have been leaked from pastes of modified cemented materials are lower to those of the OPC. In the solidification and stabilization of dust from waste collected in the scrap yard, the alkalis raised in "CKD" quicken the cement materials hydration, leading to a development of greater resistance. However, it can be established that "CKD" adjusted cementitious materials represent the greatest active influence for the heavy metals fixation, in particular waste comprising heavy metals.

2. According to the acceptance criteria. for stabilized landfills, UCS values (28-day samples) exceeded the minimum discharge limit of 0.34 N / mm2 at a disposal site in the United Kingdom. In addition, the leaching results of the metals are significantly below the suggested leaching criteria. Consequently, it can be concluded that modified OPCs from clinker dust have been effective in reducing the degradability of metals from contaminated soils to regulatory levels

5. References

1. American Society of Testing and Materials.(2000). "*Annual book of ASTM standards, section four: Construction*", Vol. 04.01. C 1362-97.
2. Cheng K.Y. (1991). "*Controlling mechanisms of metals release from cement-based waste form in acetic acid solution*". PhD thesis, University of Cincinnati, USA, p. 4–20.
3. Cullinane, M.J., Jones, L.W. and Malone, P.G. (1986). "*Handbook for stabilization/ solidification of hazardous waste Hazardous Waste Eng. Research Lab*". USEPA, Washington, DC, p. 102.
4. Ganjidoust, H., Hassani, A. and Ashkiki, A. R. (2009). "*Cement-Based Solidication/Stabilization of Heavy Metal Contaminated Soils with the Objective of Achieving High Compressive Strength for the Final Matrix*". Journal of Scientia Iranica. Vol. 16, No. 2, pp. 107-115.
5. Hills, C.D., Sollar, C.J. and Perry, R. (1993). "*Ordinary Portland cement based solidication: the role of OPC reviewed*", Cement and Concrete Research, 23, pp.196-212.
6. Musta, B. B. (2003). "*Effect of Leaching on Lime Stabilized Contaminated Soil and Mining Waste. Doctor Philosophy*". University Technology Malaysia, Skudi.
7. Mayers, T. E. and Eappi, M. E. (1992). "*Laboratory evaluation of stabilization/solidification technology for reducing the mobility of heavy metals in New Bedford Harbor superfund site sediment Stabilization of Hazardous Radioactive and Mixed Wastes*". 2nd edn. ASTM publication, Philadelphia, PA, 1992, p. 304.
8. Park, C. K. (1999). "*Hydration and solidification of hazardous wastes containing heavy metals using modified cementitious materials*". Journal of Cement and Concrete Research. 30, 429-435.
9. Saeed, K. A. H (2014). "*The physicochemical characterization of lime and cement stabilized clayey soils contaminated by heavy metals*". UTM. Ph.D:Thesis.

10. Singh, N. B., Bhattacharjee, K. N. and Shukla, A. K. (1995). "*Effect of alkali bypass dust on the hydration of granulated blast furnace slag blended cemen*". Cement Concreate Research 25 (4) 883-895.
11. Sollars CJ, Perry R.(1989). "*Cement-based stabilization of wastes: practical and theoretical considerations*". Journal of the Institution of Water and Environmental Management,3:125–32.
12. Shively,W., P. Bishop,P., D. Gress, D. and Brown,T.(1986). "*Leaching test of heavy metals stabilized with portland cement*". J Water Pollut Control Fed 58 (3) 234± 245.
13. Saeed, K. A., Kassim, K, A. , and Eisazadeh, A.(2012). "*Interferences of Cement Based- Solidification/Stabilization and Heavy Metals: A Review*". Journal of EJGE. Vol. 17 ,PP:2555- 2565.
14. Shi C, and Spence R(2004). "*Designing of cement-based formula for solidification/stabilisation of hazardous, radioactive, and mixed wastes*". Crit Rev Environ Sci Technol;34: 391–417.
15. Tashiro, C., Takahashi, H., Kanaya, M., Hirakida, I. and Yoshida, R.(1977). "*Hardening properties of cement mortar adding heav metal copmand and solubility of heavy metal from hardened morta*". Cement Concrete Research. 7(3),283-290.
16. Taylor, H.F.W. (1990). "*Cement Chemistry Academic Press*", New York, pp. 195-337.
17. U S. Environmental Protection Agency (USEPA) (1999). "*Solidification /stabilization resource guide*".EPA542-B-99-002, Adapted from http://www.epa.gow/.
18. U. S. Environmental Protection Agency (USEPA) (2004). "*Treatment technologies for site cleanup: Annual status report (11th E.)*", EPA542-R-03-009, Adapted from http://www.epa.gov/.
19. United States Environmental Protection Agency(2000). "*Solidification/stabilization use at superfund sites 2000*", EPA-542-R-00-010, p. 7.
20. United States Environmental Protection Agency. (1994). Method 1312: "*synthetic precipitation leaching procedure*" . SW-846.
21. Yin, C. Y., Shaaban, M. G. and Mahmud, H. B. (2007). "*Chemical stabilization of scrap metal yard contaminated soil using ordinary Portland cement: Strength and leachability aspects*". Building and Environment. 42,794-802.
22. Youn, J. H., Jeong, B. G. Lee, H. M. Chung, H.-S. and Park,C. (1995). "*Immobilization of heavy metals using ordinary portland cement and lime± rice husk ash*". J Korean Solid Wastes Eng Soc 12 (5) (1995) 645- 653.