Toxicity Leaching Characteristics of Cement Based Stabilized / Solidified sands Contaminated with Heavy Metals

Asst. Prof. Dr. Shahlaa E. Ebrahim
Prof. Abbas H. Sulaymon
Basim A. Hussain

Abstract

EPA Toxicity Leaching Procedure TCLP method 1313 was carried out to test the effectiveness , performance and efficiency of the solidification / stabilization treatment of five different heavy metals contaminated sands using ordinary locally produced Portland Cement type A . Three mix designs were performed on the contaminated sands at three different pollution loads and concentrations . Results showed that using (3: 1: 0.5) Sand-Cement-Water Mix ratio is very effective in retaining heavy metal contamination . Effective retention percentages of (95 , 94.1 , 97.7 , 93.3 and 94) for Cr , Cd , Cu , Ni and Pb ions respectively was obtained even when the inertial contamination load with those ions exceeded 3000 mg / kg . Particle size had a significant influence on the amount of metals leached during the extraction process. Particles with sizes above 9.5 mm showed a better effectiveness in holding and retaining metals within the Solidified / stabilized matrix. Samples with low cement mix treatments were not able to maintain the required TCLP regulatory limits for samples contaminated with Chromium, Cadmium and lead . Although the inertial extraction fluid was at pH 4.9 the final leached extractions recorded pH values above 9.5 which demonstrates the alkanet and stabilization effect of the cement matrix.

Key words: Solidification / Stabilization; Heavy Metals; TCLP; Toxicity.

1. Introduction

Solidification / Stabilization (S/S) is an attractive treatment technique for wastes contaminated with inorganic compounds .This remediation and treatment method is capable of reducing the mobility of the polluted contaminants so that they do not move through the environment . Cement based (S/S) technology currently provide a very promising solution for the disposal and remediation of polluted soils with heavy metals. In Iraq and in many other developing countries it has become an urgent and important requirement to search for proper disposal methods that is acceptable from both economic and social standpoints. Many studies have proven that industrial and municipal waste disposal sites has shown evidence of pollution escape. The release of wastes into the environment has an adversely effect on the well-being of life and also pose a permanent danger to the hydrologic cycle and the food chain [4] .

Immobilization technologies such as solidification / stabilization (S/S) can have a lot of potentials in the treatment and remediation of various types of domestic, industrial and agricultural wastes such as garbage, sledges, solids, liquids, fertilizers and even nuclear wastes. This promising technology uses the addition of a binding regent to encapsulate and reduce the mobility of hazardous waste elements [5] . Solidification / stabilization (S/S) is one of the major methods applied in hazardous waste treatment prior to land disposal .It has an effective lechability reduction for contaminated soils [3] . Moreover the U.S Environmental Protection Agency (EPA) has identified (S/S) as the best demonstrated available technology for 57 RCRA (Resource Conservation and Recovery Act) -listed hazardous wastes [9] .

Heavy Metal polluted soils and sediments could be treated by cement-based Solidification / Stabilization (S/S) technology through a number of mechanisms such as , Sorption (Physical and chemical adsorption), Complexation , and Precipitation [11] .

The rapid water-Cement reactions generate three main products : Hydrated Calcium Silicates (C_2SH_x , C_3S_2 H_x) Known by calcium Silicate Hydrate gels (C-S-H) , Hydrated Calcium aluminates (C_3AH_x , C_4AH_x) and Hydrated Lime Ca(OH) . The action rate of pure cement phases usually can be arranged in the increasing order [1] .

$$C_3A > C_3S \sim CA > C_4AF > C_2S.$$

As a result of those reactions and the formation of the primary products above , the cement particles binds the adjacent grains together and form a harden Skelton Matrix .This matrix enclosed the soil particles . Moreover the cement hydration process results in a raise in the pore water pH due to the dissociation of the hydrated lime . The strong based solution formed directly reacts with the soil silica and soil alumina strong acid . This reaction will gradually produce insoluble compounds (**Secondary Cementitiouse products**) that play a big role in the stabilization of soil .

This study focuses on the cement Solidification / stabilization (S/S) and leaching characteristics of five different synthetic prepared heavy metal wastes (Cd , Cr , Cu , Pb and Ni).

The main objectives of this study include:

- Determine the mobility of inorganic analytes from cement based solidified sands polluted with heavy metals at different mix design ratios .
- To determine the potential for toxic constituent release by leaching from waste matrix under management scenarios.

- Evaluation the Toxicity Characteristics of the leaching solutions and compare them with disposal allowable limitations.
- Studying the possibility of using an Iraqi local produced Portland Cement (Type **I**) to produce a solid stable mix to contain and capsulate heavy metals polluted sands.
- Making an assessment for this treatment and remediation method for the disposal , beneficial use and treatment effectiveness .

3. Experimental Work.

3.1 Materials and Method

3.1.1 Preparations of contaminated sand samples.

The sand used in this experiment is collected from a barrow bit located at the city of KARBALLA.

This sand is classified as a type (A) construction sand . The stock sand samples was washed with tap water and left to sundry for one week before being sieved to match the particle size distribution shown in **Figure 1** . Sand was selected to represent the contaminated media with heavy metals due to its low adsorption characteristics .This represents the worst case scenarios of contaminated sediments and soils . Heavy Metal ions were prepared from standard metal salts to form the liquid solutions of 10,000 ppm concentration using the standard procedure . **Table 1** Illustrates the characteristics of those metal ions used in this study .

The concentrated heavy metals reagents were then sprinkled on calculated amounts of weighted sand samples to obtain contamination concentrations of 500 , 1500 and 3000 mg/kg . The contaminated samples were then mixed manually for five minutes for homogeneity and left to dry to be then used to prepare the cement based solidified specimens .

3.1.2 Mixing procedure and Specimens preparations .

Solidification / Stabilization was performed according to the ordinary cement paste mixing procedure ASTM C305.Metal Oxides contaminated Sand , Ordinarily Portland cement type (A) with specifications listed in **Table 2** and water were mixed in a vessel at different mix ratios (7 , 15 and 25 % by weight) . A high water to cement ration (0.5) was employed to get an appreciable amount of contaminant release within the experimental time frame . The mix was then casted in Poly (Vinyl Chloride) plastic cylinders of size 5 cm diameter and height of 10 cm with flat Perspex endplates . Specimens were then de - molded , raped with wet tissues and left to cure for 28 days before being tested .

3.1.3 Experimental Design .

The leachate characteristics and performance of Cement - based solidified specimens were tested using TCLP standard leaching test procedures (**EPA Method 1311**) . The experiments were carried out for five heavy metals pollutants at three contamination loads . Three different mix design were applied and tested for S/S effectiveness . **Table (3)** shows the experimental design used in this study .

3.1.4 Measurement of Leaching properties .

Toxicity Characteristics leaching procedure TCLP (EPA test Method 1311) was applied in this study to express and evaluate the leachability characteristics of the cement based solidified / stabilized samples .

The TCLP tests can determine the mobility of inorganic analytes present in solid or solidified wastes . The test is done by using an extraction fluid of tap water acidified with HCL acid to obtain a pH of 4.9 . This simulates what happens to waste materials inside landfills for a period of many years. The Toxicity Characteristics leaching procedure is the only leaching procedure specified by regulation for characterizing the hazardous waste Toxicity Characteristics [2] .

EPA testing method 1311 helps in assessing the potential of a contaminated material impacts on groundwater , and surrounding soil when exposed to normal landfill circumstances . After Specimens curing period , The samples were crushed , sieved to pass 9.5 mm mesh , weight to obtain a 100 gram specimen, mixed with the standard prepared 4.9 pH extraction fluid and left for top to bottom 18 hour agitation at 30 rmp (Rounds per minute) .

Two 100 g weigh samples were taken from the crushed and sieved samples . The first for particles passing the 9.5 mm mesh and the other for the remaining particles .

After the agitation period , the test tubes were left to settle , the solid were separated from the extraction fluids , and finally the extraction fluids were collected , filtered and taken for laboratory analysis .

Figure 2 (a , b , c and d) show the cement based solidified / Stabilized heavy metal contaminated samples , experimental apparatus and extraction bottles and the agitation extraction devise used respectively .

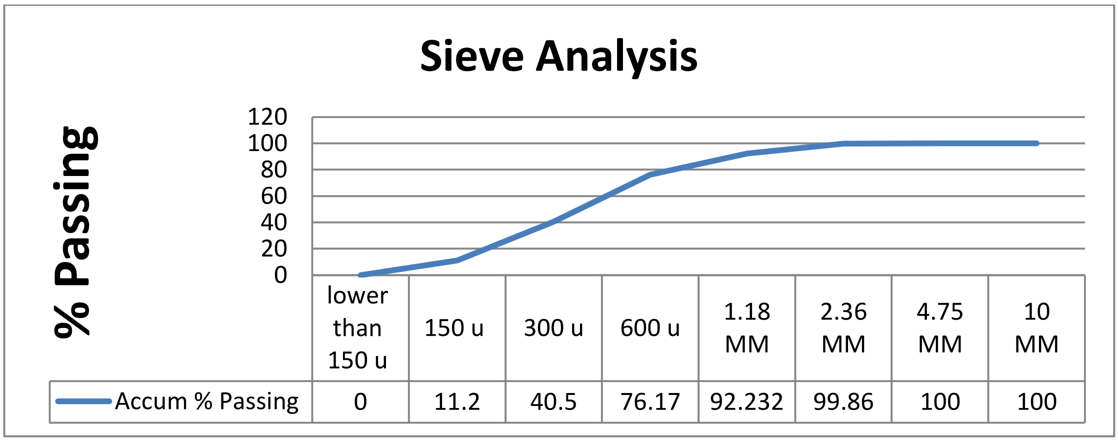

Fig.1 Sieve analysis for the Heavy metals contaminated sands Used in the study

Table 1. Characteristics of the Heavy Metal Ions

Metal salt	M.W*	Chemical Solution Formula
Nickel nitrate	290.81	Ni SO_4 .6H_2O
Copper Sulphate Hepta hydrate	249.69	Cu.SO_4 . 5H_2O
Cadimium Sulphate	208.4	Cd.SO_4
Lead Nitrate	331.2	Pb .(NO_3)$_2$
Chromium Chloride Hexa hydrate	266.48	Cr.Cl_3 .6H_2O

* **M.W** Molecular Weight

Table 2. Cement Chemical Specifications

Content	Result
Alumnae Total Content %	6.42
Magnesium Oxide Concentration %	3.13
Sulfate content SO_3 %	2.38
Total non dissolved materials %	1.02
Loss due to ignition %	3.65
Tar total Content %	0.96

Table 3. Experimental Matrix

Heavy Metals			TCLP test METHOD 1311 Particle Size	
Contamination Load Mg/Kg		Mix Design	Particle size <9.5 mm	Particle size >9.5 mm
Cd	500mg/Kg	M1,M2,M3	*	*
	1500 mg/Kg	M1,M2,M3	*	*
	3000 mg/Kg	M1,M2,M3	*	*
Cu	500mg/Kg	M1,M2,M3	*	*
	1500 mg/Kg	M1,M2,M3	*	*
	3000 mg/Kg	M1,M2,M3	*	*
Cr	500mg/Kg	M1,M2,M3	*	*
	1500 mg/Kg	M1,M2,M3	*	*
	3000 mg/Kg	M1,M2,M3	*	*
pb	500mg/Kg	M1,M2,M3	*	*
	1500 mg/Kg	M1,M2,M3	*	*
	3000 mg/Kg	M1,M2,M3	*	*
Ni	500mg/Kg	M1,M2,M3	*	*
	1500 mg/Kg	M1,M2,M3	*	*
	3000 mg/Kg	M1,M2,M3	*	*

* Three Specimens casted for each Mix design.

Fig 2. Experimental apparatus and the S/S specimens

4. Results and discussion

TCLP Leaching tests were carried after 28 days curing , solidification and stabilization using EPA method 1311 [10] .Two TCLP runs were carried out for each sample after gridding and crushing the specimens (for particles < 9.5 mm in size and for particles > 9.5 mm in size) .

The results showed that for all the samples the leachate concentrations were reduced as the cement percentage in the mix design increased **Figs (3 to 7)** .

It was noticed that as the particle size of the S/S samples increased the more effective the sample becomes in containing and retaining the heavy metal within . Samples contaminated with lead ions at 1500 mg / kg and 7 , 15 and 25 % cement mix ration had a TCLP recorded value of 14.4 , 7.6 and 4.8 mg / l respectively .

On the other hand TCLP concentrations dropped to 11.9 , 4.6 and 2.8 mg / l respectively when the same samples were tested for TCLP using particles of grain size > 9.5 mm . A similar behavior was observed for Nickel , Cadmium , Chromium and copper ions contaminated samples. This results give an indication that both S/S cement concentration and particle size has a significant effect on heavy metals leaching characteristics in acid solutions .Same observations have been found in other studies [8] .

The amount of metals released were calculated and the percentage of metals retained in the S/S samples were evaluated using the **equation (1)** below .

$$RT\ \% = \left((C_o - C_l) / C_o \right) * 100 \quad ..eq\ (1)$$

Where :

RT % : Retention Efficiency .

C_0 : Inertial Metal concentration mg.

C_l : Metal concentration in leachate mg.

The S/S samples showed a high retention efficiency exceeding 93 % for all the heavy metals when 25 % cement mix design was used even when the inertial contamination load was at 3000 mg/kg . **Table (4)** Illustrates the Retention Efficiency for Heavy Metals at different Mix designs and contamination loads .The results showed a very high retention efficiency for (S/S) specimens that used 15 % and above cement mix designs .

The Retention percentage value can be used to assess the effectiveness of the stabilization process . Although low added cement percentage S/S samples has the lowest RT% yet a reasonable degree of effectiveness was achieved for all the samples recording > 45.5 % . In general it was noticed that the highest the cement percentage ratio in the mix and the coarser of particle size of the solidified matrix. The higher the RT % is obtained leading to more effectiveness of the treatment and the remediation process as shown in **Table 4** .

Never the less and despite of the high RT % that was achieved for most of the Samples, some Heavy Metal ions that leached such as Chromium , lead and Cadmium from 7 % cement treated samples exceeded the TCLP regulatory limits that are set by the U.S EPA (50 , 50 and 10 mg/l respectively) . This may be related to the poor solidification and the high inertial contamination load of those elements in those samples. Similar observations were found in other studies [**1**] .

The pH used for the TCLP extraction solution in this study was around 4.9 .This value and after 18 hours top to bottom agitation with the S/S samples jumped to record pH values higher than 9 in the extraction solution due to the alkalinity nature of cement . This increment is due to the alkalinity of the cement used in the (S/S) treatment **[7] [6]** It is clear that there is a proportional relationship between the cement content percentage in the samples and the final extraction solution pH.

5. Conclusions and Recommendations

- Solidification / stabilization of Heavy Metals contaminated sands using cement proved to be an effective and efficient treatment method against the release of Cr, Cu, Cd, Ni and pb.
- All the samples with 15 and 25 % cement additions exhibited the TCLP regulatory limits set by the EPA for safe disposal in spite of the extremely high inertial contamination loads in the samples.
- Leaching of metals decreased with increase of cement addition and increase in particle size of the solidified / stabilized Matrix.

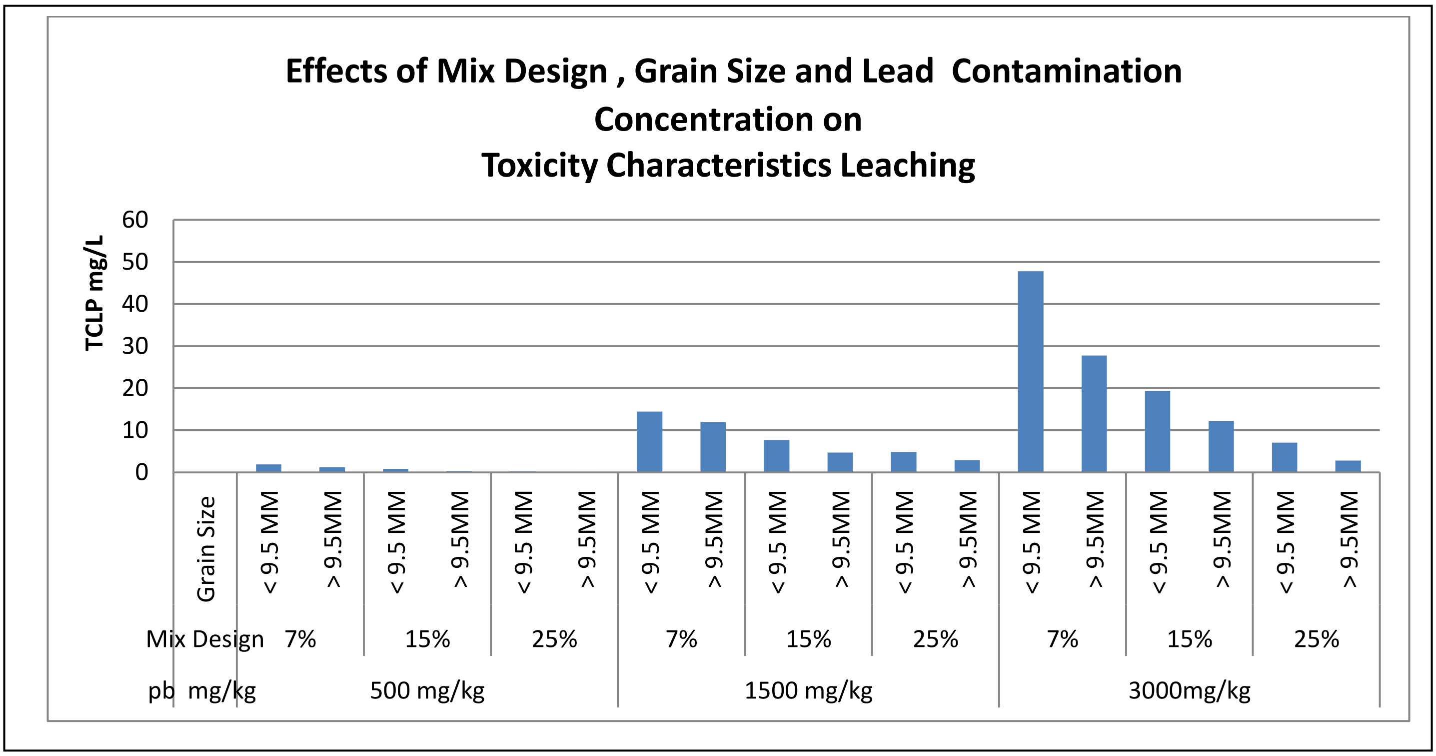

Fig 3. TCLP leachate test results for Lead ions contaminated samples

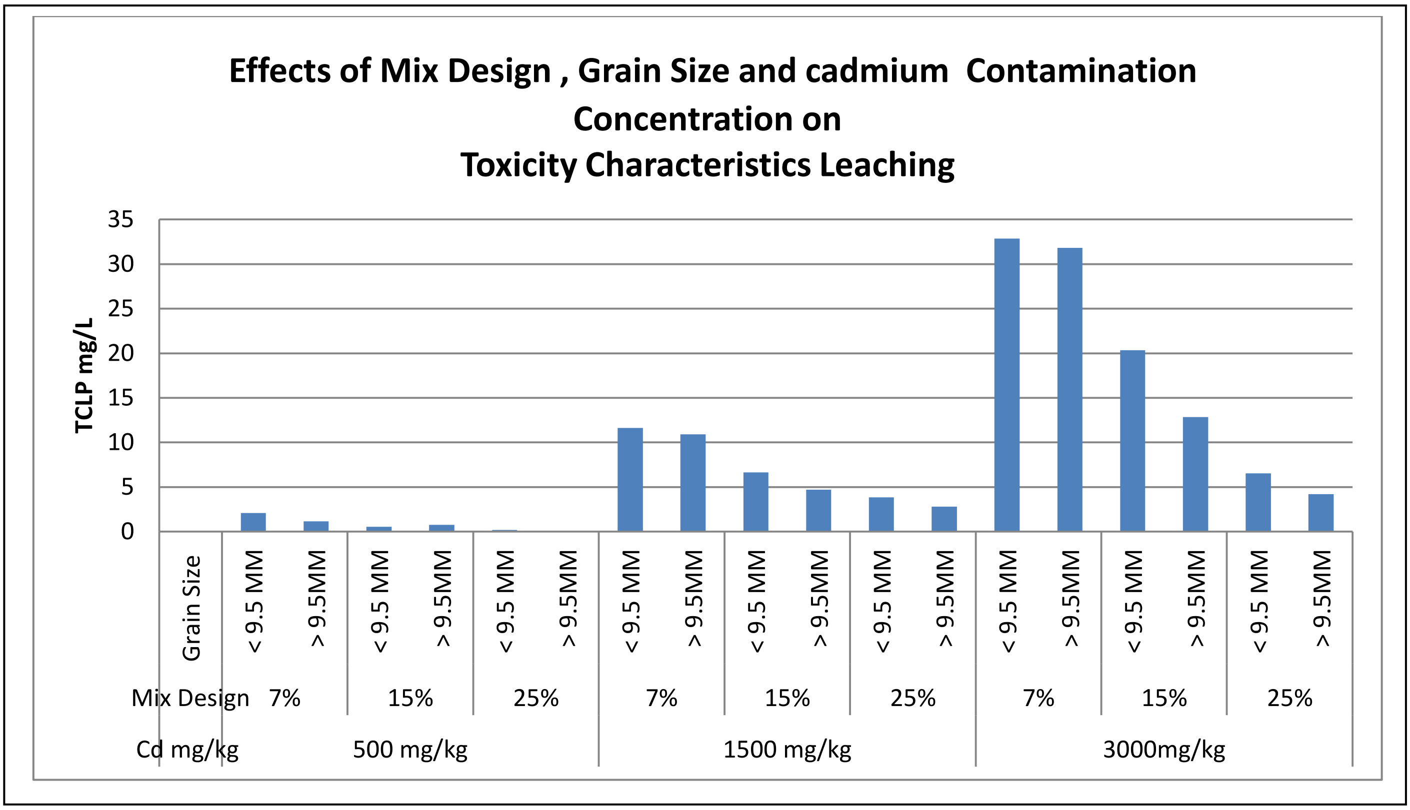

Fig 4. TCLP leachate test results for Cadmium ions contaminated samples

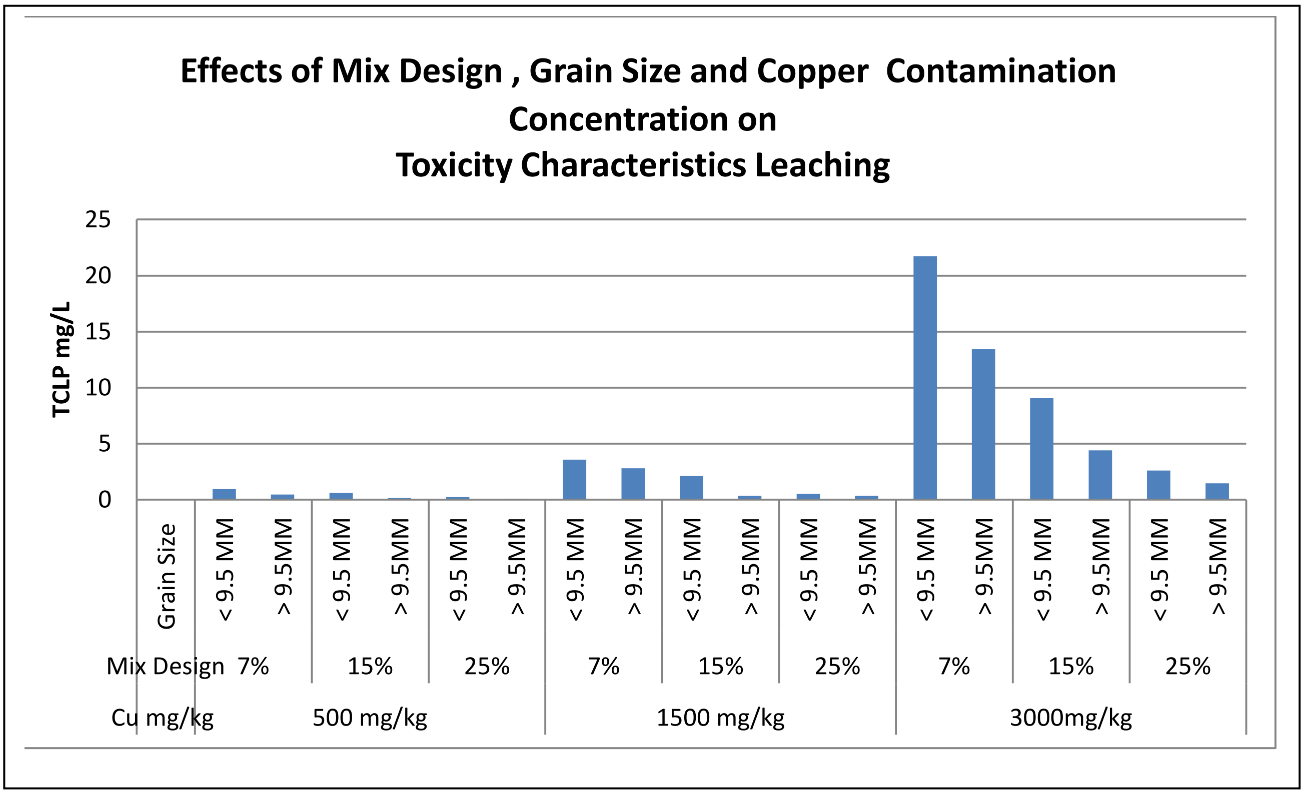

Fig 5. TCLP leachate test results for Copper ions contaminated samples

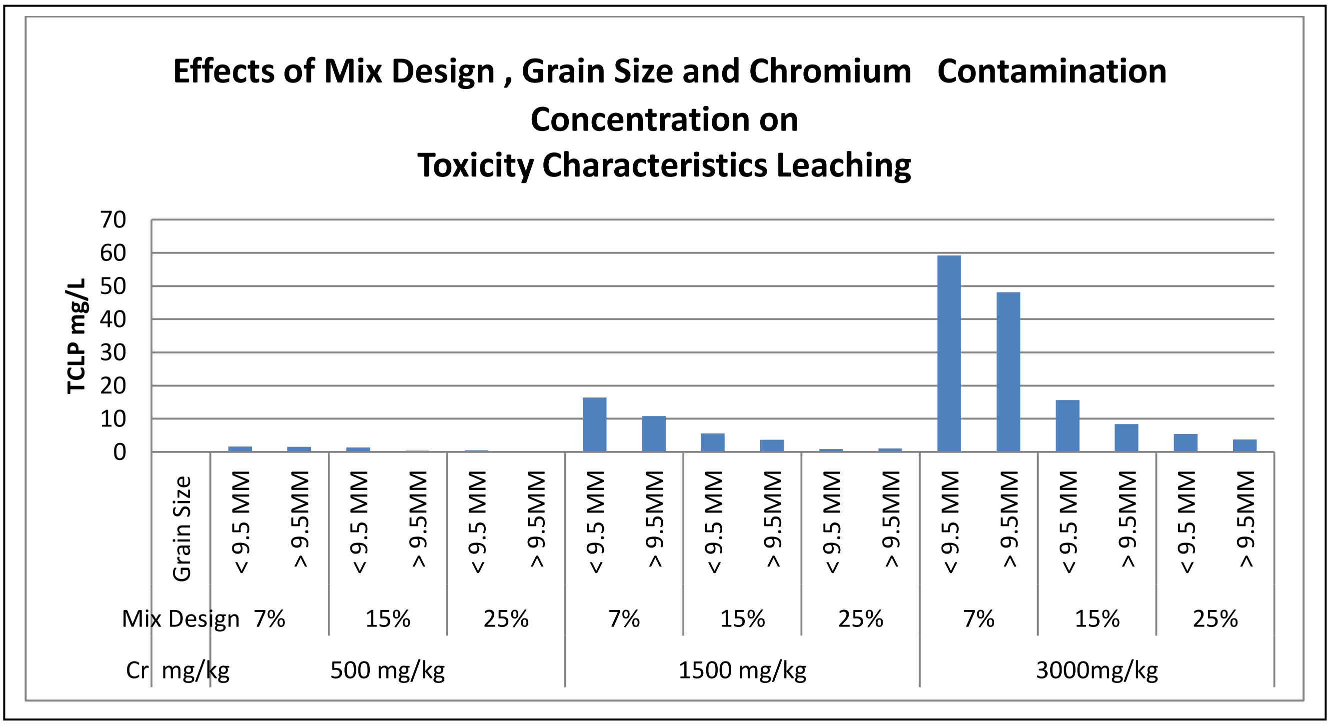

Fig 6 . TCLP leachate test results for Chromium ions contaminated samples

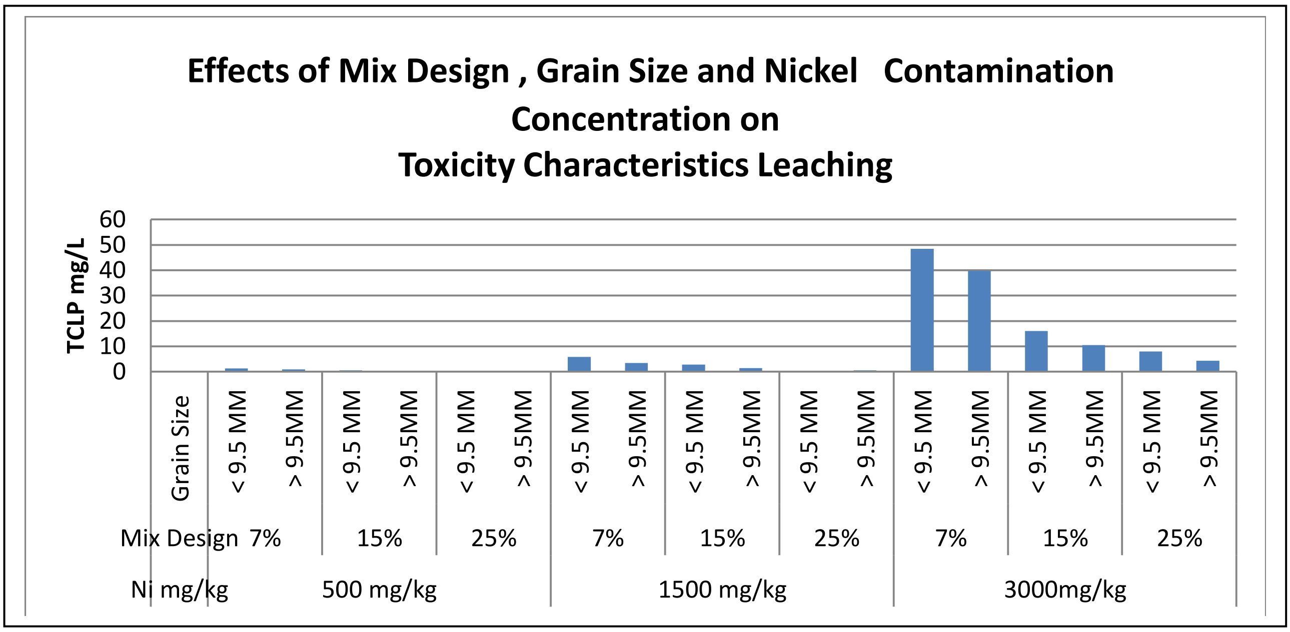

Fig 7 .TCLP leachate test results for Nickel ions contaminated samples

Table 4 . Heavy Metals Retention efficiencies for Solidified / Stabilized samples

Retention efficiency of Heavy Metals in S/S Cement based Samples %																		
Contamination Load mg/Kg	500 mg / Kg						1500 mg / Kg						3000 mg/Kg					
Mix Design Cement Addition Percentage %	7 %		15 %		25 %		7 %		15 %		25 %		7 %		15 %		25 %	
Particle size MM	< 9.5 MM	> 9.5 MM	< 9.5 MM	> 9.5 MM	< 9.5 MM	> 9.5 MM	< 9.5 MM	> 9.5 MM	< 9.5 MM	> 9.5 MM	< 9.5 MM	> 9.5 MM	< 9.5 MM	> 9.5 MM	< 9.5 MM	> 9.5 MM	< 9.5 MM	> 9.5 MM
Metal ions																		
Cr	91.5 %	93 %	93.3 %	98.3 %	97.5 %	99.4 %	73.4 %	82.4 %	91.34 %	94.3 %	98.5 %	98.2 %	45.5 %	55.7 %	87.5 %	93.3 %	95 %	96.6 %
Cd	89.4 %	94.1 %	97.4 %	96.3 %	99.1 %	99.7 %	81.1 %	82.3 %	88.8 %	92.1 %	93.3 %	95.1 %	74.3 %	75.1 %	83.2 %	89.4 %	94.1 %	96.2 %
Cu	95.2 %	97.7 %	97.1 %	99.3 %	98.9 %	99.6 %	94.1 %	95.4 %	96.3 %	99.4 %	99.1 %	99.4 %	82.4 %	89.1 %	92.4 %	96.3 %	97.7 %	98.5 %
Pb	91.3 %	94.5 %	96.3 %	98.8 %	99.1 %	99.5 %	76.1 %	80.3 %	87.3 %	92.2 %	90.4 %	94.3 %	61.2 %	77.5 %	84.3 %	90.1 %	93.4 %	97.5 %
Ni	93.4 %	95.6 %	97.8 %	99.2 %	99.7 %	100 %	89.9 %	94.1 %	95.1 %	97.6 %	99.5 %	99.1 %	62.1 %	68.9 %	87.4 %	91.8 %	93.4 %	96.5 %

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الخواص السمية للرشح الناتج من عملية التثبيت والتصلب للرمال الملوثة بالمعادن الثقيلة باستخدام المواد الاسمنتية

أ.م.د. شهلاء ابراهيم اسماعيل
باسم عبد الستار حسين
عباس حامد سليمون

الخلاصة

استخدمت طريقة المنظمة الامريكية لحماية البيئة (طريقة فحص الرشح 1313) لفحص خواص الرشح للمواد المتصلبة والمثبتة باستخدام المواد الاسمنتية . تم دراسة اداء وكفاءة عملية التثبيت لرمال ملوثة بخمس انواع مختلفة من العناصر الثقيلة باستخدام خلطات من الاسمنت البورتلندي الاعتيادي وبنسب مختلفة . ثلاث نسب من الخلطات الاسمنتية تم اضافتها الى رمال ملوثة بالمعادن الثقيلة . اظهرت النتائج بان استخدام خلطة (3 : 1 : 0,5) رمل - سمنت- ماء في عملية التثبيت والتصلب تكون فعالة جدا في الحفاظ والاحتواء لملوثات المعادن الثقيلة في داخل المصفوفة المثبتة والمتصلبة . نسب كفاءة الابقاء والاحتفاظ لهذه المعادن سجلت 95 ,94.1 , 97.7 , 93.3 و 94 ٪ لكلا من عناصر الكروم , الكادميوم , النحاس , النيكل والرصاص على التوالي باستخدام الاسمنت . حتى عندما كان تركيز هذه المعادن نسبيا عالي في الرمل المثبتة 3000 ملغم / كغم تمكنت المعالجة في الاحتفاظ بالمعادن وعدم ترشحها الى الوسط الخارجي . تأثير حجم الجزيئات كان واضح وفعال على مقدار التسرب والرشح لهذه العناصر. عندما كانت حجم الجزيئات المعرضة للفحص اكبر من 9.5 ملم كانت كفاءة الاحتفاظ بالمعادن وعدم السماح لها بالترشح خارج الوسط المثبت اعلى . النماذج التي احتوت على نسبة سمنت قليلة في خلطة التثبيت والتصلب لم تتمكن من تحقيق متطلبات نسب الاحتفاظ المحددة لهذه المعادن . على الرغم من كون الاس الهيدروجيني للماء المستخدم في فحص الترشيح بحدود 4.9 فان قيمة الاس الهيدروجيني للمحلول المستخدم للرشح ارتفع ليسجل قيم تصل الى 9.5 وهذا يعود لقاعدية مادة الاسمنت المستخدمة في عملية التثبيت والتصلب.