

The Experimental Assessment into Heavy Metal Content in Saudi Cements

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Abstract

Presence of heavy metals in cement can enhance the cement properties but can be harmful to the environment for long term due to less mobility of heavy metals. A comprehensive quantification of heavy metals contamination was carried out in the cement locally produced building materials collected from different cement factories in Riyadh city, Saudi Arabia, in which city is subject to rapid construction development. In Riyadh, it has been observed environmental issues due to heavy metal pollution from new construction projects of underground metro as well as other new infrastructural developments. Therefore, it is very important to carry out an investigation of presence of heavy metals in cement materials as major unit of construction building materials. The benefit of full statistical assessment was conducted to represent relationship models of the contents of heavy metals (Cr, Cd, Pb, Ga, and U) in cement utilized in Saudi buildings. Four different methods of matrix correlations were used to obtain full spectra of relationship between studied heavy metals and other elements. Normality tests were conducted to help the statistical performance to treat the results as parametric. Moreover, Shewhart confidence limit tests were also applied to the reported data of each heavy metals to tell us the sample out of confidence limits or not. Lucky, all the statistical tests were within good agreement with critical values. The obtained data were compared with the value of heavy metals in upper earth crust reported by Muller. Geochemical indexes calculations were performed using geochemical hazard index, background enrichment index and other useful indexes. The values of hazard indexes were compared with tabulated or recommended values. The present study was found that cement materials did not possess any significant hazard in term of heavy metals to the residents of Riyadh.

0.1 Introduction

The heavy metals are considered as member of elements that exhibit metallic characteristics. They are part of transition metals in the periodic table, some actinides, lanthanides, and metalloids. Many scientists define them based on their density, others on their chemical properties or atomic weights. Also, the definitions can be owing to their toxicity as dangerous to environment or human (Bodaghpour, S et al, 2012). Therefore, there are no common definition for heavy metals.

Cement is regarded as an important world-wide binding agent for building materials. So, cement is a chemical treatment process aiming to produce either stable compounds or excellent binder which is insoluble form. Most well recognized cement is Portland which made by firing a mixture of natural materials up to approximately 1500° (Cipurkovic, Amira et al, 2014)(Adaska, Wayne S & Taubert, Donald H, 2008).

Cement production begins with raw mineralogical content and their subsequent pre-milling in quarry site. A mixture of certain ratios of raw contents is made (Schneider, Michael et al, 2011). The mixture is crushed, milled, and cooked in large rotary kilns which are up to few metres in diameter and up to 90 metres long with a slight declined angle. The mixture is later dried to remove gases from the raw materials into the exhaust gas. This step requires a lot of energy. The mixture is combined with SiO₂, CaO, Al₂O₃, Fe₂O₃, and gypsum (Taylor, Harry FW, 1997)(Oss, Hendrik G and Padovani, Amy C, 2002). Also, waste materials containing aluminate, lime, iron, and silicate can be utilized as raw materials substitute. The cement is regulated based on its trace metals e.g. chromium content (Barnes, Paul and Bensted, John, 2002).

Interestingly, The uses of industrial wastes, e.g. inorganic wastes, have been intensively applied as suitable natural materials in cement production. These natural waste materials are including municipal solid wastes as alternative to clay, waste gypsum, red mud, iron slag, low CaO fly ash, and Al₂O. Moreover, heavy metal-containing sludges can be utilized as an alternative for cement raw material (Chen, HuXing, et al, 2010)(Shih, Pai-Haung et al, 2005). Therefore, heavy metals can be a good source for alternative of raw cement material production.

The acidity of the mixture plays major role for heavy metal release into the environment in term of long time. Nevertheless, for short period of time, the heavy metals are immobile and can not escape into the environment (Shirazi, Elham Khalilzadeh and Marandi, Reza, 2012). So, this is major concern of presence of heavy metals in cement materials.

The solubility of heavy metals heavily relies on their capability to produce aqueous phase, precipitate of controlling complexes, and their bonding in the hydration phases (Mllauer, Wolfram et al, 2012).

It has been well known in Saudia Arabia, most of modern buildings are lasting from 30 upto 40yrs, after which they must be demolished. Aftermath, the dusts of cement construction wastes are spread all over the residential areas, additionally, carrying heavy-trucks moving through the major roads which

contribute as another pollution source. In capital city, Riyadh, cement construction activities have intensified continuously and rapidly, particularly in northern and eastern portions of Riyadh city owing to underground train project. Consequently, large areas of the city have been contaminated by heavy metals of cement construction project dusts. Honestly, at night residents breathe huge amount of building dust. The question bears in mind what type of effect the building materials have on the environment. The reply can be carried out through assessment of heavy metals in cement construction building.

Therefore, this work was conducted to estimate heavy metal contamination status in cement materials produced in Riyadh as well as other cities of Saudi Arabia where there are more than 15 cement factories operating to feed the underground projects demands. The specific aims of the investigation can be summarized as follows; investigate heavy metal compositions in cement materials, carry out full statistical evaluation of the obtained data, and perform all full pollution risk assessment.

Based on heavy metal levels of input, raw, clinker, and cement materials, four heavy metals were selected in this work (Cr, Pb, Cd, U, and Ga). These elements are well recognized as toxic to humans. A literature review of these heavy metals is given below.

0.1.1 Chromium (Cr)

Cr is belonged to VIB group in the periodic table, with an atomic number 24 and atomic weight of 51.99 and density of 7.1 g/ml. The two important forms are hexa and trivalent Cr where both forms can take place in water. The solubility of hexavalent is very soluble whereas the trivalent is relatively insoluble (Zhu, Yinian et al, 2016).

Most of hexavalent Cr in the environment produces through human activities. The sources of Hexavalent Cr mainly arise from mining, metal casting, pigment industries, and fossil fuels combustion. Whereas trivalent Cr sources are glass production, photographic synthesis and building material production (Chen, Tan, et al, 2015).

Cr can enter our body through adsorption by respiratory system and gastrointestinal. When Cr is absorbed onto cells, it is rapidly excreted into the urine. The Cr can be determined in urine via routine analysis (Sedak, M, 2014).

The risk effects of Cr are linked with Cr hexavalent. It is well recognized that biological hazards of hexavalent of Cr might be reduced to Cr(III) that reacts with intracellular macromolecules. Exposure to Cr production can result in lung problems (Prasad, Ananda S, 2013).

0.1.2 Cadmium (Cd)

Cd is well known to form complexes with other organic compounds. There are four major species of Cd which are halides, sulphide, and organo-Cd compounds. Cd is primarily used in metal casting and pigment, batteries, and plastics. The

major anthropogenic sources of Cd are industries, ore mines, sludges (J He, C Ma, et al, 2013).

Cd can form many ions and compounds which can be present in freshwater. The inorganic speciation of Cd in water which is similar to Pb. The pH plays important roles in Cd reactivity, under oxidizing conditions Cd is present as hydrated form. Whereas under reducing conditions, the bisulphide ion is dominant (Aglan, Refat F and Hamed, Mostafa M. 2014).

Chronic Cd toxicity can result of long term inhalation via dust or pre-oral exposure to contaminated sources. Cd can surely cause death to human through effects on organisms. The low levels of Cd exposures are major concern. The solubility of Cd have greater toxicity than insoluble Cd compounds owing to they are more absorbed by human cells. Nevertheless, the mobility of Cd in organism is very slowly (MB McBride et al 2017).

0.1.3 Lead (Pb)

Pb is belonged to group (IVA) in the periodic table and it is often associated with other elements to form complexes. Pd can also be found in forms of organic and inorganic compounds. Pb is easily dissolved in diluted mineral acids e.g HCL, HNO₃ and organic acids, as well (Leahy, Wayne, 2013).

Pb can enter into the environment through sewage, smelters, industries, batteries, dry and wet depositions. Also, Pb contaminates water via mining. Pb might enter the human body through ingestion, skin, and intestines. Pb is easily absorbed by tissues through blood stream. When Pb is absorbed by blood stream, it can accumulate in lung, kidney, and brain cells (Mason, Lisa H et al, 2014).

0.1.4 Uranium (U)

U is the most heaviest element naturally occurring. It is belonged to actinide groups in the periodic table. The solubility of U in ground water is well-known and it also dissolves in diluted acids e.g HCL and HNO₃. U is most produced as secondary product during phosphate fertilizing processes and mining (Domingo, Jose L, et al, 2001).

The health risks caused by uranium exposure that is effects not associated with ionizing radiation. The chemical effects on the human kidney induced by the chronic ingestion of uranium in drinking water and food. Uranium effects on kidenys, was clearly shown in clinic studies on glucose, creatinine, protein, and β 2-microglobulin. It was found in urine of uranium intake for animals (Nordberg, Gunnar F, et al, 2014).

0.1.5 Gallium (Ga)

Gallium is a member of group III in the periodic Table. It is mostly used in industry for the production of semiconductor materials.

The major health effects of Ga have been concentrated on workers in semiconductor fields enveloped in production of Ga-As based devices. Few studies have shown Ga toxicity in forms of Ga-nitrate and Ga-arsenide to affect lungs, immune system, and kidneys. The International Agency for Research and Cancers has regarded Ga-As as a human carcinogen (Nordberg, Gunnar F, et al, 2014).

Mercury was not included in this work owing to its volatility as well as the used analytical technique is not suited for Hg analysis. Moreover, Hg is volatile element, thus it is less likely to be present in cement material.

0.2 Evaluation of Building Material Contamination

In recent decays, different heavy metal assessment indices applied to sediments have been developed. Metal enrichment as result of pollution can be easily detected in a number of applied risk indexes. In heavy or toxic metal researches, many researchers have compared their results to particular environment with similar environment in different regions of the globe. Environmental quality indices are the most powerful tool for evaluation of anthropogenic activities. In recent decades, many risk indexes have been proposed, applied, and developed to facilitate the assess of heavy metal studies (Caeiro et al, 2005). The contamination indexes can evaluate the degree to which the effect human and are regarded as officers for the building material quality. None of these methods has been applied on building materials.

In 1980, Hkanson was the first scientist who used contamination factor and the degree of contaminations to quantify the overall contamination roles of sediments and water.

Yovana Todorova et al (2016) studied contamination levels and ecological risks, associated with heavy metal pollution of sediments in small hydropower cascade using index approach. Yovana identified the content of As, Cd, Cu, Hg, Pb, Zn, total organic carbon and their correlations. Cd and Hg originated from different source and had specific moving. Based on the contamination and background indices the sediments were moderate contaminated and the potential ecological risk index classified the sediments with the higher risk level.

Each indices indicate the heavy metal contaminants can be broken in three categorises (Varol, Memet, 2011)(Caeiro, S, at, al ,2003) (Howard, at, al 2013):

1. Background enrichment indices which compare the results of the pollutants with baseline content of the earth crust as used in this thesis or other applied backgrounds. The enrichment factor (E.F) is defined as the ratio of the determined level to probable effect concentration. The following terminologies are used to describe the enrichment factor: ≥ 6 very high contamination factor, $3 \leq C \leq 6$ considerable contamination factors, $1 \leq C \leq 3$ moderate contamination factors, $C \leq 1$ low contamination factors.

Also, in some studies, researchers have used iron as a conservative tracer to differentiate natural from anthropogenic contents. This method is more or less qualitative analysis and thus it is less accurate than above mentioned method. To express iron enrichment factor, the following mathematical relationship does define it as (Abraham, GMS and Parker, RJ, 2008):

$$E.F = \frac{\left(\frac{m_{sample}}{Fe_{sample}}\right)}{\left(\frac{m_{shale}}{Fe_{shale}}\right)} \quad (1)$$

where;

m_{sample} is the level of the examined metal in the examined sediment or building material.

Fe_{sample} is the level of the reference metal in the examined materials.

m_{shale} is concentration of the examined metal in the average shale or the upper earth crust.

Fe_{shale} is level of the reference metal in the average shale or the upper earth crust.

Memet Varol (2011) studied enrichment factors in sediment from the Tigris River. The mean EF values for all metals studied except Cr and Mn were higher than 1.5 in the sediments of the Tigris River, suggesting anthropogenic activities on the toxic element levels in the river.

Ozkan (2012) carried out a study assessment of heavy metals using enrichment factor in inner Izmir Bay. The study showed that enrichment factor values of Hg and Cd were less than 5 indicating moderate enrichment whereas Pb and Cr were highly enriched.

2. Contamination indices which compare pollutant with clean areas. The contamination indices are common criterion to estimate the presence of heavy metals in uncontaminated sediment or the upper earth crust. The geo-accumulation index introduced by Muller to quantify heavy metals in sediments and the index can be computed through the following relationship:

$$I_{geo} = \log\left[\frac{C_n}{1.5B_n}\right] \quad (2)$$

where C_n is the reported concentration of the heavy metal (n), B_n is the geochemical level value of heavy metal in the upper earth crust (n), and factor 1.5 is the correction factor due to the variations of background data. The upper earth rock given by Turkman is regarded as the background values of heavy metals in this work as illustrated in Table.1. Table.2, the scale of geo-accumulation index consists of six grades ranging from 0-6 (Caeiro, S, et al, 2005).

In addition, I_{geo} can offer an advantage of reducing the effects of mother rocks and prominent anthropogenic effects on building heavy metal contamination.

Nevertheless, I_{geo} is only used for a single heavy metal contaminant, so this index cannot furnish a comprehensive details of the contamination status of the building materials (Guan, Yang et al, 2014).

S Odat (2013) studies the levels of heavy metal along the highway of Irbid/Zarqa in Jordan. The study used The geo-accumulation index in which Cd exhibited high level with I_{geo} of 1.4. The rest of reported heavy metals I_{geo} values were below 0.2 demonstrating background levels.

3. Metal contamination Index (MTI). In order to estimate the overall degree of sediment material contamination, the metal contamination index can be computed according to the relationship

$$MPI = (M1 * M2 * M3..Mn)^{\frac{1}{n}} \quad (3)$$

where Mn is the content of heavy metal n expressed in ppm (mg/kg) of dry weight basis (Qingjie, Gong, at, al, 2008).

Therefore; Metal contamination index (MTI) approach can be used for the estimate which shows the composite influence of individual parameters on the overall quality of building materials. It is also a combined physio-chemical and microbial index which makes it possible to compare the quality of building materials and sediments.

The following description is used for MTI: ≤ 150 , low risk; $150 \leq 300$, moderate risk; $300 \leq 600$, considerable risk, ≥ 600 , very high risk as reported by Muller.

4. Degree of contamination (CD) was defined as the sum of all contamination factors of heavy metal M. CD classification can be found in Table.3
5. Other contamination indexes like Vector modulus and root product, and Nemerow pollution indexes are not used in this work. Newerow was applied (Jie, Chen Qing, Liu Hui, Qian, 2012). Thus, Newerow is a comprehensive pollution index and a single factor used to assess the pollution of toxic metals in building materials (Hong-gui, Deng et al, 2012).

0.3 Analytical Work

The marble materials were collected from different houseware stores in Riyadh. The proposed materials weathering-effect were removed at the spot and later transported to the our lab. The materials were then crushed using crushing machine. A polyamide screen sieve (mesh size 1mm) was used and then the crushed materials were spread on the sieve by using plastic spatula and soft-shaking. Later, crushed materials were placed in an oven at $110 \pm 5^\circ\text{C}$ for overnight in order to ensure no moisture is present in the crushed materials.

Approx. 5gm of each sample was milled to reduce the particle size, and to homogenize the powder sample. After drying, roughly 0.2 gm of of the

Table 1: Concentrations of heavy metals in upper earth crust

Element	ppm	Element	ppm
V 51	20	Sr 88	610
Cr 52	11	Mo 98	0.4
Mn 55	1100	Cd 111	0.035
Fe 57	3800	Te 130	
Co 59	0.1	Ba 138	10
Ni 60	20	Tl 205	
Cu 63	4	Pb 208	9
Zn 66	20	Bi 209	
Ga 69	4	U 238	2.2
As 75	1		

Table 2: Muller's classification for the geo-accumulation index

<i>I_{geo}</i>	Value	Class	Material Quality
	≤0	0	Uncontaminated
	0-1	1	Uncontaminated to moderately contaminated
	1-2	2	Moderately contaminated
	2-3	3	Moderately to strongly contaminated
	3-4	4	Strongly contaminated
	4-5	5	Strongly to extremely contaminated
	≥6	6	Extremely contaminated

Table 3: Muller's classification for the degree of contamination (CD)

Values	Material quality
≤ 1.5	Very low degree of contamination
$1.5 \leq CD \leq 2$	Low degree of contamination
$2 \leq CD \leq 4$	Moderate degree of contamination
$4 \leq CD \leq 8$	High degree of contamination
$8 \leq CD \leq 16$	Extremely degree of contamination

homogenised sample weight was very carefully measured out into vessel, and weight was recorded with an accuracy of ± 0.0001 gm. A solution of HCl, HF, and HNO_3 was added to the vessel.

The performance was done by microwave assisted digestion using 0.2 g dried sample. After digestion H_3BO_3 was added for complexation of fluorides. Adding boric acid to the digested solution not only complexes the free fluoride ions in the solution, but also facilitates the dissolution of the precipitated fluorides. The solution in the bottle was the sample diluted to 50 ml in 3.5% HNO_3 .

Microwave conditions were: 60 bar in PTFE (polytetrafluoroethylene) vessels; 35 minutes at 1400 W using a Multiwave 3000 (Anton Paar; Graz, Austria) microwave digestion system. All acids were Merck Suprapur. Determination of heavy metals was carried out by ICP-MS (Inductively Coupled Plasma-Mass Spectrometer): NexION 300D (Perkin Elmer, USA) at the chemistry department, King Saud University. The selected parameters of operational system used in this analysis are listed in Table.4.

Table 4: Instrumentation operating System for ICP-MS

RF power	1600 W
Nebulizer gas flow	0.92 L/min
Lens Voltage	9.25 V
Analog Stage Voltage	-1762.5 V
Pulse Stage Voltage	1050 V
Number of Replicates	3
Reading / Replicates	20
Scan Mode	Peak Hopping
Dwell Time	40 ms
Integration	1200ms

ICP standard solution was created for the analysis with eight varying levels for each element. High purity certified elemental standard (6 CertiPUP, Merck Plasma Standards) was used in this analysis. To ensure that acids used in this work did not affect the ICP-MS reported data, blank was carried out and acids were used in the standard to the same levels as the sample digestion. It was found out that the acids did not have any affect. Every 8th sample run by ICP-MS was standard, to monitor the quality of instrument. Moreover, an internal standard was used to ensure that the instrument did not go out of calibration.

For quality assurance, five certified reference materials were used. The used reference materials were purchased from USGS and they were 69 b bauxite, 1646 a Estaurine Sediment, 1 d Limestone, GBW 07106 Rock, and GBW 07108 Rock.

The reported results of the certified reference materials by ICP-MS lab are listed in Table.5. For major elements of the certified material, the target relative standard deviation was less than 10% and thus all the results above this target were rejected and repeated. Similarly for minor and trace elements, the target relative standard deviation was less than 20%.

The target accuracy of the certified materials has to be above 85% to produce very healthy and comparable results. Fortunately, the obtained result accuracy were above 90% by ICP-MS lab. The accuracy can be computed through equation:

$$R = \frac{\text{measured value}}{\text{true value}} \tag{4}$$

Also, t-tests were conducted for the reference materials analysed in this work. The obtained results were less than the tabulated values indicating good agreement of the reported data. Nevertheless, the t-test results were not reported here.

Therefore, from the obtained results of the reference materials, the precision was less than 10% and the accuracy was better than 90% indicating the obtained data of heavy metals in the study marble material were very comparable.

Table 5: Reported results of reference materials using ICP-MS

lab results	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Sr	Mo	Cd	Te	Ba	Tl	Pb	Bi	U	
69 b bauxite	147.6	75.7	685.8	6.94	1.3	12.9	11.4	27	96	27.7	9.2	26.5	2.1	0.3	76	0.5	10.3	7.1	9.3	
1646 a Estaurine Sediment	49	36.2	219.4	1.73	4.9	21.4	10.8	46.6	4.5	5.2	71	1.8	0.2	0.3	192	0.2	8.8	0.3	1.3	
1 d Limestone	9.3	9.1	227.3	0.17	24.4	4.7	3.4	15.2	0.9	10.6	236.7	0.9	0.6	0.1	22.3	0	0.4	0.1	0.9	
GBW 07106 Rock	36	18.3	157.7	2.32	6.7	15.3	17.4	15.7	0.49	6.2	63.7	4.7	27	200	129.3	0.3	6.1	0.2	1.9	
GBW 07108 Rock	35.3	24.9	414.4	1.68	8.8	18.5	22.9	47.8	0.23	7.2	876.2	6.3	29	57	110	0.2	10.4	3.3	1.4	
Certified material																				
69 b bauxite	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Sr	Mo	Cd	Te	Ba	Tl	Pb	Bi	U	
1646 a Estaurine Sediment	156	75	850	7.14	1.1	23	10	48.9	5	6.23	68	1.8	0.148	0.214	80	11.8			
1 d Limestone	45	40.9	234.5	2.01	5	4	18	1	1	260	58	5.3	29	214	210	<0.5	11.7		2	
GBW 07106 Rock	10		233	0.22											30					1
GBW 07108 Rock		32		1.70	9	17.8	23.4	52	0.38	6.6	913	7.1	32	62	143		7.6			2.1
															120					3.16

0.4 Analytical Results and Discussion

The studied cement materials chemical data are listed in Table.20. The statistical calculations are also reported in Table.20. The matrix mathematical calculations using four different methods are found in Table.21 and Table.22. The result calculations were subjected into statistical examination which obviously showed all the reported data herein passed the statistical examination indicating the reported data were confident.

Heavy metals associated with marbles are discussed herein with more emphasized on statistical models. As carried in previous sections, only Cr, Cd, Pb, and U are given in details.

0.4.1 Chromium (Cr)

Cr levels in cement materials were slightly elevated as shown in Table.20 with range¹ of 27. The range showed the data were not much different. The highest reported value was 36 ppm for Cr in cements whereas the lowest value was 9 ppm. The data distribution was as follows: 24% was 19 ppm, 49% was 22 ppm, and 74% was 28 ppm.

The normality test of Cr results was obtained through A-D test and showed very comparable data in Fig.1. The Shewhart confidence limit test of Cr in cement material proved the study materials were normal distribution as shown in Fig.2. All the reported results passed the Shewhart confidence limit test.

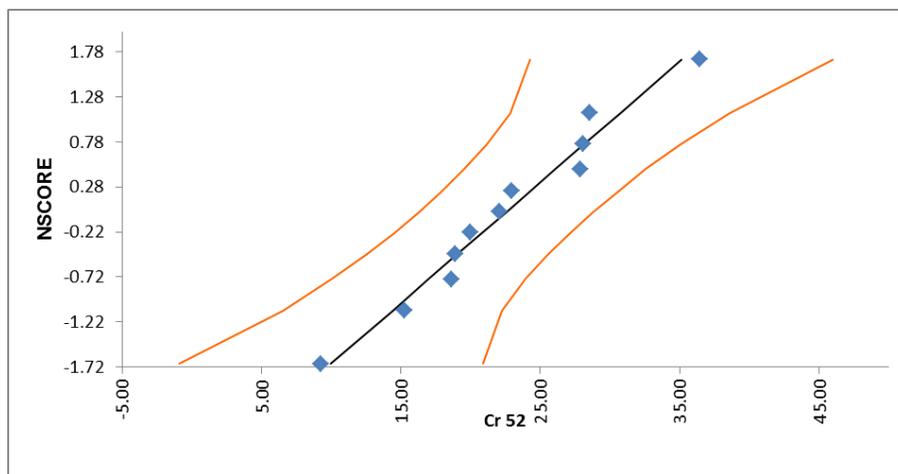


Figure 1: Normal distribution of Cr level in cement materials

Matrix correlation calculations using Pearson Correlations and Pearson Probabilities in Table.21 and Table.22 indicated Cr had strong positive correlation

¹Range is the difference between upper and lower values

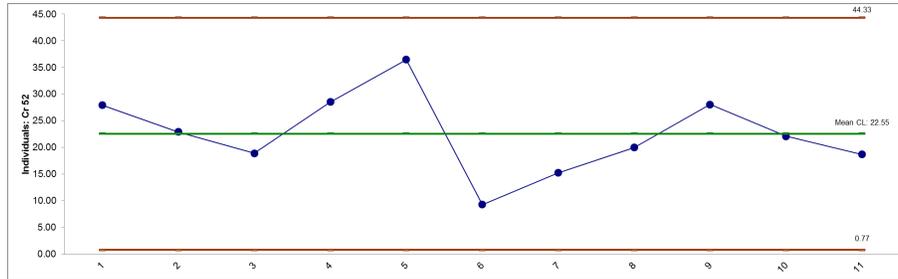


Figure 2: Shewhart confidence limit for Cr level in cement material

with V and model relationship can be computed through Table.6 as follows:

$$Cr = (2.395) + (0.291100) * V \tag{5}$$

Cr had very strong positive matrix correlation with Fe as computed in Table.21 and Table.22. Thus, the computed multi regression model via Table.7 was related as:

$$Cr = (11.125) + (0.001026) * Fe \tag{6}$$

Also, Cr had very strong positive relationship with heavy metal as computed in Table.21 and Table.22 and it can be modelled via Table.8 as:

$$Cr = (4.295) + (0.641228) * As \tag{7}$$

In Tables 21 &.22, Cr had significant relationship with Co (R=0.88) which can be modelled using Table.9 as:

$$Cr = (13.254) + (1.379) * Co \tag{8}$$

In Tables 21 &.22, Cr with Ni were strongly correlated (R= 0.86) and it can be shaped in mathematical relationship using Table.10 as:

$$Cr = (-5.759) + (1.956) * Ni \tag{9}$$

Mathematical correlation calculations showed Cr was correlated with Cu with R values of 0.86; thus, the multi regression model in Table.11 can be as

$$Cr = (6.681) + (0.375894) * Cu \tag{10}$$

Table 6: Summary of Cr and V model in cement material

R-Square	61.81%					
R-Square Adjusted	57.57%					
S (Root Mean Square Error)	4.845					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	2.395	5.480	0.436994	0.6724		
V 51	0.291100	0.076264916	3.817	0.0041	1	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	341.96	341.96	14.569	0.0041	
Error	9	211.24	23.471			
Total (Model + Error)	10	553.20	55.320			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	1.964					
P-Value Positive Autocorrelation	0.4639					
P-Value Negative Autocorrelation	0.5116					

Table 7: Summary of Cr and Fe model in cement material

R-Square	75.93%					
R-Square Adjusted	73.25%					
S (Root Mean Square Error)	3.847					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	11.125	2.439	4.562	0.0014		
Fe 57	0.001026258	0.000192623	5.328	0.0005	1	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	420.02	420.02	28.385	0.0005	
Error	9	133.17	14.797			
Total (Model + Error)	10	553.20	55.320			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	1.798					
P-Value Positive Autocorrelation	0.4040					
P-Value Negative Autocorrelation	0.6719					

Table 8: Summary of Cr and As model in cement material

R-Square	68.80%					
R-Square Adjusted	65.33%					
S (Root Mean Square Error)	4.379					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	4.295	4.306	0.997330	0.3447		
As 75	0.641228	0.143941	4.455	0.0016	1.00000	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	380.60	380.60	19.845	0.0016	
Error	9	172.60	19.178			
Total (Model + Error)	10	553.20	55.320			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	2.323					
P-Value Positive Autocorrelation	0.6973					
P-Value Negative Autocorrelation	0.2755					

Table 9: Summary of Cr and Co model in cement material

R-Square	62.27%					
R-Square Adjusted	58.07%					
S (Root Mean Square Error)	4.816					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	13.254	2.817	4.706	0.0011		
Co 59	1.379	0.357834	3.854	0.0039	1	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	344.46	344.46	14.852	0.0039	
Error	9	208.74	23.193			
Total (Model + Error)	10	553.20	55.320			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	1.10236981					
P-Value Positive Autocorrelation	0.0639					
P-Value Negative Autocorrelation	0.9568					

Table 10: Summary of Cr and Ni model in cement materials

R-Square	73.99%					
R-Square Adjusted	71.10%					
S (Root Mean Square Error)	3.998					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	-5.759	5.724	-1.006	0.3407		
Ni 60	1.956	0.386532	5.060	0.0007	1	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	409.31	409.31	25.601	0.0007	
Error	9	143.89	15.988			
Total (Model + Error)	10	553.20	55.320			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	1.597					
P-Value Positive Autocorrelation	0.1929					
P-Value Negative Autocorrelation	0.7029					

Table 11: Summary of Cr and Cu model in cement materials

R-Square	62.75%					
R-Square Adjusted	58.61%					
S (Root Mean Square Error)	4.785					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	6.681	4.324	1.545	0.1567		
Cu 63	0.375894	0.096535782	3.894	0.0037	1	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	347.14	347.14	15.162	0.0037	
Error	9	206.06	22.895			
Total (Model + Error)	10	553.20	55.320			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	1.790					
P-Value Positive Autocorrelation	0.3479					
P-Value Negative Autocorrelation	0.6301					

0.4.2 Cadmium (Cd)

Cd levels present in cement materials were regarded as low as it can be seen later in hazard risk discussion. The Cd concentrations were in average of 1 ppm with range of 0.5 indicating the normality test can be easily calculated. the highest level of Cd was 2 ppm and the lowest level was 0.7 ppm. The data distribution was as follows: 24% was 0.7 ppm, 49% of data was 1 ppm, and 74% was 1.5 ppm. The normality test showed very good agreement with tabulated value as diagrammed in Fig.3.

All samples for Cd Shewhart confidence limit test passed the test as illustrated in Fig.4.

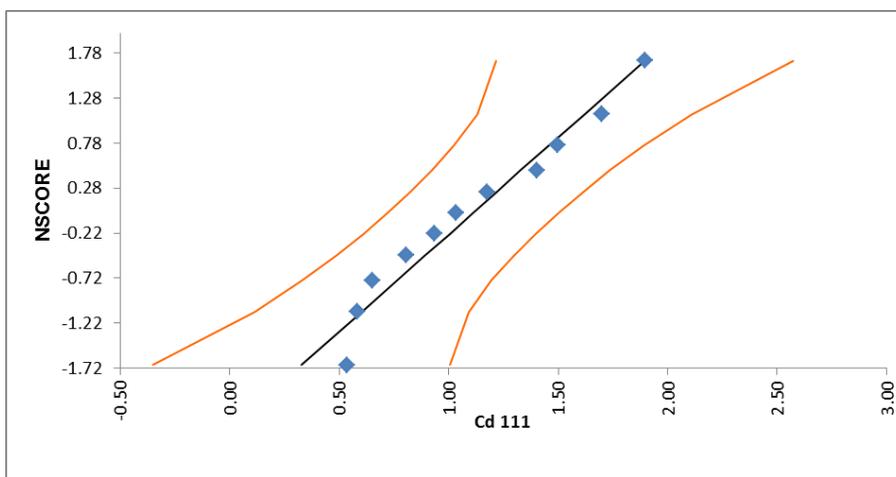


Figure 3: Normal distribution of U level in cement materials

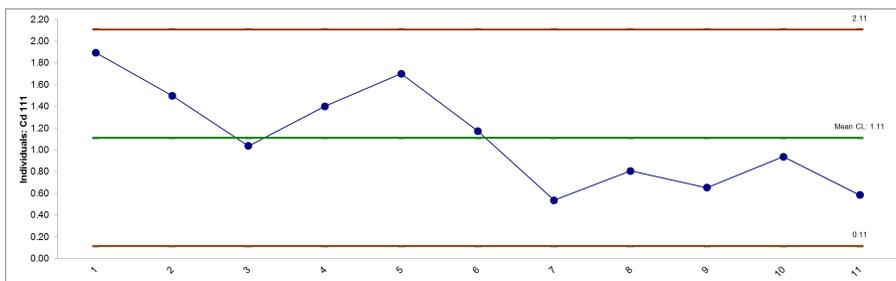


Figure 4: Shewhart confidence limit for Cd level in cement materials

The correlation probabilities calculations showed that there was slightly significant positive correlation between Cd and Ni with $R=0.66$. The obtained

model of this relationship can be calculated using Table.12 as follows:

$$Cd = (-0.233157) + (0.092821) * Ni \tag{11}$$

As shown in Table 21 and Table.22, there was a strong positive correlation between Cd and Cu (R=0.70). Using the summery model in Table.13 one can obtain the relationship between Cd and Cu as :

$$Cd = (0.229408) + (0.020868) * Cu \tag{12}$$

Cd and Zn were positively correlated using matrix correlation calculation. The multi regression model was calculated using parameters in Table.14 to obtain the following relationship as:

$$Cd = (0.753047) + (0.013211) * Zn \tag{13}$$

Cd and As were strongly correlated with positive sign. Using Table.15 to predict the model, it can lead to the following equation:

$$Cd = (0.261627) + (0.029814) * As \tag{14}$$

Table 12: Summary of Cd and Ni model in cement materials

R-Square	42.91%					
R-Square Adjusted	36.57%					
S (Root Mean Square Error)	0.369179					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	-0.233157	0.528507	-0.441162	0.6695		
Ni 60	0.09282067	0.035688355	2.601	0.0287	1	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	0.921956	0.921956	6.765	0.0287	
Error	9	1.227	0.136293			
Total (Model + Error)	10	2.149	0.214859			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	1.138					
P-Value Positive Autocorrelation	0.0393					
P-Value Negative Autocorrelation	0.9191					

Table 13: Summary of Cd and Cu model in cement materials

R-Square	49.79%					
R-Square Adjusted	44.21%					
S (Root Mean Square Error)	0.346211					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	0.229408	0.312876	0.733222	0.4821		
Cu 63	0.020867584	0.006984805	2.988	0.0153	1	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	1.069836029	1.069836029	8.926	0.0153	
Error	9	1.078757675	0.119862			
Total (Model + Error)	10	2.149	0.214859			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	1.162					
P-Value Positive Autocorrelation	0.0565					
P-Value Negative Autocorrelation	0.9275					

Table 14: Summary of Cd and Zn model in cement materials

R-Square	49.20%					
R-Square Adjusted	43.56%					
S (Root Mean Square Error)	0.348246					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	0.753047	0.160283	4.698	0.0011		
Zn 66	0.013210661	0.004474561	2.952	0.0162	1.00000	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	1.057113386	1.057113386	8.717	0.0162	
Error	9	1.091480318	0.121276			
Total (Model + Error)	10	2.149	0.214859			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	1.269					
P-Value Positive Autocorrelation	0.0763					
P-Value Negative Autocorrelation	0.8686					

Table 15: Summary of Cd and As model in cement materials

R-Square	38.29%					
R-Square Adjusted	31.44%					
S (Root Mean Square Error)	0.383818					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	0.261627	0.377416	0.693204	0.5057		
As 75	0.029813518	0.012615549	2.363	0.0424	1.00000	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	0.822745	0.822745	5.585	0.0424	
Error	9	1.326	0.147316			
Total (Model + Error)	10	2.149	0.214859			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	0.967648					
P-Value Positive Autocorrelation	0.0240					
P-Value Negative Autocorrelation	0.9668					

0.4.3 Lead (Pb)

Pb is well-known severe toxic heavy metal. Pb concentrations in the studied adhesive materials were in average value of

Pb average concentration in cement material was approx. 4.8 ppm with range of 3 ppm. The highest level of Pb was 8.1 ppm and the lowest level was 3.1 ppm. The distribution of data was as follows: 24% was 4 ppm, 49% was 4.2 ppm, and 74% was 5.4 ppm. The reported results of Pb clearly followed normal distribution as proven by A-D test and shown in Fig.5.

Luckily, all Pb results passed the confidence limit test of Shewhart proven that all the data were comparable as shown in Fig.6.

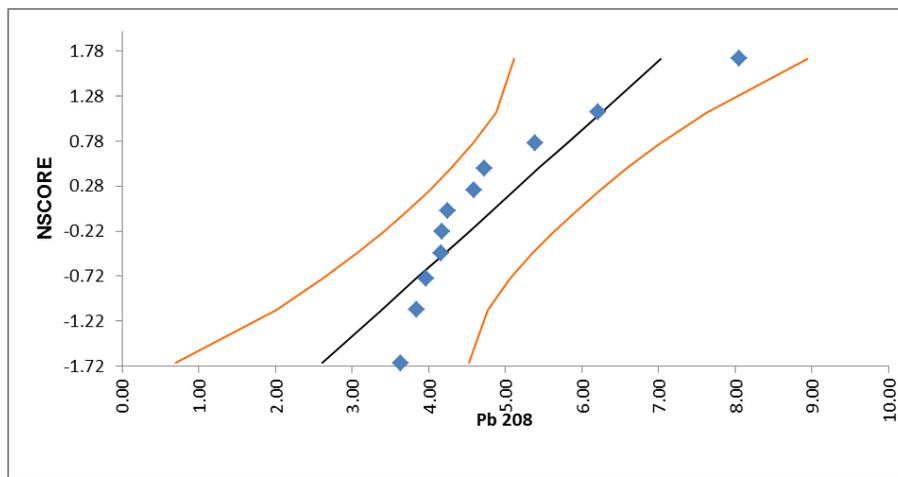


Figure 5: Normal distribution of Pb level in cement material

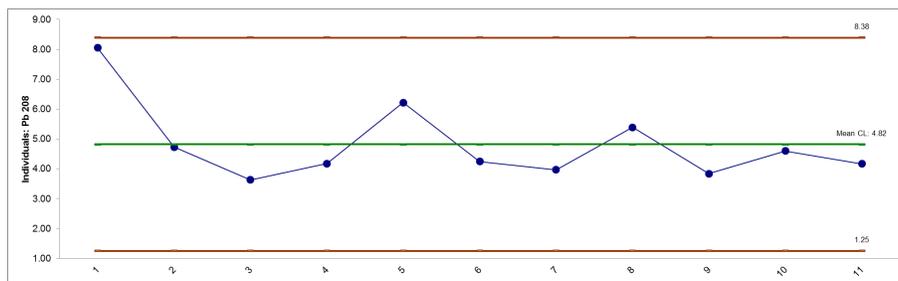


Figure 6: Shewhart confidence limit for Pb level in cement material

The Pearson probabilities calculations showed between Pb and Zn with R=0.92 and the calculated multi regression model in Table.16 is

$$Pb = (3.493) + (0.048971) * Zn \tag{15}$$

Pb and Cd were positively correlated and the regression model can be calculated from Table.17 as

$$Pb = (2.578) + (2.017) * Cd \tag{16}$$

Pb and Ba were significantly correlated and their regression model using Table.18 is :

$$Pb = (2.953) + (0.035596) * Ba \tag{17}$$

Table 16: Summary of Pb and Zn model in cement materials

R-Square	85.25%					
R-Square Adjusted	83.61%					
S (Root Mean Square Error)	0.528449					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	3.493	0.243223	14.361	0.0000		
Zn 66	0.048970693	0.006789955	7.212	0.0001	1.00000	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	14.526	14.526	52.016	0.0001	
Error	9	2.513	0.279258			
Total (Model + Error)	10	17.039	1.704			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	2.932					
P-Value Positive Autocorrelation	0.9359					
P-Value Negative Autocorrelation	0.0325					

Table 17: Summary of Pb and Cd model in cement materials

R-Square	51.30%					
R-Square Adjusted	45.89%					
S (Root Mean Square Error)	0.960207					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	2.578	0.783002	3.293	0.0093		
Cd 111	2.017	0.655070	3.079	0.0132	1.00000	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	8.741	8.741	9.481	0.0132	
Error	9	8.298	0.921998			
Total (Model + Error)	10	17.039	1.704			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	1.538					
P-Value Positive Autocorrelation	0.1421					
P-Value Negative Autocorrelation	0.7104					

Table 18: Summary of Pb and Ba model in cement materials

R-Square	83.59%					
R-Square Adjusted	81.77%					
S (Root Mean Square Error)	0.557319					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	2.953	0.322702	9.150	0.0000		
Ba 138	0.035595877	0.005256414	6.772	0.0001	1.00000	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	14.244	14.244	45.859	0.0001	
Error	9	2.795	0.310604			
Total (Model + Error)	10	17.039	1.704			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	2.039					
P-Value Positive Autocorrelation	0.4767					
P-Value Negative Autocorrelation	0.4242					

0.4.4 Uranium (U)

U levels in cement materials were regarded as low with an average of 1.5 ppm. The highest level of U was found to be 2 ppm and the lowest level was 1.3 ppm. The data pattern was as follows: 24% was 1.3 ppm, 49% was 1.6 ppm, and 74% was 1.8 ppm. The reported data of U in cement materials followed very good normal distribution as shown in Fig.7. Also, A-D test proved the normal distribution for U.

The Shewhart confidence limit test for U levels indicated all analysed material passed the test as figured in Fig.8.

Pearson probability calculations showed no correlation with U. Nevertheless, Spearman rank correlations in Fig.22 showed U was correlated with V. The relationship between U and V can be modelled using Table.19 as:

$$U = (0.821700) + (0.010161) * V \quad (18)$$

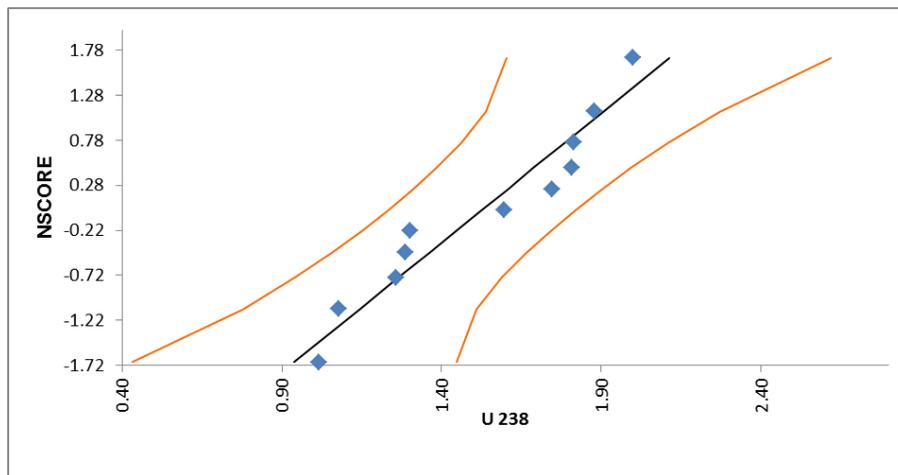


Figure 7: Normal distribution of U level in cement material

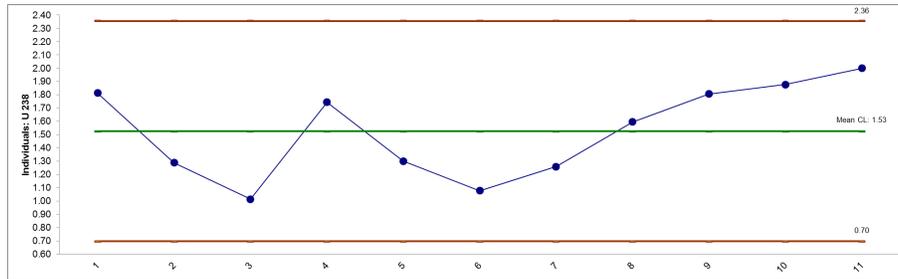


Figure 8: Shewhart confidence limit for Pb level in cement materials

Table 19: Summary of U and V model in cement materials using Spearman ank correlations

R-Square	34.60%					
R-Square Adjusted	27.34%					
S (Root Mean Square Error)	0.295782					
Parameter Estimates:						
Predictor Term	Coefficient	SE Coefficient	T	P	VIF	Tolerance
Constant	0.821700	0.334558	2.456	0.0364		
V 51	0.010160686	0.004656169	2.182	0.0570	1	1
Analysis of Variance for Model:						
Source	DF	SS	MS	F	P	
Model	1	0.416613	0.416613	4.762	0.0570	
Error	9	0.787385	0.087487173			
Total (Model + Error)	10	1.204	0.120400			
Durbin-Watson Test for Autocorrelation in Residuals:						
DW Statistic	1.603					
P-Value Positive Autocorrelation	0.2418					
P-Value Negative Autocorrelation	0.7420					

Table 20: Elemental Analysis and Statistical Evaluation for Cement Materials

Sample Id	Sample code	V	51 Cr	52 Mn	55	Fe 57	Co 59	Ni 60	Cu 63	Zn 66	Ga 69	As 75	Sr 88	Mo 98	Cd 111	Te 130	Ba 138	Tl 205	Pb 208	Bi 209	U 238
Cement S1	D01	76.1	27.9	170	9470	4.8	17.5	42.8	96.8	9.9	27.2	70.5	6.7	7.8	1.9	0.04	140.6	0.23	8.05	4.58	1.81
Cement S2	D02	69.1	22.9	56	12052	5.5	17.8	53.9	19.7	9.8	37.0	60.2	7.8	5.3	1.5	0.03	39.6	0.08	4.73	36.54	1.29
Cement S3	D03	56.7	18.9	56	10125	4.6	15.0	37.6	15.5	8.1	27.6	37.2	5.3	1.0	0.06	47.6	0.04	3.63	0.44	1.01	
Cement S4	D04	81.0	28.5	273	12660	8.1	17.8	51.5	22.0	10.3	39.7	46.1	5.7	1.4	0.04	51.8	0.06	4.17	0.30	1.75	
Cement S5	D05	95.0	36.5	594	27290	18.0	17.9	81.2	43.9	16.2	46.4	174.5	9.1	1.7	0.00	80.2	0.04	6.21	57.44	1.30	
Cement S6	D06	30.9	9.3	13	783	0.7	8.2	30.0	11.7	5.9	14.9	118.2	7.0	1.2	0.04	28.7	0.04	4.25	42.22	1.08	
Cement S7	A01142	CSC44.8	15.2	187	7821	6.5	10.2	27.8	14.3	8.4	18.6	352.7	3.1	0.5	0.06	45.5	0.04	3.97	0.28	1.26	
Cement S8	A01142	OPC37.0	20.0	240	11270	8.3	12.5	41.0	19.1	9.6	28.5	330.4	4.8	0.8	0.08	57.5	0.05	5.39	0.17	1.60	
Cement S9	A01146	68.7	28.1	291	12184	7.2	14.8	35.8	20.9	8.6	25.7	36.5	3.6	0.7	0.04	30.7	0.02	3.84	0.12	1.81	
Cement S10	A01062	100.0	22.1	167	11121	5.7	14.5	37.0	17.6	7.0	29.8	29.8	4.8	0.9	0.06	34.8	0.02	4.60	0.16	1.88	
Cement S11	C 0557	72.5	18.7	191	7727	4.8	13.0	26.0	16.4	6.2	17.9	23.3	3.8	0.6	0.04	19.4	0.04	4.17	0.28	2.00	
Count		11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11
Mean		69	23	203	11137	7	14	42	27	9	28	116	6	1.1	0.05	52	0.06	4.8	13.0	1.5	
Stdev		20	7	158	6315	4	3	16	25	3	10	120	2	0.5	0.02	34	0.06	1.3	21.4	0.3	
Range		69	27	581	26506	17	10	55	85	10	31	329	6	1.4	0.08	121	0.21	4.4	57.3	1.0	
Minimum		31	9	13	783	1	8	26	12	6	15	23	3	0.5	0.00	19	0.02	3.6	0.1	1.0	
24th Percentile (Q1)		57	19	56	7821	5	12	30	15	7	19	36	4	0.7	0.04	31	0.04	4.0	0.2	1.3	
49th Percentile (Median)		69	22	187	11121	6	15	38	19	9	28	60	5	1.0	0.04	45	0.04	4.2	0.3	1.6	
74th Percentile (Q3)		81	28	273	12184	8	18	51	22	10	37	174	7	1.5	0.06	58	0.06	5.4	36.5	1.8	
Maximum		100	36	594	27290	18	18	81	97	16	46	353	9	1.9	0.08	141	0.23	8.1	57.4	2.0	
95.0% CI Mean		55 to 82	27 to 308894	15339 to 52.710.5	919 to 43.57.1	10.23 to 3.493.616	2103 to 0.05929.8	74.30.02 to 0.3.9	5.61.4 to 1.7	14 to 35.10 to 110239	72.40.507.9 to 21.7.196 to 43.19.19	10.638 to 2103	0.232 to 0.033.427	58.06.4 to 0.039.1	2.139.9 to 37.0.4	0.6	0.89	1.86	0.45	0.00	0.22
95.0% CI Sigma		0.24	0.21	0.58	1.01	0.96	0.43	0.61	1.97	0.64	0.28	1.20	0.21	0.24	0.45	0.92	58.06.4	2.01	0.89	1.86	0.45
Anderson-Darling Normality Test		0.69	0.80	0.10	0.01	0.01	0.25	0.08	0.00	0.07	0.58	0.00	0.82	0.72	0.23	0.01	0.01	0.00	0.01	0.00	0.22
p-value (A-D Test)		-0.37	0.11	1.47	1.47	1.87	-0.67	1.65	2.73	1.65	0.43	1.42	0.48	0.37	-0.55	2.08	2.98	1.80	1.38	0.00	0.17
Skewness		0.56	0.86	0.03	0.03	0.01	0.30	0.02	0.00	0.02	0.50	0.03	0.45	0.56	0.39	0.00	0.00	0.01	0.04	0.79	
p-value (Skewness)		0.23	0.31	3.41	5.04	5.47	-0.43	3.36	7.72	4.14	-0.32	0.68	-0.54	-1.11	1.77	4.96	9.36	3.22	0.31	-1.63	
Kurtosis		0.70	0.65	0.04	0.01	0.01	0.86	0.04	0.00	0.02	0.94	0.47	0.77	0.34	0.18	0.01	0.00	0.05	0.65	0.08	
p-value (Kurtosis)																					

Table 21: Martix Correlation Calculations using Pearson Methods for Cement Materials

Pearson Correlations	V 51	Cr 52	Mn 55	Fe 57	Co 59	Ni 60	Cu 63	Zn 66	Ca 69	As 75	Sr 88	Mo 98	Cd 111	Te 130	Ba 138	Tl 205	Pb 208	Bi 209	U 238	
V 51	1.0000																			
Cr 52		1.0000																		
Mn 55			1.0000																	
Fe 57				1.0000																
Co 59					1.0000															
Ni 60						1.0000														
Cu 63							1.0000													
Zn 66								1.0000												
Ca 69									1.0000											
As 75										1.0000										
Sr 88											1.0000									
Mo 98												1.0000								
Cd 111													1.0000							
Te 130														1.0000						
Ba 138															1.0000					
Tl 205																1.0000				
Pb 208																	1.0000			
Bi 209																		1.0000		
U 238																			1.0000	

Pearson Probabilities	V 51	Cr 52	Mn 55	Fe 57	Co 59	Ni 60	Cu 63	Zn 66	Ca 69	As 75	Sr 88	Mo 98	Cd 111	Te 130	Ba 138	Tl 205	Pb 208	Bi 209	U 238	
V 51																				
Cr 52		0.0041																		
Mn 55			0.0040																	
Fe 57				0.0005																
Co 59					0.0000															
Ni 60						0.1150														
Cu 63							0.0145													
Zn 66								0.3279												
Ca 69									0.2133											
As 75										0.0010										
Sr 88											0.7290									
Mo 98												0.0432								
Cd 111													0.0004							
Te 130														0.0134						
Ba 138															0.0122					
Tl 205																0.0271				
Pb 208																	0.2883			
Bi 209																		0.0001		
U 238																			0.0014	

Table 22: Martix Correlation Calculations using Spearman Methods for Cement Material

Spearman Rank Correlations	V 51	Cr 52	Mn 55	Fe 57	Co 59	Ni 60	Cu 63	Zn 66	Ga 69	As 75	Sr 88	Mo 98	Cd 111	Te 130	Ba 138	Tl 205	Pb 208	Bi 209	U 238	
V 51	1.0000																			
Cr 52		1.0000																		
Mn 55			1.0000																	
Fe 57				1.0000																
Co 59					1.0000															
Ni 60						1.0000														
Cu 63							1.0000													
Zn 66								1.0000												
Ga 69									1.0000											
As 75										1.0000										
Sr 88											1.0000									
Mo 98												1.0000								
Cd 111													1.0000							
Te 130														1.0000						
Ba 138															1.0000					
Tl 205																1.0000				
Pb 208																	1.0000			
Bi 209																		1.0000		
U 238																			1.0000	

Spearman Rank Probabilities	V 51	Cr 52	Mn 55	Fe 57	Co 59	Ni 60	Cu 63	Zn 66	Ga 69	As 75	Sr 88	Mo 98	Cd 111	Te 130	Ba 138	Tl 205	Pb 208	Bi 209	U 238	
V 51																				
Cr 52		0.0128																		
Mn 55			0.0289																	
Fe 57				0.0289																
Co 59					0.0037															
Ni 60						0.3118														
Cu 63							0.0010													
Zn 66								0.0098												
Ga 69									0.0006											
As 75										0.0073										
Sr 88											0.8325									
Mo 98												0.4500								
Cd 111													0.6500							
Te 130														0.6500						
Ba 138															0.2229					
Tl 205																0.0128				
Pb 208																	0.2345			
Bi 209																		0.0767		
U 238																			0.0604	

0.4.5 Gallium (Ga)

The levels of Ga in the study cement materials were likely to be in trace level and thus, it is decided not to further discuss it.

0.5 Risk Assessment Discussion

As the aim of our study to figure out the risk assessment of presence of heavy metals in marble materials, in this section, risk evaluation of heavy metal based in the previous analytical data are given and discussed.

Enrichment factors of the selected heavy metals were used by normalizing each value of heavy metals to their values reported by Mullers in Table.2. This can offer us an indication of presence of heavy metals in marble materials. It was chosen the upper earth crust shale heavy metal values as reference values (free heavy metal values) for normalization

Geo-accumulation Index can be very helpful to trace back the presence of heavy metals and their chemical environment. It was decided to include this index in the study due to its importance in geo-science and contamination of sediments.

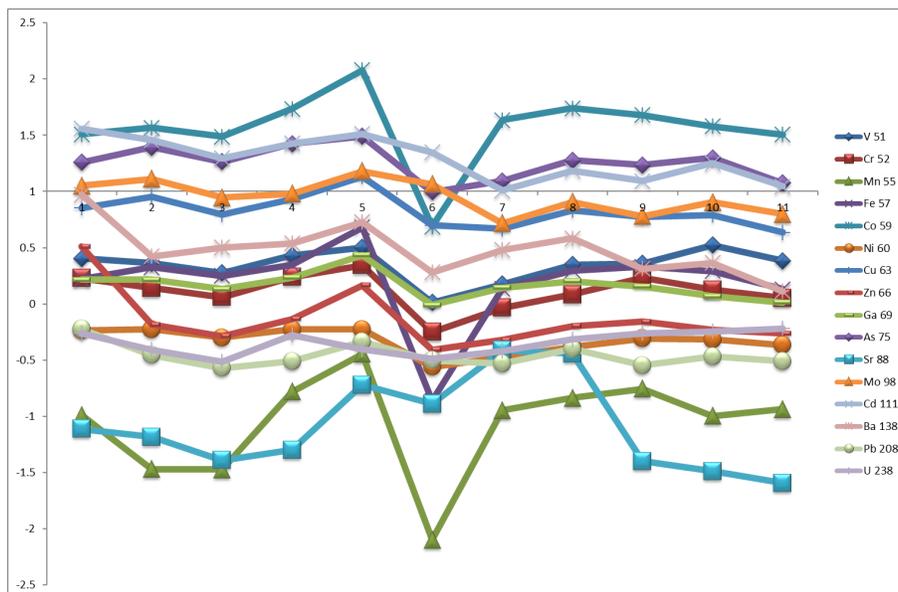


Figure 9: The distribution of Geo-accumulation index in cement material

0.5.1 Chromium (Cr)

The calculated E.F of Cr in cement materials are listed in Table.23. The reported results of E.F were approx. 2 which can be regarded as low as seen in Fig10.

The reported geo-accumulation index in Table.24 were below 0.1 which is regarded unpolluted. Similarly, the other calculated indexes in Table.25 proved cement materials were not contaminated with Cr. Fig.11 showed most of calculated geo-accumulation index for Cr in cement materials were located in negative area.

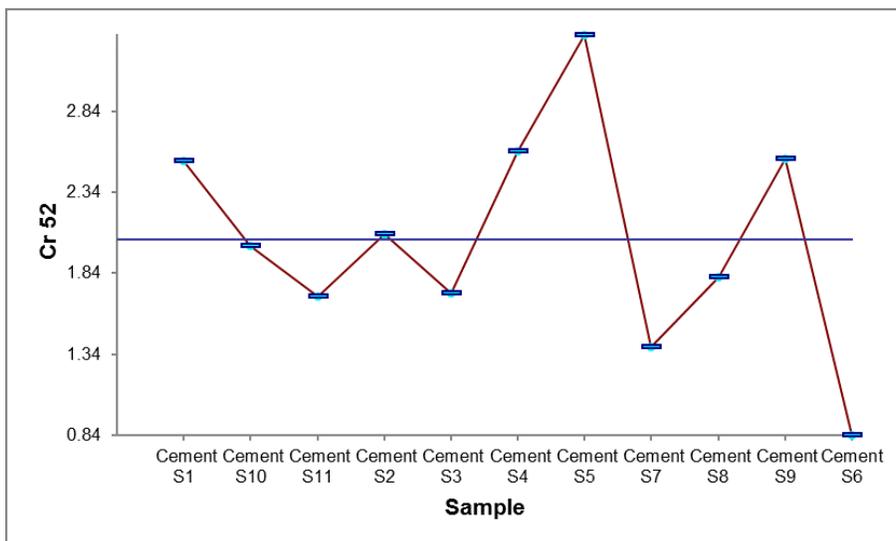


Figure 10: Enrichment distribution of Cr level in marble materials

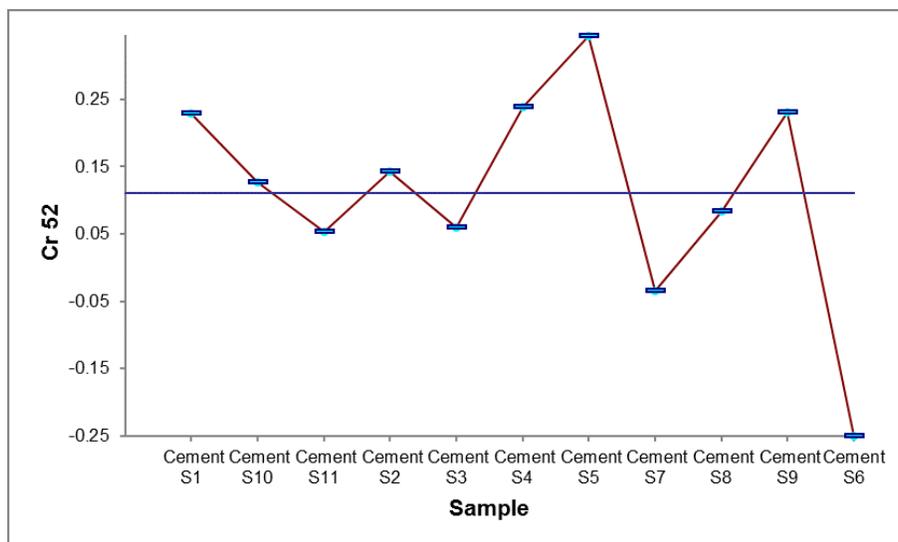


Figure 11: The distribution of Geo-accumulation index of Cr in cement material

0.5.2 Cadmium (Cd)

In Table.23 as well as Fig.12, E.Fs of Cd showed high level of enriched Cd present in marbles. Nevertheless, as stated previously, enrichment factor is not taken as indicator of hazard parameter in pollution science.

The Table.24 showed the calculated geo-accumulation indexes for Cd were less than 1.1 in average. These values of geo-accumulation can offer an answer that marble materials were not contaminated with Cd.

The other pollution indexes calculated in Table.?? proved that Cd levels in marble materials were not polluted.

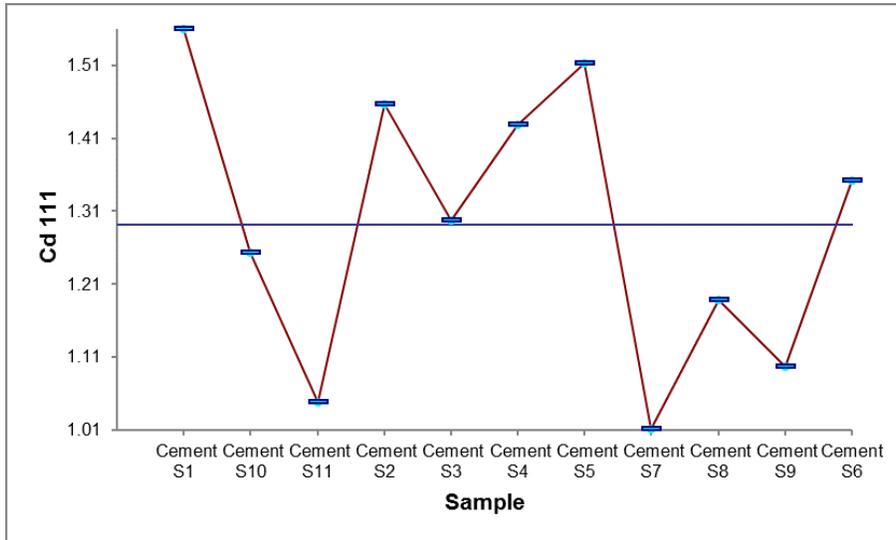


Figure 12: Enrichment distribution of Cd level in marble materials

0.5.3 Lead (Pb)

All the reported values of E.F of Pb in cement materials were below unite meaning cement materials were free of contamination of Pb as proven in Fig14.

Fortunately, all the reported values of geo-accumulation were in negative area as shown by Table.24. The other calculated hazard indexed listed in Table25 as well as Fig.15.

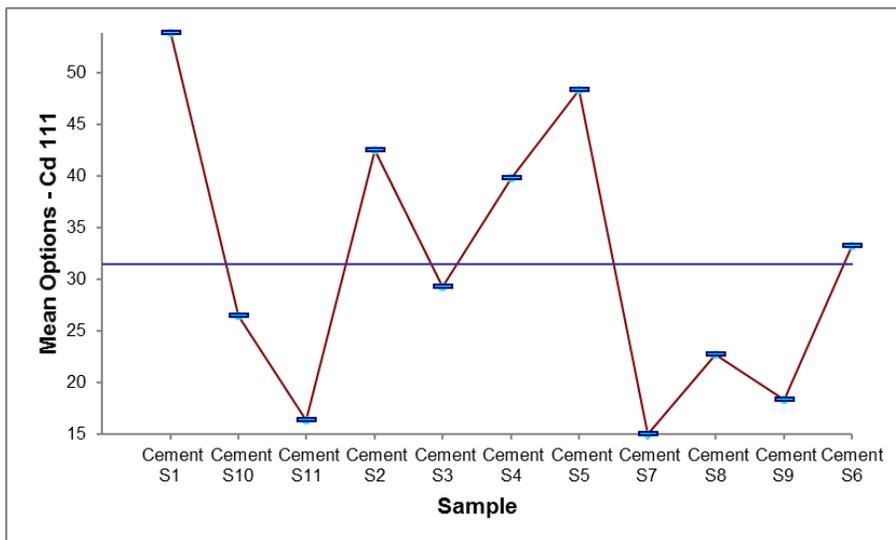


Figure 13: The distribution of Geo-accumulation index of Cd in cement material

0.5.4 Uranium (U)

U is regarded as very low level in cement materials which can be noted through Table.23. The values of E.F were less than 0.8.

Table.24 presents the geo-accumulation index of U in cement materials. The reported values were in negative region proving all cement materials were free of uranium contamination. The other pollution hazard indexes in Table.25 showed the same patterns.

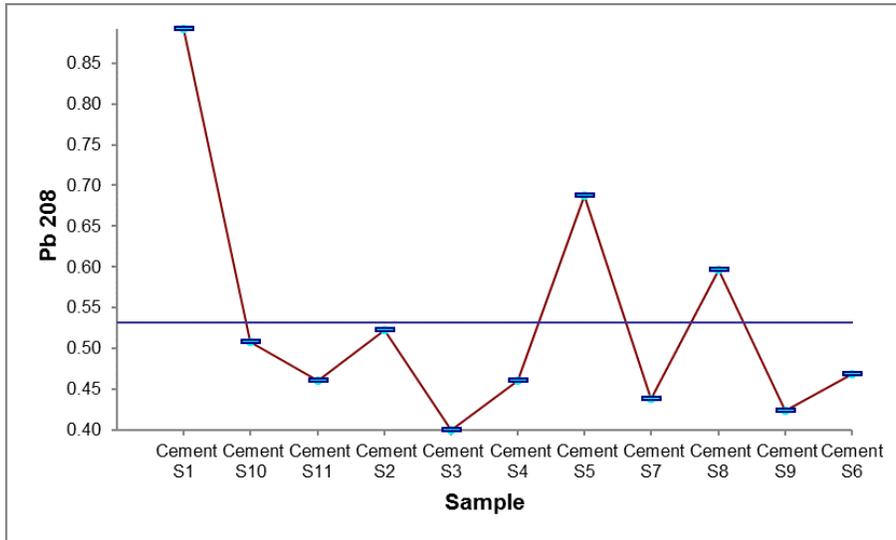


Figure 14: Enrichment distribution of Pb level in cement materials

0.5.5 Gallium (Ga)

The computed E.Fs in Table.23 showed Ga was poorly enriched in cement materials owing the values of E.F were less than the unit.

Similarly, the obtained geo-index in Table.24 proved the analyzed material of cements were uncontaminated with Ga. Also, the other calculated hazard index were very comparable with geo-index. Therefore, it can be stated all studied cement materials were free of Ga contamination.

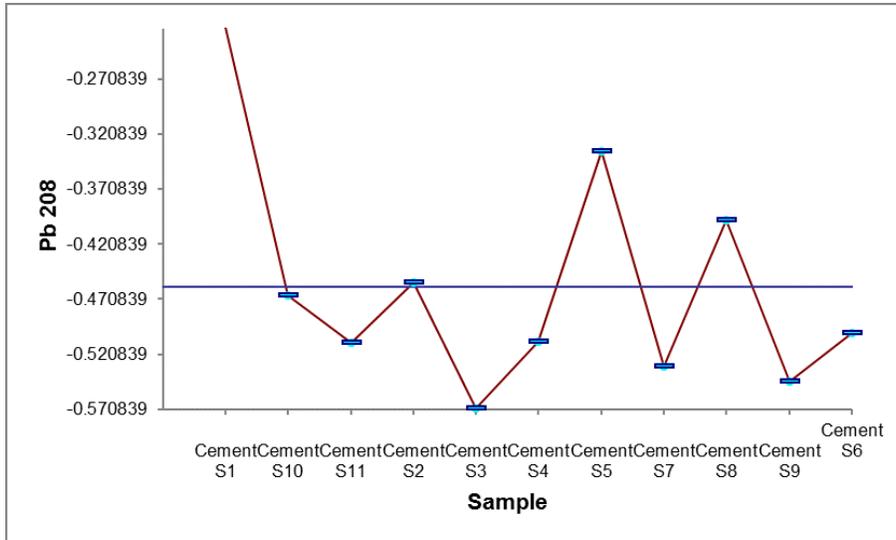


Figure 15: The distribution of Geo-accumulation index of Pb in cement material

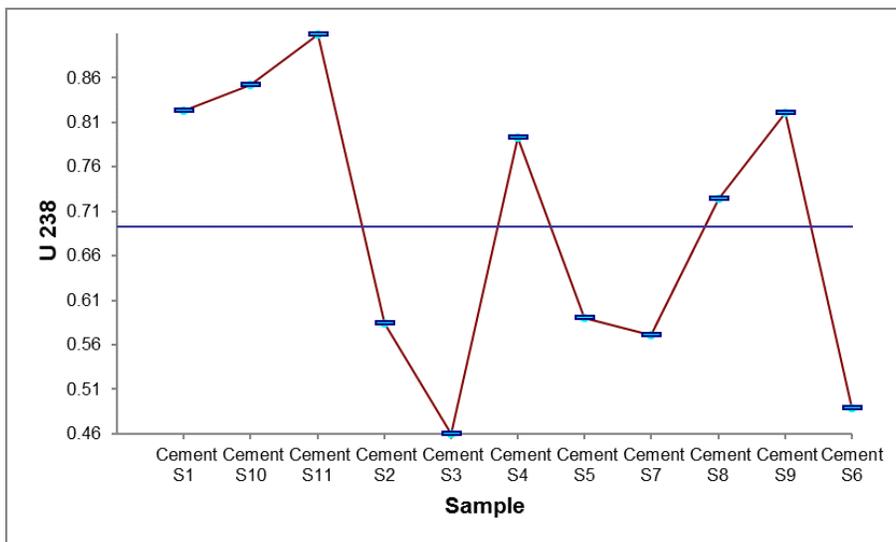


Figure 16: Enrichment distribution of U level in cement materials

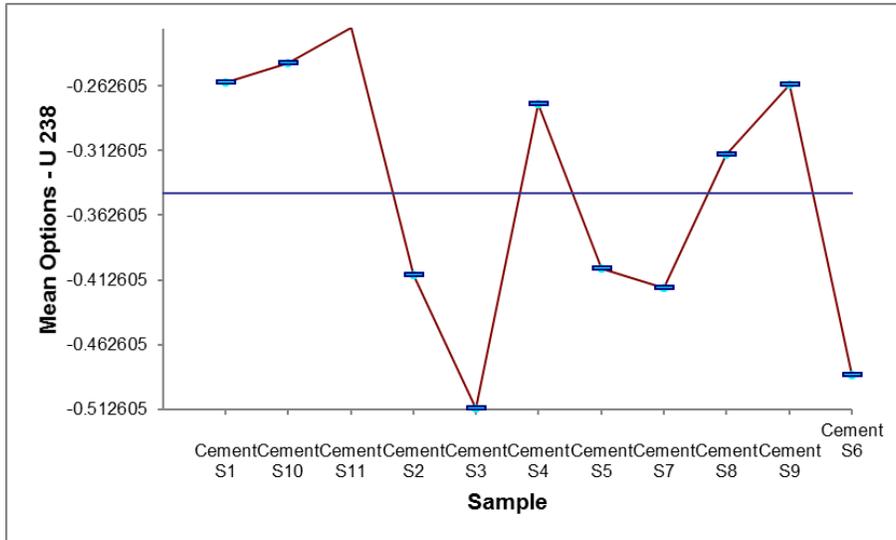


Figure 17: The distribution of Geo-accumulation index of U in cement material

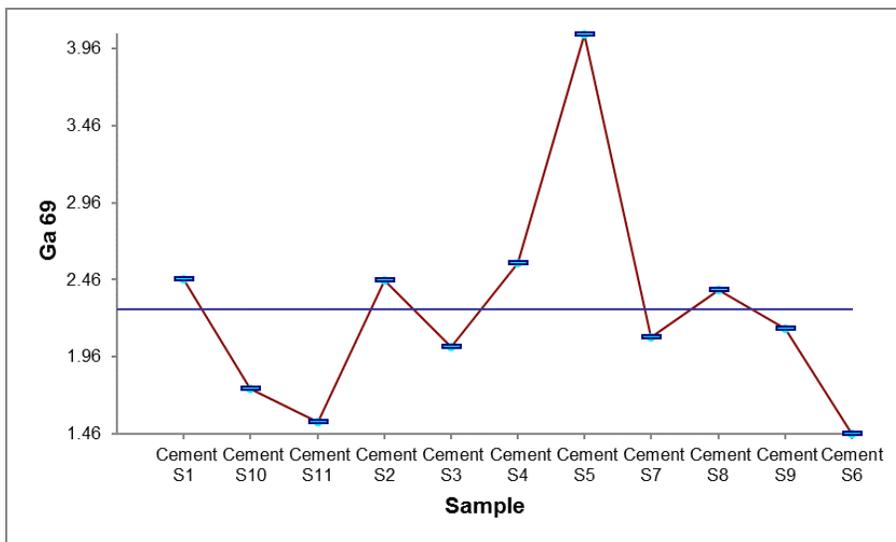


Figure 18: Enrichment distribution of Ga level in cement materials

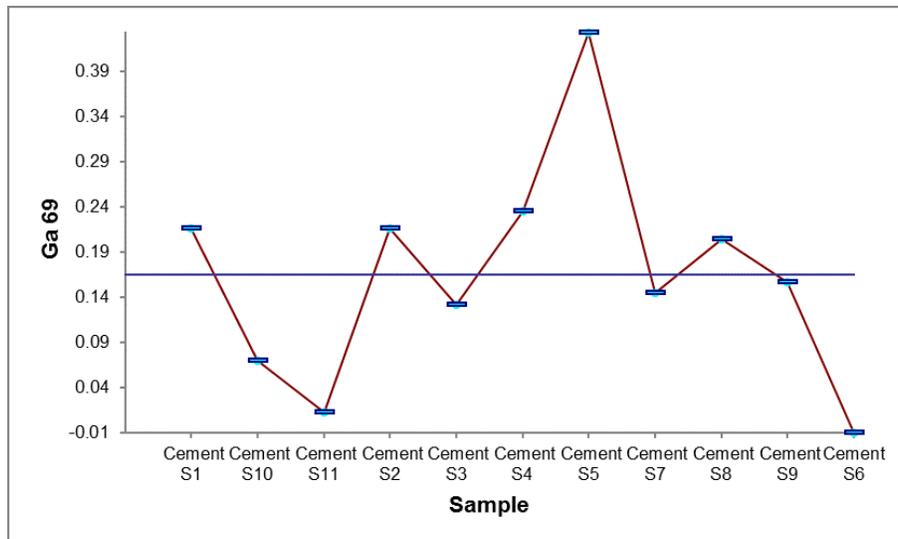


Figure 19: The distribution of Geo-accumulation index of Ga in cement material

Table 23: Enrichment Factor for Cement Materials

	V 51	Cr 52	Mn 55	Fe 57	Co 59	Ni 60	Cu 63	Zn 66	Ca 69	As 75	Sr 88	Mo 98	Cd 111	Ba 138	Pb 208	U 238
Cement S1	3.81	2.54	0.15	2.49	48.39	0.88	10.69	4.84	2.46	27.17	0.12	16.86	54.15	14.06	0.89	0.82
Cement S2	3.45	2.08	0.05	3.17	35.21	0.89	13.47	0.98	2.46	37.01	0.10	19.41	42.77	3.96	0.53	0.59
Cement S3	2.83	1.72	0.05	2.66	46.00	0.75	9.39	0.77	2.03	27.56	0.06	13.24	29.58	4.76	0.40	0.46
Cement S4	4.05	2.59	0.25	3.33	81.24	0.89	12.87	1.10	2.57	39.75	0.08	14.32	40.05	5.18	0.46	0.79
Cement S5	4.75	3.32	0.54	7.18	179.70	0.89	20.31	2.19	4.06	46.36	0.29	22.71	48.57	8.02	0.69	0.59
Cement S6	1.54	0.84	0.01	0.21	7.33	0.41	7.49	0.59	1.46	14.90	0.19	17.43	33.54	2.87	0.47	0.49
A01142 GSC	2.24	1.38	0.17	2.06	64.63	0.51	6.96	0.72	2.09	18.62	0.58	7.81	15.31	4.55	0.44	0.57
A01142 OPC	3.35	1.82	0.22	2.97	52.55	0.62	10.24	0.96	2.39	28.47	0.54	12.07	23.00	3.75	0.60	0.73
A01146	3.44	2.55	0.26	3.21	71.60	0.74	8.94	1.04	2.15	25.72	0.06	9.07	18.64	3.07	0.43	0.82
A01062	5.00	2.01	0.15	2.93	57.08	0.73	9.26	0.88	1.76	29.81	0.05	12.02	26.73	3.48	0.51	0.85
C 0657	3.62	1.70	0.17	2.03	48.13	0.65	6.50	0.82	1.54	17.87	0.04	9.47	16.67	1.94	0.46	0.91
Count	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00
Mean	3.46	2.05	0.18	2.93	67.44	0.72	10.56	1.35	2.27	28.48	0.19	14.04	31.73	3.24	0.54	0.69
Stdev	1.00	0.68	0.14	1.66	42.56	0.16	3.92	1.23	0.70	9.62	0.20	4.65	13.24	3.35	0.18	0.16
Range	3.46	2.47	0.53	6.98	172.38	0.48	13.81	4.25	2.59	31.46	0.54	14.90	38.84	12.12	0.49	0.48
Minimum	1.54	0.84	0.01	0.21	7.33	0.41	6.90	0.59	1.46	14.90	0.04	7.81	15.31	1.94	0.40	0.46
25th Percentile (Q1)	2.83	1.70	0.05	2.06	48.13	0.62	7.49	0.77	1.76	25.62	0.06	9.47	18.64	3.07	0.44	0.57
50th Percentile (Median)	3.45	2.01	0.17	2.93	57.08	0.74	9.39	0.96	2.15	27.56	0.10	13.24	29.58	4.55	0.47	0.73
75th Percentile (Q3)	4.05	2.55	0.25	7.21	81.24	0.89	12.87	1.10	2.46	37.01	0.29	17.43	42.77	5.75	0.60	0.82
Maximum	5.00	3.32	0.54	1.18	179.70	0.89	20.31	4.84	4.09	46.36	0.58	22.71	54.15	14.06	0.89	0.91
95.0% CI Mean	2.79 to 4.13	1.59 to 2.90	0.09 to 0.28	1.81 to 4.04	38 to 96	0.61 to 0.87	9 to 13.20	0.52 to 2.18	1.8 to 2.7	22 to 34.04	0.06 to 0.30	10 to 17.22	17.22 to 40.29	7.40 to 14.06	0.44 to 0.65	0.59 to 0.82
99.0% CI Sigma	0.7 to 1.70	0.47 to 1.19	0.1 to 0.23	0.16 to 2.89	7.4 to 74.06	0.11 to 0.22	7.4 to 6.86	0.56 to 2.16	1.49 to 1.26	7.72 to 10.86	0.14 to 0.33	2.25 to 8.19	23.24 to 53.81	3.34 to 5.85	0.1 to 0.23	0.11 to 0.23
Anderson-Darling Normality Test	0.24	0.21	0.38	1.01	0.96	0.43	0.61	1.97	0.64	0.28	1.20	0.21	0.24	0.92	0.89	0.45
P-Value (A-D Test)	0.69	0.80	0.10	0.01	0.17	0.23	0.08	0.00	0.07	0.38	0.00	0.82	0.32	0.04	0.01	0.37
Skewness	0.57	0.16	1.17	1.07	1.87	0.67	1.65	2.73	1.65	0.43	1.42	0.48	0.37	2.08	1.80	0.70
P-Value (Skewness)	0.59	0.86	0.03	0.03	5.47	0.43	3.36	7.72	4.14	-0.32	0.63	0.45	0.56	0.00	0.01	0.70
Kurtosis	0.23	0.31	3.41	5.04	5.47	0.43	3.36	7.72	4.14	-0.32	0.63	-0.54	-1.11	4.96	3.22	-1.63
P-Value (Kurtosis)	0.70	0.65	0.04	0.01	0.01	0.86	0.04	0.00	0.02	0.94	0.47	0.77	0.34	0.01	0.05	0.08

Table 24: Geo-accumulation Index for cement materials

	V 51	Cr 52	Mn 55	Fe 57	Co 59	Ni 60	Cu 63	Zn 66	Ga 69	As 75	Sr 88	Mo 98	Cd 111	Ba 138	Pb 208	U 238
Cement S1	0.40	0.23	-0.99	0.22	1.51	-0.23	0.85	0.51	0.22	1.26	-1.11	1.05	1.56	0.97	-0.22	-0.26
Cement S2	0.36	0.14	-1.47	0.33	1.57	-0.23	0.95	-0.18	0.22	1.39	-1.18	1.11	1.46	0.42	-0.46	-0.41
Cement S3	0.28	0.06	-1.47	0.25	1.49	-0.30	0.80	-0.29	0.13	1.26	-1.39	0.95	1.29	0.50	-0.57	-0.51
Cement S4	0.43	0.24	-0.78	0.35	1.73	-0.23	0.93	-0.14	0.23	1.42	-1.30	0.98	1.43	0.54	-0.51	-0.28
Cement S5	0.50	0.34	-0.44	0.68	2.08	-0.23	1.13	0.17	0.43	1.49	-0.72	1.18	1.51	0.73	-0.34	-0.40
Cement S6	0.01	-0.25	-2.10	-0.86	0.69	-0.56	0.70	-0.41	-0.01	1.09	-0.89	1.07	1.35	0.28	-0.50	-0.49
Cement S7	0.17	-0.03	-0.95	0.14	1.63	-0.47	0.67	-0.32	0.14	1.09	-0.41	0.72	1.01	0.48	-0.53	-0.42
Cement S8	0.35	0.08	-0.84	0.30	1.74	-0.38	0.83	-0.20	0.20	1.28	-0.44	0.91	1.19	0.58	-0.40	-0.32
Cement S9	0.36	0.23	-0.75	0.33	1.68	-0.31	0.78	-0.16	0.16	1.23	-1.49	0.78	1.09	0.31	-0.55	-0.26
Cement S10	0.52	0.13	-1.00	0.29	1.58	-0.31	0.79	-0.23	0.07	1.30	-1.49	0.90	1.25	0.37	-0.47	-0.24
Cement S11	0.38	0.05	-0.94	0.13	1.51	-0.36	0.64	-0.26	0.01	1.08	-1.59	0.80	1.05	0.11	-0.51	-0.22
Count	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00	11.00
Mean	0.34	0.11	-1.07	0.20	1.56	-0.33	0.82	-0.14	0.16	1.26	-1.08	0.95	1.29	0.48	-0.46	-0.35
Stdev	0.15	0.16	0.45	0.38	0.33	0.11	0.14	0.26	0.12	0.15	0.41	0.15	0.19	0.23	0.10	0.10
Range	1.65	1.59	1.65	1.54	1.39	0.34	0.49	0.92	0.44	0.49	1.18	0.46	0.55	0.86	0.35	0.29
Minimum	0.01	-0.25	-2.10	-0.86	0.69	-0.56	0.64	-0.41	-0.01	1.00	-1.59	0.72	1.01	0.11	-0.57	-0.51
25th Percentile (Q1)	0.28	0.05	-1.47	0.14	1.51	-0.38	0.70	-0.29	0.07	1.09	-1.40	0.80	1.09	0.31	-0.53	-0.42
50th Percentile (Median)	0.36	0.13	-0.95	0.29	1.58	-0.31	0.80	-0.20	0.16	1.26	-1.18	0.95	1.29	0.48	-0.50	-0.32
75th Percentile (Q3)	0.43	0.23	-0.78	0.33	1.73	-0.23	0.93	-0.14	0.22	1.39	-0.72	1.07	1.46	0.58	-0.40	-0.26
Maximum	0.52	0.34	-0.44	0.68	2.08	-0.23	1.13	0.51	0.43	1.49	-0.41	1.18	1.56	0.97	-0.22	-0.22
95.0% CI Mean	0.24 to 0.60	0.03 to 0.23	-0.76 to 0.67	0.45 to 0.67	0.45 to 0.64	-0.76 to 0.64	0.42 to 0.67	0.25 to 0.67	0.03 to 0.23	0.24 to 0.64	-0.36 to 0.79	0.26 to 0.67	0.11 to 0.26	0.11 to 0.26	0.40 to 0.60	0.18 to 0.48
95.0% CI Sigma	0.11 to 0.26	0.11 to 0.26	0.32 to 0.79	0.26 to 0.67	0.23 to 0.69	0.09 to 0.34	0.10 to 0.26	0.18 to 0.34	0.03 to 0.18	0.26 to 0.64	-0.42 to 0.79	0.21 to 0.67	0.03 to 0.26	0.03 to 0.26	0.40 to 0.60	0.18 to 0.48
Anderson-Darling Normality Test	48	34	65	152	103	54	26	101	36	27	40	16	21	23	60	48
P-Value (A-D Test)	0.18	0.44	0.07	0.00	0.00	0.12	0.62	0.01	0.39	0.59	0.30	0.92	0.82	0.76	0.09	0.19
Skewness	-1.20	-0.96	-1.21	-2.36	-1.70	-1.08	0.82	1.87	0.70	-0.23	0.62	-0.06	-0.13	0.67	1.38	-0.38
P-Value (Skewness)	0.07	0.14	0.07	0.00	0.01	0.10	0.20	0.01	0.28	0.71	0.34	0.92	0.83	0.29	0.04	0.55
Kurtosis	1.70	1.63	1.74	7.36	5.43	0.62	0.86	3.61	1.51	-0.58	-0.97	-0.91	-1.33	1.09	1.61	-1.42
P-Value (Kurtosis)	0.19	0.20	0.18	0.00	0.01	0.50	0.40	0.03	0.22	0.74	0.44	0.49	0.21	0.33	0.20	0.17

Table 25: Degree of contamination and Pollution load Index for cement materials

Degree of contamination		Pollution load Index	
V 51	38.09	V 51	3.31
Cr 52	22.55	Cr 52	1.94
Mn 55	2.03	Mn 55	0.13
Fe 57	32.24	Fe 57	2.35
Co 59	741.88	Co 59	54.95
Ni 60	7.96	Ni 60	0.70
Cu 63	116.12	Cu 63	10.01
Zn 66	14.89	Zn 66	1.09
Ga 69	24.98	Ga 69	2.19
As 75	313.23	As 75	26.99
Sr 88	2.10	Sr 88	0.12
Mo 98	154.42	Mo 98	13.35
Cd 111	349.04	Cd 111	29.19
Ba 138	57.65	Ba 138	4.55
Pb 208	5.89	Pb 208	0.52
U 238	7.63	U 238	0.68

0.6 Conclusion

A comprehensive assessment of presence of heavy metals in cement building materials used in Saudi building market was conducted. Over 10 samples were assembled from major cement producers in Saudi Arabia. Quality control measurements were precisely performed to offer us very good reported data with regard to the carried out statics. The reported precision of used reference materials which are matrix-matched was over 93% and relative standard deviation was better than 7%.

In this assessment, the risk indexes indicated the levels of Cr, Cd, Pb, U, Ga concentrations were likely to be insignificant with regard to the critical values reported in literature of sediments in the upper earth crust. The calculation of enrichment factor was located within less Muller scale. Also, the geo-accumulation calculations were in negative values indicating the study cement materials free of heavy metals contamination.

Therefore, using Saudi produced cement materials can be considered safe for workers as well as residents.

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