JJEES
Jordan Journal of Earth and Environmental Sciences
Volume 6, (Special Publication, Number 3), June, 2014
ISSN 1995-6681
Pages 23- 28

High Calcium Ash Incorporated Into Clay, Sand and Cement Mortars Used For Encapsulating of Heavy Metals

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Abstract

Many heavy and toxic metals are found in variable concentrations contained in the High Calcium Ash (HCA) produced by direct combustion of the bituminous limestone. Huge quantities of ash will be produced when bituminous limestone is utilized as energy source for electricity production or retorting process to produce crude oil in Jordan. One of the main serious environmental impact of this ash is the leachability of heavy metals and its potential contamination of the surface and groundwater reservoirs in the catchment area of Wadi Al-Mujieb.

Encapsulation of Lead, Zinc, and Manganese ions were investigated by mixing of HCA with sand, cement and clay (kaolin) mortars. HCA was added with different percentages (e.g. 0%, 3.5% and 10%) to variable ratios of sand-cement-clay mixtures. Beside heavy metal encapsulation analysis; the unconfined compressive strength, water consumption and permeability were carried out for the produced mortars. The results shows that an effective heavy metal encapsulation were achieved with 10% HCA added to 25% clay, 50% sand and 25% cement mixture. Pb and Mn was encapsulated, very low Zn was detected and leached from the mortars. On the other hand, the maximum unconfined compressive strength (16.83 MPa) was reached when 10% HCA was added to the mixture of 25% clay, 25% sand and 50% cement. The permeability was decreasing with increasing HCA, because of the pozzolanic composition of HCA similar to Ordinary Portland Cement (OPC).

Keywords: High Calcium Ash, Heavy Metals, Encapsulation, Compressive Strength, Leaching, Permeability.

1. Introduction

Huge amounts estimated as billions of tons of bituminous limestone are considered as promising reserves to solve the increasing energy demands in Jordan in the foresight future. Extraction of crude oil by retorting and generation of electricity by direct combustion of organic rich bituminous limestone will produce bulk quantities of high alkali ash which is rich in calcium oxide and various heavy metals Abdel Hadi et al. (2008).

Organic-rich rocks such as black shale are potentially hosted economic metal accumulations, and many have been discovered all over the world (Pasava, 1991 a). Moreover, Many studies indicated that black shales are very important host for Platinum Group of Elements (PGE) Pasava et al. (1993). Pasava (1990), reported a higher trace elements concentrations in the Barrandian Upper Proterozoic (Bohemian Massif) accompanied with high organic carbon. This metal enrichment was attributed to the role of organic matter that acts as geochemical reduction barrier for metal precipitation and accumulation. El-Hasan (2008), indicates that XRF analysis for trace elements in shale samples collected from El-Lajjoun, shows moderate contents of trace element enrichments compared to the average shale, where enrichment series is Cd > Mo > U > Cr > Zn > Ni > Cu > V. It seems that the poly-elemental ores sources in black shales became a significance resource for Ni, Mo and precious metals Pasava (1991 a).

The source of these metals is most probably volcanogenic-hydrothermal exhalations. Rimmer, (2004) has used the paleoredox indicators to elucidate the paleo-environmental nature of Devonian black shales at central Appalachian basin. Particularly C-S-Fe analysis and the enrichment of Mo, Pb, Zn, V, Cu, Cr, and Co. Algeo and Maynard (2004) found that trace elements commonly exhibit considerable enrichment in laminated, organic-rich facies, especially those deposited under euxinic conditions. Moreover, previous study showed that Jordanian organic-rich Oil shale contains high amounts of trace and toxic elements such as Mo, V, Cr, Zn and other (El-Hasan, 2008). Han et al. (2014), Found that the concentrations of biogenic elements, implying a genetic relationship between Mo and Ni enrichment and organic matter.

The combustion process of Oil shale is expected to produce huge ash tailing that is considered as hazardous pollution source to the environment due to its friable nature and its enrichment of toxic elements. Among those elements chromium is the most hazardous. Especially Cr(IV) which are highly mobile and could reach water resources easily. El-Hasan et al. (2011), used the synchrotron based XANES analytical procedure and found a potential environmental risk in the form of high oxidation state toxic elements particularly

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the Cr (IV), which was highly increased due to the aerobic combustion process.

Al-Haraheshah et al. (2010) found that surface water at the area of oil shale utilization are facing medium to high potential to pollution risk. The leachability tests showed that there will be substantial amounts of amany pollutants such as Pb, Cr possibly leached out to surface water from oil shale utilizations plant. Abdel Hadi et al. (2008), has tested the change in engineering properties of the limy ash produced from the direct combustion of El-Lajjun oil shale mixed with brown clayey soil from various locations of Jordan. The results revealed a very high increase in the unconfined compressive strength and California Bearing Ratio values.

This work aims to carryout a comprehensive investigation regarding the metallogenesis and leachability of heavy metals and other chemical elements by infiltration of water through dumped ash. The geochemical mobility of these metals accompanied with their toxicity to human and animal paid the attention toward finding suitable technologies or designs aims to maximize the remediation or solidification for these metals. Therefore, in this work two percentages (3.5% and 10%) of HCA is added to the sand-cement-clay mixture. In order to determine the best mix ratio of (Sand-Cement-Clay and HCA) that would show higher compressive strength and at the same time encapsulates higher concentrations of heavy metals within its structure.

2. Materials and Methodology

Unconfined compressive test after 1 and 4 weeks, heavy metals leaching test and the permeability test were carried out for different mixtures.

2.1. Materials

2.1.1 High Calcium Ash (HCA)

Calcium ash was brought from EL-Lajjun area. Ash is the solid waste product of surface combustion of the EL-Lajjun bituminous limestone. The ash has a plasticity index less than 10 limit of 25 according to ASTM D4318 and thus; classified as a non plastic material, with specific gravity equal to 2.39. The chemical composition and the concentrations of major oxides and trace elements of the three representative bituminous limestone samples are given in Table (1). Moreover, the physical properties of the ash samples from El-Lajjun are given in Table (2).

The ashing process was done on the labs of Natural Resources Authority . More than 5 kilogram of gravel size oil shale were burned directly on an aerobic conditions, then smaller amount of samples were completely burned using muffle furnace at different temperature up to 925 ºC. The chemical composition of major oxides of the ash samples compared with standard Ordinary Portland Cement (OPC) are given in Table (3).

Table 1: Chemical composition of the bituminous limestone samples from El-Lajjun

	Sample 1	Sample 2	Sample 3	Average
SiO_2 %	12.2	12.6	13.6	12.8
Al_2O_3 %	2.5	2.7	2.9	2.7
Fe_2O_3 %	1.3	1.8	1.5	1.5
CaO %	25.7	26.9	28.4	27.0
MgO %	0.46	0.45	0.47	0.46
MnO %	0.005	0.005	0.003	0.004
TiO_2 %	0.13	0.14	0.14	0.14
K_2O %	0.5	0.47	0.44	0.47
P_2O_5 %	2.40	2.96	2.42	2.59
Li ppm	5	6	6	6
B ppm	22	22	26	23
V ppm	133	174	154	154
Cr ppm	474	467	534	492
Co ppm	46	48	56	50
Ni ppm	268	241	285	265
Cu ppm	110	124	118	117
Zn ppm	472	507	539	506
As ppm	91	117	87	98
Sr ppm	796	900	817	838
Y ppm	22	20	23	22
Nb ppm	16	20	19	18
Mo ppm	122	160	155	146
Ag ppm	3	4	4	4
Sn ppm	90	100	113	101
La ppm	8	5	5	6
Ce ppm	44	52	57	51
Pb ppm	34	38	41	38
W ppm	23	28	33	28
Zr ppm	661	722	415	599

*Analysis was accomplished by using the coupled plasma technique (ICP).
* Loss on ignition is 51.98 %.

Table 2: Physical characteristics of El-Lajjun bituminous limestone

Physical property	**Sample (1)**	**Sample (2)**	**Sample (3)**	**Average**
Bulk density g/cm^3	1.96	1.94	1.95	1.95
Specific gravity	2.39	2.38	2.41	2.39
Moisture content %	0.9	0.75	1.05	0.9

Table 3: Chemical composition of ash sample compared with standard Ordinary Portland Cement (OPC). The analysis was done using XRF technique.

Oxide Wt. %	Ash Sample	OPC
SiO_2	25.30	23
Al_20_3	2.35	4
Fe_2O_3	1.37	2
CaO	45.21	64
MgO	1.63	2
P_2O_5	5.47	---
Na_2O	0.85	---
TiO_2	0.14	---
MnO	0.02	---

2.1.2 Natural clay

As a source for natural clay, a bulk disturbed brown soil sample was obtained from the vicinity of Al Karak - Mutah area which is located about 130 km south of Amman. Its chemical composition is determined by ICP and listed in Table (4). The sample was tested to determine natural moisture content, grain size distribution, and its classification according to the Unified Soil Classification System (USCS) (Evett & Cheng, 2007) in addition to Atterberg limits. The sample parameters are given in Table (5).

Table 4: Chemical composition of the brown soil determined by using ICP technique.

Oxide	**Wt %**
SiO_2	67.1
Al_2O_3	12.4
Fe_2O_3	7.1
CaO	1.9
MgO	0.8
MnO	0.16
TiO_2	1.7
K_2O	0.8
P_2O_5	0.11
L.O.I	7.5

Table 5: Physical and mechanical properties of brown soil.

Parameter	
Liquid limit (LL)	46.3
Plastic limit (PL)	23.5
Shrinkage limit(SL)	11.7
Plasticity index	22.8
Passing #200%	93.65
Clay fraction %	56.6
Specific gravity	2.64
Unconfined compressive strength Kg/cm^2	6.5
Maximum dry density g/cm^3	1. 88
California Bearing Ratio	4.2

2.1.2.1 Characterization of brown soil

The XRD analysis revealed that quartz and smectites (montmoorillonite) are the major components of the brown soil. The chemical analysis for major oxides was determined using the ICP. The major chemical constituents are given Table (4). Which indicates that SiO_2 is the major constituent, while Al_2O_3 and Fe_2O_3 are present in considerable amounts as compared with the very low CaO content. P_2O_5 is presented in relatively low concentration and the organic matter content is measured as (3%).

The physical and mechanical properties are determined and listed in Table (5). Atterberg limits have revealed that the soil is medium to high plastic clay. The maximum dry unit weight is 1.81 g/cm^3 and the optimum water content is 16% at standard Proctor effort (ASTM D 698).

The soil is classified into A-7-6 according to the American Association of Highway and Testing Organization (AASHTO), and classified as silty clay according to the Unified Soil Classification System (USCS) as shwon in Fig. (1).

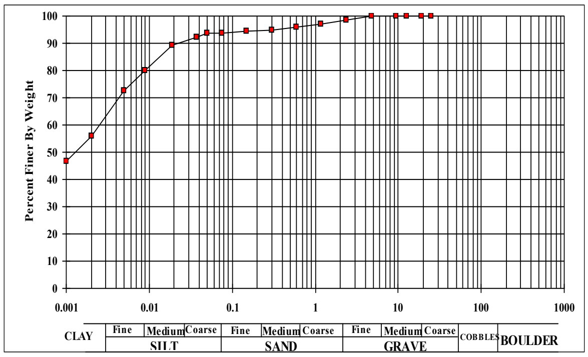

Figure 1: USCS plotting of particle size distribution of the brown soil used in the study

2.1.2.2 Unconfined Compressive Strength of the brown soil

The sample for the test was obtained with optimum moisture content and prepared using a Harvard miniature compaction device and measured the height and diameter of sample. The average of unconfined compression strength of clay equal (353.36 kN/m^2 = 3.60 Kg/cm^2) OR (347.16 kN/m^2 = 3.54 Kg/cm^2).

2.1.3 Sand

Sand was brought from Sweileh area western Amman. Flesh color and has a specific gravity equal to (2.66).

2.1.4 Cement

Ordinary Portland Cement (OPC), type-1 manufactured by Jordan Cement Factories Company was used.

2.2. Analytical methods

The study procedure of heavy metal encapsulation was done for Zn, Mn and Pb only. The conditions during the analytical procedure were done at room temperature. The permeability test was carried out for Sand-Clay mixture with 0, 3.5 and 10% of HCA, because the hydration reaction of the cement continued more than 28 days. The samples of this study were inserted into tight plastic bags during the study period (1 and 4 weeks) for curing purpose. Unfortunately, there is no standard basics to explain or predict the behavior of the mixture when adding the calcium ash so far due to the lack of similar results.

Chemical composition of the HCA samples was investigated using X-Ray Fluorescence machine (XRF-Pioneer F4), manufactured by Broker at the labs of Natural Resources Authority (NRA), Amman. The machine has an attached 72-position sample changer. The pellets were made by fusing 0.8 g of sample powder and 7.2 g of $L_2B_4O_7$ in Au/Pt crucible using a flexor machine (Leco 2000) for 4 minutes at 1200 ºC. The melt was poured in a mold and left to cool to form glass disc. The machine was calibrated with international standards, the analytical error was within ± 5%.

For the unconfined compressive strength test, the samples were obtained from mixtures of sand, clay and cement in percentages given in Table (6). Then HCA was added to mixture with (0.0%, 3.5% and 10%), herethen they will be called HCA0, HCA1 and HCA2 respectively. Three trials were done of each test. Water was added to make the sample saturated and the sample was compacted and prepared using Harvard miniature compaction device. The height and diameter were measured of each sample. The curing of samples is to put the sample in package, this sample contain the moisture content to time of test after one and four week. Because the compressive strength of samples were expected to be high we used the CBR machine.

Table 6: Percentage of mixed sand, clay and cement in the sample

Sample #	Sand (%)	Clay(%)	Cement (%)
1	25	50	25
2	25	25	50
3	50	25	25

3. Results and Discussion

3.1 Mixtures

3.1.1 Compressive strength of Mixture for HCA0

The procedure unconfined compressive strength test was done for mixture without HCA. The result are shown in Fig. (2).

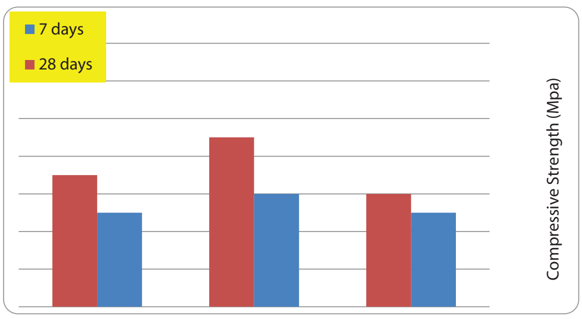

Figure 2: Compressive strength of samples of HCA0

3.1.2 Compressive strength of Mixture for HCA1

The procedure of the test unconfined compressive strength test was repeated but with adding 3.5% of HCA to the mixture, results are illustrated in Fig. (3).

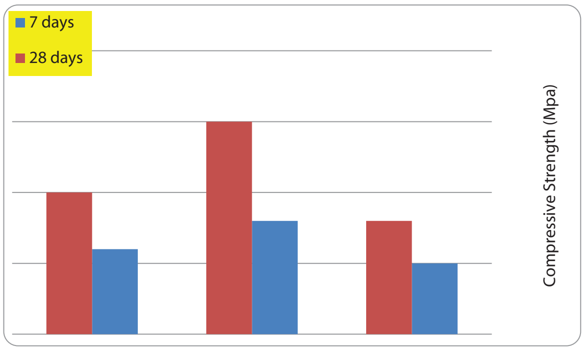

Figure 3: Compressive strength of samples of HCA1

3.1.3 Compressive strength of Mixture for HCA2

The same procedure of the unconfined compressive strength test was repeated with addition of 10% of HCA to the mixture, the results are shown in Fig. (4).

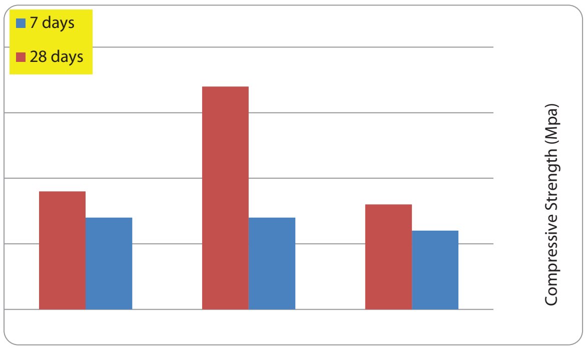

Figure 4: Compressive strength of samples of HCA2

3.1.4 Water Consumption

Table (7) shows that among the best mortars that contain all components (i.e. samples No. 1, 2, and 3), Sample No. 2 was the lowest consuming water mortars. The highest Cement percentages (50%) and equal Clay (25%) and Sand (25%) is the reason for that. However, this sample shows the highest compressive strength as shown in Figs. (2, 3 & 4). In general the effect of HCA percentage on the water consumption was clear and it found to be of proportional trend.

Table 7: Amount of water consumed by the three mixtures.

Sample #	Water (ml) in mixture with 10% high calcium ash (HCA2)	Water (ml) in mixture with 3.5% high calcium ash (HCA1)	Water (ml) in mixture without high calcium ash (HCA0)
1	29	24.9	24.94
2	29.1	28.3	26.5
3	25.2	18.5	20.35

3.1.5 Permeability of Mixture HCA0, HCA1 and HCA2

The permeability test was done for samples (HCA0, HCA1 and HCA2). Permeability coefficient (K) was decreased with increasing HCA content as revealed in Table (8). The highest K value was recorded for the HCA0 sample. Therefore, the lowest value of K was recorded in Sample No. 2 of HCA2, which was equal to 2.7x 10-6 cm/sec. This might be attributed to the mixing ratio of mixture components that affects the water consumption.

Table 8: Result of permeability test for all mixture samples.

Sample No.	h_1 (cm)	h_2 (cm)	K (cm/sec)		
			HCA0	HCA1	HCA2
1	143	133	$1.29*10^{-5}$	$7.74*10^{-6}$	$3.5*10^{-6}$
2	143	133	$3.1*10^{-5}$	$4.74*10^{-6}$	$2.7*10^{-6}$
3	143	133	$2.8*10^{-5}$	$5.17*10^{-6}$	$4.35*10^{-6}$

3.2 Heavy Metal Encapsulation

The samples submerged in the water put into the permeability mold for 24 hours before tested. Table (9) shows the results of the analyzed water. It shows that sample No. 3 has the lowest leached Zn % of mortars of HCA2, while Pb and Mn were not detected in all samples.

The sample of high ratios of cement (50% of mixture) reflects increasing compressive strength with increasing both the percentage of ash and curing period as shown in Figs. (2, 3 & 4). High calcium ash played the role as a cementing binder of binding for sand so it increased the mixture compressive strength. The sample with mixed ratio (25 % sand, 25 % clay, 50 % cement) has the maximum compressive strength of (16.83 Mpa) of HCA1, there is no big difference if compared with samples of HCA2 mortars. While the sample with mixed ratio (50% sand, 25% clay, 25 % cement) of HCA2 has highest ability to encapsulation the metal ions. Where Mn and Pb were not detected and has the lowest Zn content released to the solution. However, the mixture sample that proved the test result with high compressive strength of (16.83 Mpa) and proper encapsulation of heavy metals from solution was with mixed ratio (25% sand, 25 % clay, and 50% cement) of HCA1. Shawabkeh and Mahasneh (2004), had studied the encapsulation of Lead ions in Sand-Cement-Clay mixture, and assured the ability of such mixture with mass percentages of 25% sand, 50% cement and 25% clay to encapsulate metal ions from solution. This mass ratio showed the maximum adsorption capacity toward lead with high compressive strength.

El-Hasan et al. (2011) found that oil shale ash produced from aerobic combustion is composed mainly from Calcite and Quartz beside clay, gypsum and apatite as gangue minerals. Such assemblage is considered as composite of OPC and clay. Moreover, the HCA has a pozzolanic composition similar to OPC, which reacts with the alkali portion of the mixture to produce self-cementaceous compounds. Eventually, an increase in HCA would increase the compressive strength, which is similar to the increase of OPC to the mixture. This might be attributed to the fact that HCA act as the role of OPC, therefore it enhances the compressive strength of mixture. And therefore, sample No. 2 of HCA2 is showing the higher compressive strength because of its higher cement content and this would explain the reverse relationship between the HCA and permeability.

Moreover, there is no relationship between permeability and water consumption. Which can be explained as HCA increased it needs more water for mixing, this was obvious from the proportional relation between HCA and water consumption as shown in Table (7).

Table 9: Result of permeability test for all mixture samples.

Sample No.	Zn (ppm)	Mn (ppm)	Pb (ppm)
1	0.68	Nd	Nd
2	0.53	Nd	Nd
3	0.38	Nd	Nd

4. Conclusions

Before starting this study we were expecting a negative results on compressive strength and water consumption after adding the high calcium ash to the mixture. But the research outputs revealed positive results. The encapsulation of heavy metals are acceptable too. The HCA1 and HCA2 with percentages 3.5% and 10% are the best to achieve higher compressive strength. Moreover, the HCA2 (10%) are the better in attain the higher metal encapsulation. Further studies needed to investigate the fate of toxic elements such as Cr, V and As.

Acknowledgemnet

The authors are grateful to the Natural Resources Authority (NRA) for providing the Oil Shale samples and helping in the ashing and chemical analysis procedures. As well we are thankful to Lafarge Cement Factory for providing the OPC.

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