

# Geo Polymerization of Kaolin and Metakaolin Incorporating NaOH and High Calcium Ash

Nafeth Abdel Raman A. Hadi<sup>1</sup>

<sup>1</sup> Al Balqa' Applied University, Jordan

Corresponding author: Nafeth Abdel Raman A. Hadi, Dep. of Civil Engineering, Faculty of Engineering Technology, Al Balqa' Applied University, Jordan. E-mail: nafeth22@yahoo.com

Received: December 2, 2015

Accepted: December 27, 2015

Online Published: January 24, 2016

doi:10.5539/esr.v5n1p67

URL: <http://dx.doi.org/10.5539/esr.v5n1p67>

## Abstract

This research work aims to investigate the possibility to produce Ordinary Portland Cement free construction materials depending on the reactivity of high alkali liquids or solids with rich silica-alumina clay through geo polymerization process. Different mixtures of kaolin, metakaolin, bituminous limestone ash and NaOH were prepared and molded with different ratios. Standard cylindrical samples were prepared from each mixture and cured at ambient laboratory temperature for 28 days to investigate their physical and mechanical properties.

The unconfined compressive strength results of Kaolin-NaOH mixtures have ranged from 19 to 30 kg/cm<sup>2</sup> after 24 hours. The unconfined compressive strength results of kaolin ash mixtures have ranged from 23 to 36 kg/cm<sup>2</sup> at 28 days. The unconfined compressive strength results of ash-metakaolin mixtures have ranged from 32 to 56 kg/cm<sup>2</sup> at 28 days.

Kaolin-NaOH samples revealed various degrees of efflorescence when subjected to wetting and drying conditions, on the other hand, ash-kaolin samples showed efflorescence free surfaces and increasing of strength with increasing the curing time.

**Keywords:** bituminous lime stone ash, kaolinite, metakaolin, NaOH, efflorescence, construction materials

## 1. Introduction

Utilization of some natural resources for different engineering purposes in Jordan as kaolin and high calcium ash waste could be achieved through chemical polymerization reactions or through alkali pozzolanic reaction. Clay can be hardened and transformed into useful construction materials (Abdel Hadi et al., 2008; Alshaaer et al., 2002).

Metakaolin was prepared by heating Kaolinitic clay from Batn el Ghouh deposits at 700 C° for two hours. The burning or calcination temperature of clay affects the pozzolanic reactivity of the resulting product. The clay is in its most reactive state when the calcining temperature leads to loss hydroxyls and results in a collapsed and disarranged structure (Sabir et al., 2001).

The reactivity of metakaolin depends on calcination temperature, it has been found that 700 C° is optimal, calcination below this temperature results in a less reactive material containing more residual kaolinite (Ambrose et al., 1985).

Huge quantities of bituminous limestone are distributed over different locations in Jordan. These rocks are considered as the future energy source in the country. Ash is produced through treating these rocks to squeeze out crude oil by retorting process at 550 C° or direct combustion at 950 C° for electricity production. In both cases ash is produced and considered as one of the major negative environmental impacts (Nafeth et al., 2008). In this research, ash was prepared by direct combustion at 950 C°

Glass sand from Dabbet Hanout, south of Jordan was used as a filler to improve mechanical properties of various mixtures. It is characterized as inert filler in cement-based materials, low price, high stability and resistance to chemical attack. Glass sand is well crystalline and does not include impurities such as organic matter or swelling/shrinking minerals.

Brown sandy silty clay from the vicinity of Amman area was treated by high alkali calcium ash at ambient temperature, unconfined compressive strength and California Bearing Ratio increased dramatically (Nafeth et al.,

2008).

In this research, Batn el-Ghoul kaolin was collected. Batn el-Ghoul kaolin is Ordovician age and located about 65 km south-south east of Ma'an city (<http://www.nra.gov.jo>). It is characterized as fine grained, present as successive layers (Bender, 1974) and mainly composed of hydrous aluminum silicate,  $Al_2Si_2O_5(OH)_4$ .

Different mixtures of kaolin (K0), metakaolin (MK), were activated by NaOH and high calcium ash through various designated mixtures.

Low temperature inorganic amorphous glassy polymer produced by the reaction of metakaolin and alkaline sodium silicate solution below 100 C° was studied by Rahier, et al. (1996 a).

Calcium silicate hydrate (C-S-H) and calcium alumina silicate hydrate (C-A-S-H) formed at ambient temperature were responsible for strength build up in brown clay and clayey marl when treated with high calcium ash (Nafeth et al., 2008).

Inorganic polymers don't use the formation of calcium silica hydrates (C-S-H) for matrix and strength (Sofi, 2007). The increased curing temperatures going up to 105 C° or 130 C°, showed decreased or limited improvements in the material's stability and strength under different conditions for clays activated by NaOH solution (Alshaaer, 2000).

Khoury(2006) concluded that enhancement of the mechanical properties of the geopolymer depends on the particle size of clay, sand and their ratio in the mixture in addition to sodium hydroxide percentage and concentration.

The following work will focus on investigation and evaluation of the physical and mechanical performance of low temperature alkali activated clays from Jordanian kaolin and its calcined product (metakaolin (MK) to produce simple construction items utilizing NaOH and high calcium ash.

## 2. Materials and Testing

Kaolinitic clay from Batn el Ghoul deposits was used. The kaolin sample was crushed and ground using Los Angeles machine and sieved using sieve #100. The passing dry portion was collected and divided into 10 parts. Each part was labeled and stored in tight plastic bags. About 500 g from each portion was heated to a certain temperature to produce calcined kaolin at different temperatures. Four calcined kaolin samples were heated for 2 hours at 500, 600, 700 and 800 C°. The samples were nominated as Mk500, Mk 600, Mk700 and Mk 800 respectively. Silica sand from Dabbet Hanout, south of Jordan was used as a filler to improve mechanical properties of various mixtures. NaOH solution with fixed concentration of 12.35 was used as an alkaline activator for the dissolution of aluminum silicate in kaolin and calcined kaolin (MK) mixtures.

High calcium ash was used as an additive to kaolin and metakaolin mixtures instead of NaOH in some trial mixtures. Ash was prepared by heating bituminous limestone at 950 C° (Nafeth et al., 2008). All mixtures and testing procedures were carried out at ambient temperature. NaOH active Clay was tested after 24 hours while ash treated samples were tested after 28 days.

### 2.1 Chemical and Physical Characterization of Raw Materials

X-ray fluorescence (XRF) was carried out to identify the chemical composition as oxide% for each ingredient. The samples showed major variation in their major oxides content. The results for the raw materials used in various mixtures are summarized in Table 1.

Table 1. X-ray fluorescence of raw materials

	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	SO <sub>3</sub> (%)
<b>Kaolin</b>	49.3	26.2	6.9	0.7	0.18	2.87
<b>Glass sand</b>	99.03	0.43	0.1	0.1	0.0	0.02
<b>Ash</b>	22	2.57	1.22	44.3	2.41	5.8
<b>Metakaolin</b>	59.9	32.3	2.5	1.2	0.5	0.01

All solid ingredients of the mixtures were used at their dry condition. Some physical properties of raw materials are shown in Table 2.

Table 2. Physical properties of raw material

Material	Absorption (%)	Specific gravity	Passing # 200 sieve (%)
<b>Kaolin</b>	-		93
<b>Glass sand</b>	1.1	2.55	3
<b>Ash</b>	1.4	2.46	2
<b>Metakaolin</b>		2.64	90

## 2.2 Mixtures

### 2.2.1 Mixing-Molding and Curing of NaOH–Clay Mixtures

Homogeneous mixtures with different ingredients and proportions were prepared. A controlled speed mixer was used to insure proper mixing of each mixture ingredients.

All mixtures were molded directly after mixing. Cylindrical samples with length/diameter (L/D) = 2.0 were obtained. Each molded sample was labeled and stored into a tight plastic bag away from disturbance to prevent evaporation of NaOH from the sample and hence to insure continuous reaction until testing. It has been found that the NaOH content is very critical for metakaolin-sand mixtures. This is related to the non plastic mixtures. Poor consistency and deformation of the samples was adjusted by adding kaolin.

### 2.2.2 Metakaolin-Kaolin-Sand-NaOH Mixtures

Metakaolin revealed poor cohesion and none plastic behavior, so kaolin (K<sub>0</sub>) was added to metakaolin to improve consistency and cohesion in order to facilitate molding the mixtures into standard cylindrical samples. The optimum calcination temperature for kaolin to get maximum compressive strength will be determined through this set of trials. Metakaolin mixtures were designated as MK followed by calcination temperature.

The ingredients and their proportions in these mixtures are shown in Table 3. All mixtures were mixed under the same conditions and proportions.

Table 3. Metakaolin-Kaolin-Sand-NaOH Mixtures

Sample.	No.	MK(g)	K0 (g)	Sand (g)	NaOH (g)
<b>70</b>	MK-500	25	10	15	11
<b>71</b>	MK-600	25	10	15	11
<b>72</b>	MK-700	25	10	15	11
<b>73</b>	MK-800	25	10	15	11

### 2.2.3 Kaolin-Sand-NaOH Mixtures

Passing 100 sieve of dry of dry kaolin-sand with NaOH were prepared. The target of these trial mixtures is to investigate the effect of calcined kaolin compared with untreated kaolin on the geopolymerization process when both are treated with High alkali NaOH solution. The proportions of the mixtures are shown in Table 4.

Table 4. Proportions of Kaolin-sand-NaOH mixtures

Mixture	K01(g)	Sand (g)	NaOH (g)
<b>K01</b>	25	75	15
<b>K02</b>	50	50	15
<b>K03</b>	75	25	15
<b>K04</b>	100	0	15

### 2.2.4 Metakaolin-Sand-Ash Mixtures

#### 1) Ash-Kaolinite-Glass Sand Mixtures

High calcium ash was used as an additive to kaolin in these mixtures instead of NaOH solution; the mixtures were nominated as K0A1, K0A2, K0A3 and K0A4. Water was added carefully in each mixture until reaching wet plastic state. The mixtures showed good cohesion and consistency before molding. The mix proportions for each trial are shown in Table 5.

Table 5. Mix proportions of kaolin-ash and glass sand

Mixture	K0 (g)	Sand (g)	Ash (g)	Water(g)
K0A1	25	75	10	35
K0A2	50	50	15	50
K0A3	75	25	25	62
K0A4	100	0	50	77

## 2) Metakaolin (MK)–Kaolin-Glass Sand-Ash Mixtures

The purpose of these trials is to verify and compare the effect of replacing kaolin with metakaolin on the physical and mechanical properties of the prepared mixtures. In these trials kaolin was replaced by metakaolin with different proportions in kaolin - glass sand mixtures.

The mixtures were designated as MK1, MK2, MK3 and MK4. The mix proportions are shown in Table 6.

Table 6. Mix proportions of metakaolin-kaolin with sand and ash

Mixture	K0 (g)	MK	Sand (g)	Ash (g)	Water(g)
K0A1	25	0	75	10	35
K0A2	30	20	50	15	50
K0A3	35	40	25	25	62
K0A4	50	50	0	50	77

## 3. Results

Unconfined compressive strength (UCS) of 15 to 30 kg/cm<sup>2</sup> after 24 curing hours were obtained for mixtures with MK prepared at different temperatures. Mixtures with Mk-700 showed the higher compressive strength results as shown in Figure 1.

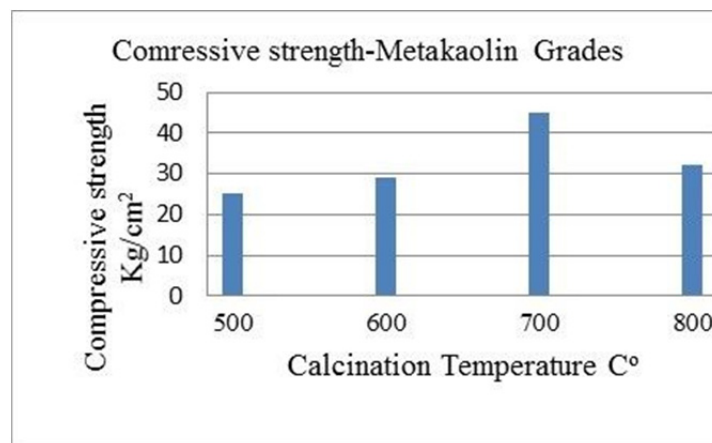
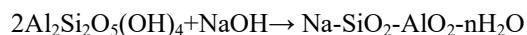


Figure 1. Compressive strength for Mk at different temperatures

The compressive strength results for Kaolin-sand-NaOH mixtures showed lower compressive strength compared with metakaolin mixtures under the same conditions. However the compressive strength was increased with increasing the glass sand content in the mixture until equal weights of kaolin and sand. Strength build up for the tested samples is referred to polymerization reaction of NaOH with silica-aluminum content in the natural kaolin and calcined kaolin according to the following equation:



Compressive strength was not increased with increasing the curing time for 28 days, Strength buildup and geopolymerization reactions took place and completed at early age and did not continue for 28 days to produce extra polymerized materials. Strength build up in these samples is not related to dissolution of silica as in the

case of NaOH-micro silica from siliceous sources Optimum results were obtained by mixing equal weights of kaolin and glass sand with 15% of NaOH by weight of kaolin and glass sand. Glass sand played an important role as inert filler in the mixtures. The results are shown in Figure 2.

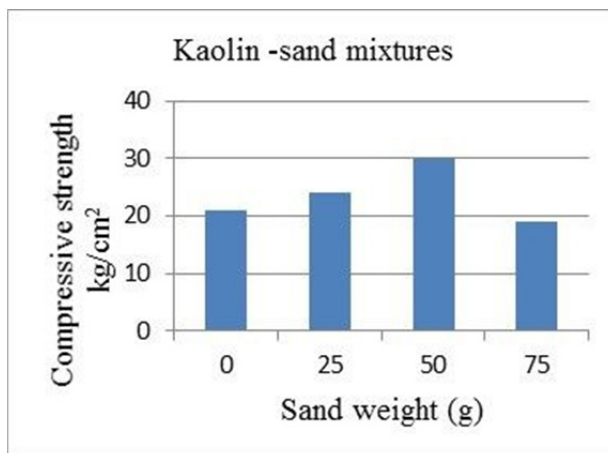


Figure 2. Strength variation with sand content

The problem of fluorescence was obvious on the tested samples when NaOH solution was used as an activator as seen in Figure 3. The ultra fine powdery material forms a semi viscous layer when the samples became with contact with water.



Figure 3. Fluorescence phenomena on NaOH- metakaolin mixtures

The strength of kaolin-ash mixtures showed higher compressive strength results compared with the same mixtures treated with ash instead of NaOH solution.

Geopolymer gel can be observed in different parts of the samples, coexistence of geopolymer gel, and partially unreacted kaolinite layers in the kaolin-glass sand and NaOH mixture is shown in Figure 4A. According to EDX elemental analysis, Figure 4B, this gel is composed from Sodium Aluminosilicates. The geopolymer gel is considered as binding material of the partially dissolved kaolinite layers and other fillers such as glass sand.

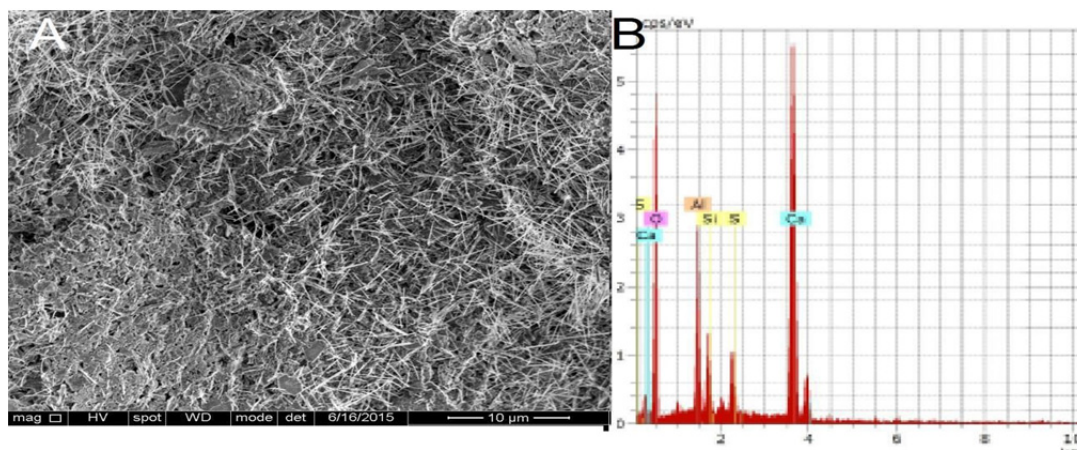


Figure 4. A:SEM image of kaolinite –glass sand and NaOH mixtures; A: distorted kaolinite layers; B: geopolymer gel; B: The EDX analysis of geopolymer gel (region B in Figure 4A)

The reaction in these mixtures is related to alkali pozzolanic reactions that took place between the high calcium ash and the pozzolanic part in kaolin represented by  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ . The alkali pozzolanic reactions are time dependent and strength builds up with increasing curing time which may extend to 90 days. Compressive strength results for these mixtures were conducted at 28 days. The results of compressive strength results for kaolin-ash mixtures are shown in Figure 5.

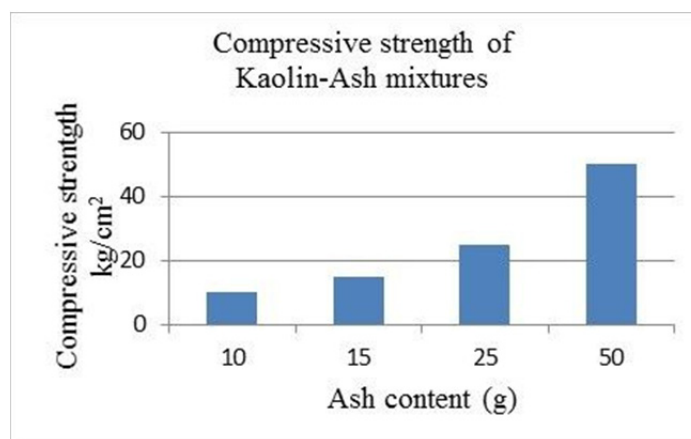


Figure 5. Compressive strength results for kaolin-ash-mixtures

The Compressive strength results showed higher values when Mk700 is used. The destruction of kaolin structure through calcination at  $700\text{ C}^\circ$  increased its reactivity with the rich calcium ash. The compressive strength results for the metakaolin-ash mixtures are shown in Figure 6.

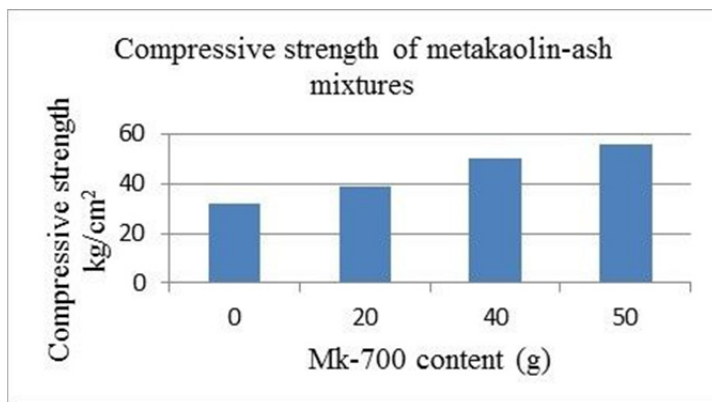


Figure 6. Compressive strength of Mk-700 mixtures

Scanning electron microphotographs in Figure 7A shows the fiber structure of the ash mixtures.

The fibers indicates the C-S-H and C-A-S-H, Figure 6B, shows the EDX of crystals with fibrous structures which is responsible for the strength build up in ash mixtures

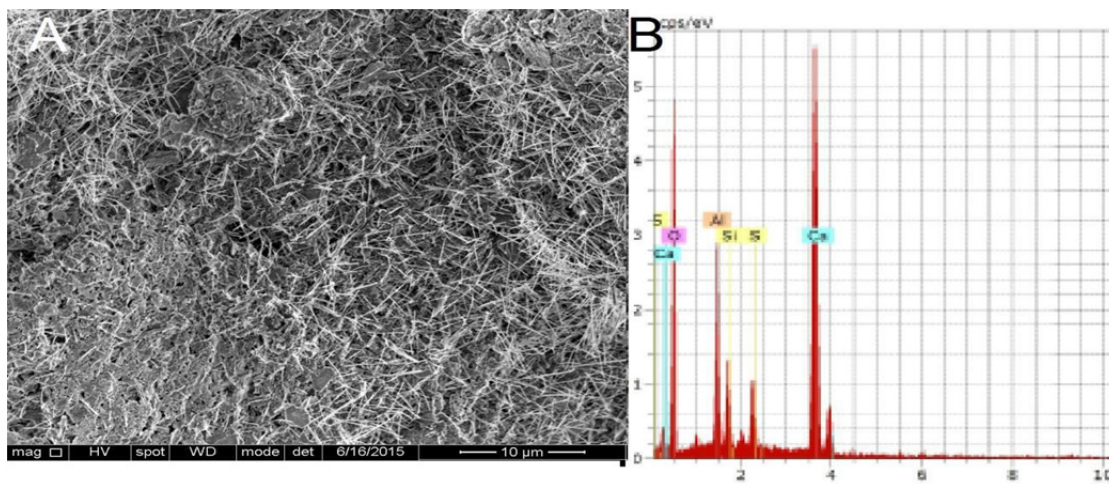


Figure 7. A) SEM image of K0-A geopolymer; B) the EDX of crystals with fibrous structure

Efflorescence disappeared on the surfaces of the tested samples. as shown in Figure 8. This is related to complete reaction and the consumption of the CaO through bonding with silicates and alumina to produce strong  $\text{CaO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O}$  and  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot n\text{H}_2\text{O}$  respectively in the mixtures.



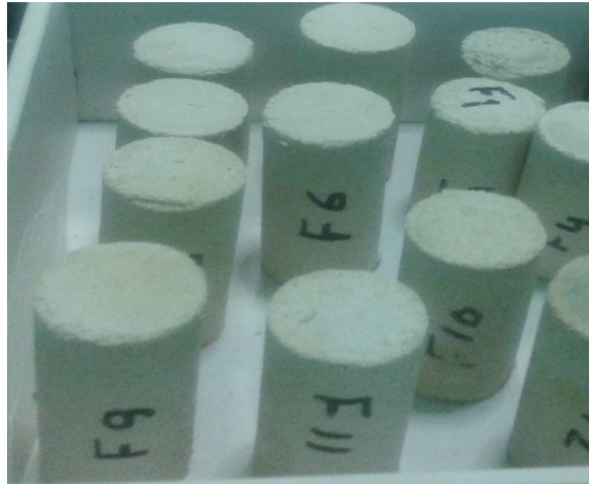


Figure 8. Efflorescence free samples in Mk-ash mixtures

#### 4. Discussion

Intensive research work concerning the production of green low cost construction materials have been carried out by different authors. NaOH activated kaolin showed variable compressive strength results at early ages. Strength buildup in these mixtures is mainly related to the formation of sodium aluminum silicates and sodium zeolite phases which are characterized as strong phases. Loss of strength and efflorescence were obvious features of these samples if they are subjected to wetting and drying cycles regardless of the dry curing time

Compressive strength increased from 36 to 56 kg/cm<sup>2</sup> when kaolin was replaced partially with metakaolin, this is related to higher reactivity of ash with aluminum silicate in the calcined kaolin. Dissolution of un reacted or free NaOH crystals through wetting followed by water evaporation through drying leads to accumulation of salts on the surfaces of the samples. Successive wetting and drying cycles lead to more dissolution of NaOH and more voids and hence decreasing of compressive strength. For post utilization of such materials, loss of strength through wetting and drying is considered as obstacles.

High calcium ash geopolymers showed higher compressive strength results when they used instead of NaOH if the samples are normally compacted and cured at laboratory ambient temperature. The bituminous limestone ash is rich in CaO; the weight percent of CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> are 44%, 22%, 2.57 and 1.22% respectively. It means that the used ash is composed of two parts, an alkali part represented by CaO and pozzolanic part represented by SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> as revealed by the XRF analysis. An alkali pozzolanic reaction will proceed at ambient temperature upon the addition of water similar to the hydration reaction of

Ordinary Portland cement to produce Calcium Aluminum Silicates (C-A-S) and Calcium

Silicate Hydrate (C-S-H). So the bituminous limestone ash is considered as a self cementitious material bonding the mixture ingredients. The compressive strength results of the ash mixtures showed an increasing trend with increasing of ash content and curing time. This is related to the increase of C-S-H and C-A-S-H as a cementing material in the mixtures. Successive wetting and drying did not cause efflorescence or decrease the compressive strength of the samples since no dissolution of the cementing materials.

#### 5. Conclusions and Recommendations

Compressive strength results are not the only factor for the determination of quality of construction materials. Stability under various moisture conditions, safe chemical composition and cost of production are major factors.

Utilization of the bituminous limestone ash as a self cementitious material instead of high alkali for geopolymerization of kaolinite is recommended to produce low cost, safe and stable construction materials as masonry bricks and similar items. Geopolymerization of pozzolanic clays utilizing high alkali NaOH is not recommended from the engineering point of view to be used as construction materials due to the following results:

1-The efflorescence phenomenon on the surfaces of product if utilized as masonry block or where there is a need for plastering works, the bonding characteristics of the geopolymer with cement mortars is poor.

2-The strength of the tested polymers is based on dry conditions. The geopolymers are sensitive



to moisture content variation and compressive strength decreases through increasing of moisture content.

3-High alkali NaOH is dangerous to hold, mix and it is irritate for labors to handle the product due to salt accumulation (efflorescence) on the geopolymer surfaces.

### References

- Abdul Hadi, N. (2008). Stabilization of the phosphatic wastes using high calcium ash In Jordan. *Canadian Journal of Civil Engineering*, 35, 1-7.
- Abdul Hadi, N., Khoury, H., & Kharabsheh, M. (2008). Utilization of bituminous limestone ash from EL-LAJJUN area for engineering applications. *Acta Geotechnica*, 3, 139–151. Retrieved from <http://www.nra.gov.jo>
- Abdul Hadi, N., Khoury, H., & Kharabsheh, M. (2009). Utilization of bituminous limestone ash from EL-Lajjun area in production of lightweight Masonry block. *Acta Geotechnica*, 4(3), 215-222.
- Alshaer, M. (2000). *Stabilization of kaolinitic soil from Jordan for construction purposes*. Vrije Universiteit Brussel, Brussels, Belgium.
- Alshaer, M., Cuypers, H., & Wastiels, J. (2002). *Stabilization of kaolinic soil for construction purposes by using mineral polymerization technique*. Proceedings of the 6<sup>th</sup> International Conference on Concrete Technology for Developing Countries, 3, 1085-1092.
- Ambroise, J., Murat, M., & Pera, J. (1985). Hydration reaction and hardening of calcined clays and related minerals: V. Extension of the research and general conclusions. *Cement and Concrete Research*, 15, 261-268.
- ASTM D2166 / D2166M. (2013). *Standard Test Method for Unconfined Compressive Strength of Cohesive Soil*. ASTM International.
- Benachour, Y., Davy, C. A., Skoczylas, F., & Houari, H. (2008). Effect of a high calcite filler addition upon microstructural, mechanical, shrinkage and transport properties of a mortar. *Algeria. Elsevier Ltd. Cement and Concrete Research*, 38(6), 727-736.
- Bender, F. (1974). *Geology of Jordan*. Borntraeger. Berlin, Germany.
- Khoury, H. (2006). *Industrial rocks and minerals in Jordan*. Publications of the University of Jordan, Amman.
- Rahier, H., Van Mele, B., Biesemans, M., Wastiels, J., & Wu, X. (1996a). Low-temperature synthesized aluminosilicate glasses. Part I Low-temperature reaction stoichiometry and structure of a model compound. *Journal of materials science*, 31(1), 71-79.
- Sabir, B. B., Wild, S., & Bai, J. (2001). Metakaolin and Calcined Clays: Metakaolin and calcined clays as pozzolans for concrete. *Cement and Concrete Composites*, 23(6), 441–454.

### Copyrights

Copyright for this article is retained by the author(s), with first publication rights granted to the journal.

This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).