Experimental Studies on Effects of Alkaline Solution Type on Behavior of Zeolite & Red-Mud Based Geopolymer Mortar

El-Kholy, S.A.[1], Hasan, H. El Deen[2], Asran, A. Gomaa [3], Abd Al-Kader, A. Al Sayed [4]

[1]Prof, Civil Engineering Department, Al Azhar University, Cairo, Egypt,
[2]Civil Engineering Department, Banha University, Shoubra, Egypt,
[3]Prof, Civil Engineering Department, Al Azhar University, Cairo, Egypt,
[4] Teaching Ass., Civil Engineering Department, Higher Technological Institute, 10th of Ramadan City, Egypt,
ahmed_abdelkader_86@hotmail.com

Abstract: This paper presents an experimental study on the effective usage of Red-Mud (Aluminum slag) and Zeolite in geopolymer mortar. Potassium and Sodium based alkaline activators with sodium Meta silicate (Na_2SiO_3) were used for different mix proportions. The parameters in this study were the NaOH or KOH solution molarity and the Na_2SiO_3/NaOH, KOH ratio. Three NaOH or KOH concentrations (8, 12, and 16 molars) were inspected. The results showed that the studied parameters significantly affected the properties of the produced geopolymer mortars. Pozzolanic activity, Workability, setting time and accelerated mortar bar test (AMBT) were investigated and presented.

[El-Kholy, S.A., Hasan, H. El Deen, Asran, A. Gomaa, Abd Al-Kader, A. Al Sayed. **Experimental Studies on Effects of Alkaline Solution Type on Behavior of Zeolite & Red-Mud Based Geopolymer Mortar.** *Life Sci J* 2018;15(4):31-39]. ISSN: 1097-8135 (Print) / ISSN: 2372-613X (Online). http://www.lifesciencesite.com. 4. doi:10.7537/marslsj150418.04.

Keywords: Zeolite, Red Mud (Aluminum slag), Pozzolanic activity, Geopolymer mortar, Alkaline-Activators; Alkali-aggregate reaction.

1. Introduction:

Geopolymers are a new class of three-dimensional inorganic polymer obtained by reaction of an alumino-silicate material (e.g., metakaolin, fly ash, natural pozzolan, zeolite, etc.) with an alkaline solution. The basic monomer unit is called sialate (O-Si-O-Al-O), which consists of SiO4 and AlO4 tetrahedral linked alternatively by sharing all the oxygen [1]. Also, Geopolymer is an inorganic alumino-hydroxide polymer synthesized from predominantly silicon and aluminum materials of geological origin and industrial by-product material such as FA (with low calcium, Class F) [7]. In the present scenario, it is not sufficient to replace the cement partially. A need is felt to develop an alternative binding material to cement which is having less foot print than cement [2].

Geopolymer is a term that was firstly used by Ahmed et, al. and Davidovits [4] to describe the alumino-silicate binders, which formed by the alkali activation of a source material that is rich in content of aluminum and silicon. These binders have superior properties that promote them as cement replacement materials [3].

Geopolymerization is based on alumino-silica chain. It is a polymeric reaction that takes place between certain amount of alumina and silica in the presence of a strong alkaline solution (i.e., NaOH, KOH, etc.). Geopolymerization is often referred as alkali activation, transforms the amorphous ingredients of materials into a composite that have strong binding property [5].

Geo-polymerization process, although not fully understood, may be divided into three main phases; namely dissolution of Si and Al species found in the raw materials through the effect of hydroxide ions followed by condensation of precursor ions into monomers and finally polymerization of monomers into three dimensional polymeric structures. These three steps can either take place simultaneously or concurrently with each other. Water is produced through the polymerization process as discontinuous a nono-pores in the paste. Water plays no role in the chemical reaction; it merely provides workability and initial reaction medium to the geopolymer [6].

Alkali-aggregate reaction (***AAR***) is a prejudicial reaction that occurs in OPC structures in the presence of reactive aggregates (with amorphous or poorly crystallized silica) if the amount of alkali is too high. As geopolymers are alkali-activated materials, the risk of damage due to AAR need to be assessed. The study of alkali-aggregate reaction in OPC is carry out by the use of accelerated test described by standards as ASTM C1260 [8] (which consists of in accelerating the reaction by curing mortar samples at 80^{o} C in 1 M NaOH) [9].

AAR is a rapid test method applied to determine the potential alkali-silica reactivity (***ASR***) of aggregates by testing mortar specimens which called "Accelerated mortar bar test (***AMBT***)" as a test method. This test is a rapid, since the results are available in two weeks, but the conditions of the tests are relatively harsh and one can wonder if this test is really representative of what can be found in real structures.

Use of supplementary cementitious materials (SCM) such as fly ash, blast-furnace slag and silica fume is usually considered as a mitigating measure against the ASR expansion of concrete. However, the effectiveness of an SCM in reducing the ASR depends on the type and dosage of the SCM, and the type of the reactive aggregate. The effectiveness of an SCM depends on its alkali content, with higher alkali content exhibiting higher expansion. Ashish and Prabir [12] stated that expansion of mortar specimens containing reactive aggregates was reduced by the use of fly ash as a partial replacement of cement. Fly ash can significantly reduce the alkalinity of pore solution resulting in a reduction of the ASR. The addition of reactive aggregates in powder form with the binder can also reduce the ASR as the powder acts as a pozzolan and reduces the alkalinity of the pore solution [12].

2. Experimental Programme:

2.1 Materials

2.1.1 Zeolite

Zeolite was obtained with specific gravity ***2.15 g/cm³***, volumetric weight was ***1.08 g/cm³***, specific surface area was ***6150 cm²/g*** and the soundness was ***1 mm***. The particle size distribution of Zeolite is shown in Fig. 2. It is off-white in colour and substantially lighter than Portland cement. The chemical composition of Zeolite is shown in Table 1; while its physical properties are given in Table 2.

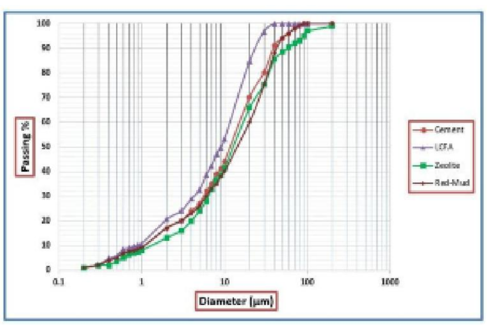

Fig. 2: particle size distribution

2.1.2 Red-Mud (Aluminum slag)

Red-Mud (Water – Cooled aluminum slag) was obtained with specific gravity is ***2.65 g/cm³***, volumetric weight is ***1.18 g/cm³***, specific surface area is ***5200 cm²/gm*** and the soundness was ***1.12 mm***. The particle size distribution of Red-Mud is shown in Fig. 2. It is dark-grey in colour. The chemical composition of Red-Mud is shown in Table 1; while its physical properties are given in Table 2.

Table 1: Chemical composition of constituent materials

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO
Zeolite	0.66	0.02	12.14	64.79	0.08	0.55	Nil	3.21	3.6
Red-Mud	0.65	2.27	56.8	23.6	0.45	1.18	0.8	0.61	6.18
Oxides	**TiO_2**	**MnO**	**Fe2O3**	**ZnO**	**ZrO_2**	**BaO**	**CuO**	**L.O.I***	
Zeolite	0.44	Nil	4.06	Nil	Nil	Nil	Nil	10.1	
Red-Mud	2.29	0.06	2.99	0.14	0.12	0.72	0.11	0.79	

2.1.3 Ordinary Portland cement (OPC) & Fly ash (FA)

Ordinary Portland cement (CEM - 42.5 N) was used. The specific gravity was ***3.13 g/***cm³, specific surface area was 3000 cm²/gm. Fly ash (FA) was obtained from Sika Egypt for construction chemicals, Egypt. According to ASTM: C618-12a, FA is divided into two distinct categories i.e., low-calcium FA (Class F, CaO < 10%) and highcalcium FA (Class C, CaO > 10%). In this study low-calcium FA was used. The chemical composition of OPC and FA shown in Tables 3, while its physical properties are given in Table 2.

2.1.4 Sand

Natural siliceous sand has been used as fine aggregate with a specific gravity of ***2.54 gm/cm³***, fineness modulus of ***2.60*** and volumetric weight was ***1.81 g/cm³.***

Table 2: Physical composition of constituent materials

Materials	Properties
Zeolite	Specific gravity: 2.15 g/cm³
	Specific surface area: 6150 cm²/g
	Soundness: 1 mm
	Colour: off-white
Red-Mud	Specific gravity: 2.65 g/cm³
	Specific surface area: 5200 cm²/g
	Soundness: 1.12 mm
	Colour: dark-grey
LCFA	Specific gravity: 2.40 g/cm³
	Specific surface area: 3640 cm²/g
	Colour: grey
Cement	Specific gravity: 3.13 g/cm³
	Specific surface area: 3000 cm²/g

Table 3: Chemical composition of OPC and FLY ASH

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO
OPC	0.29	1.24	5.48	20.29	0.17	0.45	63.11
Fly ash	0.43	1.1	27.28	54.72	1.12	1	5.31
Oxides	**TiO_2**	**MnO**	**Fe2O3**	**SO_3**	**Cl**	**CuO**	**L.O.I***
OPC	0.27	0.08	2.85	2.49	NIL	0.02	3.39
Fly ash	1.82	0.1	5.15	1.01	0.01	0.01	6.8

2.1.5 Activator materials/Solution

The alkaline activator used was sodium silicate (Na_2SiO_3), sodium hydroxide (NaOH) and potassium hydroxide (KOH) solution.

Sodium meta-silicate ($Na_2SiO_3.9H_2O$) solution (Na = 16.17%, O = 67.55%, H = 6.38% and Si = 9.88% by mass). Density 2.4 g/cm^3 and melting point 1.088 ^{0}C. It is colourless crystals and molecular weight (M.W) 284.2 g/mole with 98% purity. Sodium meta-silicate also known as high specific gravity glass water.

Sodium hydroxide (NaOH) was in flakes form as shown in Fig. 4 with 96% purity, density 2.13 g/cm^3, melting point 318 ^{0}C and molecular weight (M.W) 40 g/mole.

Potassium hydroxide (KOH) was in flakes form with 85% purity, density 2.12 g/cm^3, melting point 360 ^{0}C and molecular weight (M.W) 56.11 g/mole.

2.2 Specimen preparation and curing

2.2.1 Material preparation

Zeolite and Red-Mud (Aluminum slag) as raw materials are shown in Fig. 6. Obtaining a particle size that pass a # 200 ASTM sieve (75 µm) of Zeolite and Red-Mud by grinding using Retsch grinder. The particle size distribution of Zeolite and Red-Mud is shown in Fig. 2.

(a) (b)

Fig. 6: (a) Zeolite, (b) Red-Mud (Aluminum slag) as raw materials

2.2.2 Activator Solution

A combination of sodium meta-silicate (Glass water) and sodium hydroxide or potassium hydroxide solution was used as an alkaline activator. The parameters involved in this study were the NaOH or KOH solution molarity and the [Na_2SiO_3/NaOH or Na_2SiO_3/KOH] ratios. Three NaOH and KOH concentrations (8, 12, and 16 molarity (M)) were investigated. The Na_2SiO_3/NaOH or KOH ratio was varied between 1 and 2.5 with 0.5 as step.

2.2.3 Fresh mortar and casting

The mortars were prepared with the binder (Cement, low-calcium fly ash ***LCFA***, Zeolite or Red-Mud) to sand ratio of 1 to 3. The alkali solution/ binder ratio of 0.55 was used for all of the mixes. The details of mixes are shown in Table 4 with two phases. The mixing procedures were similar to that specified for the OPC mortars by the ASTM standards C305. Mortar bar specimens of ***25 x 25 x 285 mm*** were cast also. The specimens were cured at room temperature for 24 hours in a relative humidity of at least 95%. After that, mortar bars are put in the solution of 1M NaOH that is already at 80°C for 24 hours. After that, the initial length of mortar bars is measured as the zero reading. Until the next reading, samples remained in 1M NaOH for a period of 14 days according to ASTM C1260 standard [8].

3. Results and Discussion:

3.1 Pozzolanic Activity

Table 4: Mix parameters and proportions of the FA based geopolymer, *Phase 1* with NaOH as alkaline activator

Mix. Designation	OPC (g)	LCFA (g)	Zeolite (g)	Red-Mud (g)	Sand (g)	(Na_2SiO_3 / NaOH)	NaOH Solution (g)			Na_2SiO_3 (g)	W/B
							8 M	12 M	16 M		
C-M	200	—	—	—	600	—	—	—	—	—	0.55
LCFA-M	140	60	—	—	600	—	—	—	—	—	
Z-8Na-1	—	—	200	—	600	1	55	—	—	55	0.55
Z-8Na-1.5	—	—	200	—	600	1.5	44	—	—	66	
Z-8Na-2	—	—	200	—	600	2	36.7	—	—	73.3	
Z-8Na-2.5	—	—	200	—	600	2.5	31.4	—	—	78.6	
Z-12Na-1	—	—	200	—	600	1	—	55	—	55	
Z-12Na-1.5	—	—	200	—	600	1.5	—	44	—	66	
Z-12Na-2	—	—	200	—	600	2	—	36.7	—	73.3	
Z-12Na-2.5	—	—	200	—	600	2.5	—	31.4	—	78.6	
Z-16Na-1	—	—	200	—	600	1	—	—	55	55	
Z-16Na-1.5	—	—	200	—	600	1.5	—	—	44	66	
Z-16Na-2	—	—	200	—	600	2	—	—	36.7	73.3	
Z-16Na-2.5	—	—	200	—	600	2.5	—	—	31.4	78.6	
RM-8Na-1	—	—	—	200	600	1	55	—	—	55	0.55
RM-8Na-1.5	—	—	—	200	600	1.5	44	—	—	66	
RM-8Na-2	—	—	—	200	600	2	36.7	—	—	73.3	
RM-8Na-2.5	—	—	—	200	600	2.5	31.4	—	—	78.6	
RM-12Na-1	—	—	—	200	600	1	—	55	—	55	
RM-12Na-1.5	—	—	—	200	600	1.5	—	44	—	66	
RM-12Na-2	—	—	—	200	600	2	—	36.7	—	73.3	
RM-12Na-2.5	—	—	—	200	600	2.5	—	31.4	—	78.6	
RM-16Na-1	—	—	—	200	600	1	—	—	55	55	
RM-16Na-1.5	—	—	—	200	600	1.5	—	—	44	66	
RM-16Na-2	—	—	—	200	600	2	—	—	36.7	73.3	
RM-16Na-2.5	—	—	—	200	600	2.5	—	—	31.4	78.6	

Phase 2 with KOH as alkaline activator

Mix. Designation	OPC (g)	LCFA (g)	Zeolite (g)	Red-Mud (g)	Sand (g)	(Na_2SiO_3 / KOH)	KOH Solution (g) 8 M	12 M	16 M	Na_2SiO_3 (g)	W/B
C-M	200	—	—	—	600	—	—	—	—	—	0.55
LCFA-M	140	60	—	—	600	—	—	—	—	—	
Z-8K-1	—	—	200	—	600	1	55	—	—	55	0.55
Z-8K-1.5	—	—	200	—	600	1.5	44	—	—	66	
Z-8K-2	—	—	200	—	600	2	36.7	—	—	73.3	
Z-8K-2.5	—	—	200	—	600	2.5	31.4	—	—	78.6	
Z-12K-1	—	—	200	—	600	1	—	55	—	55	
Z-12K-1.5	—	—	200	—	600	1.5	—	44	—	66	
Z-12K-2	—	—	200	—	600	2	—	36.7	—	73.3	
Z-12K-2.5	—	—	200	—	600	2.5	—	31.4	—	78.6	
Z-16K-1	—	—	200	—	600	1	—	—	55	55	
Z-16K-1.5	—	—	200	—	600	1.5	—	—	44	66	
Z-16K-2	—	—	200	—	600	2	—	—	36.7	73.3	
Z-16K-2.5	—	—	200	—	600	2.5	—	—	31.4	78.6	
RM-8K-1	—	—	—	200	600	1	55	—	—	55	0.55
RM-8K-1.5	—	—	—	200	600	1.5	44	—	—	66	
RM-8K-2	—	—	—	200	600	2	36.7	—	—	73.3	
RM-8K-2.5	—	—	—	200	600	2.5	31.4	—	—	78.6	
RM-12K-1	—	—	—	200	600	1	—	55	—	55	
RM-12K-1.5	—	—	—	200	600	1.5	—	44	—	66	
RM-12K-2	—	—	—	200	600	2	—	36.7	—	73.3	
RM-12K-2.5	—	—	—	200	600	2.5	—	31.4	—	78.6	
RM-16K-1	—	—	—	200	600	1	—	—	55	55	
RM-16K-1.5	—	—	—	200	600	1.5	—	—	44	66	
RM-16K-2	—	—	—	200	600	2	—	—	36.7	73.3	
RM-16K-2.5	—	—	—	200	600	2.5	—	—	31.4	78.6	

***e.g.:** (RM-16Na-2) refers to red-mud mixture with 16 mole of NaOH solution and Na_2SiO_3/NaOH ratio is 2, Equation no. 1 was followed to achieve a molarity of NaOH or KOH as shown

The hydraulic reactivities of used geo-polymer binders (Zeolite and Red-Mud) were done using hydrated lime Ca $(OH)_2$ as an alkaline activator. Each ground dried solid was mixed in the dry state with solid: Ca $(OH)_2$ ratio of 80:20, respectively. The hydration process was carried out by mixing ratio of 1:1 by weight. The hydration kinetics were studied by the determination of the remaining (un-reacted) free lime content as well as the chemically combined water content at different ages of hydration (2 and 6 hours and 1, 2 and 7 days). The free lime content remaining during hydration showed in Table 5.

Wt. of chemical hydroxide (gm) = [Molarity x volume of water (L) x specific gravity of chemical hydroxide (gm/mole)]… Eq. 1

From the results obtained, it is evident that the free lime content decreases with increasing age of hydration; this is due to its consumption as a result of pozzolanic reaction with each of the solids under investigation.

Obviously, Red-Mud (Aluminum slag) proved to have very high pozzolanic activity as all the free lime consumed with in the first 6 hours of the hydration process. Meanwhile, Zeolite possess a medium pozzolanic activity as the free lime content is almost consumed after 7 days of hydration.

Table 5: Free lime content remaining during hydration, H means Hours & d means days

Geo-polymer mortar binder	CaO, % 2 H	6 H	1 d	2 d	7 d
Red-Mud	0.5	0.3	0	0	0
Zeolite	8.8	5.8	4.8	3.2	0.41

3.2 Workability of Fresh Mortars

Flow table test was used to measure the mortar flow diameter percentage (%) as an indicator of workability and according to ***ASTM C230 M-08*** [13]. OPC and LCFA mortars with flow table 56% and 63% shows higher workability than zeolite or red-mud geopolymer mortars, this may refer to the higher viscosity of the NaOH, KOH and Na_2SiO_3 alkaline solutions used in different geopolymer mixtures. Table. 6 shows the effect of the NaOH and KOH molarity with different Na_2SiO_3/NaOH, KOH ratios on workability.

Table 6: Effect of NaOH & KOH molarity with different Na_2SiO_3/NaOH ratios

Flow Table (%)	NaOH (M)	8 M				12 M				16 M			
	(Na_2SiO_3 / NaOH)	1	1.5	2	2.5	1	1.5	2	2.5	1	1.5	2	2.5
	Zeolite	48	46	43	43	45	43	43	39	43	40	39	35
	Red-Mud	45	45	39	38	44	40	39	35	38	37	34	31
	KOH (M)	8 M				12 M				16 M			
	(Na_2SiO_3 / KOH)	1	1.5	2	2.5	1	1.5	2	2.5	1	1.5	2	2.5
	Zeolite	43	41	39	36	40	38	37	36	38	36	32	28
	Red-Mud	35	34	31	29	32	31	31	29	29	28	26	24

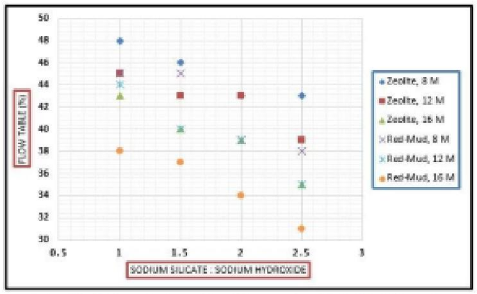

Fig. 9: Effect of the NaOH molarity with different Na_2SiO_3/NaOH ratios on flowability

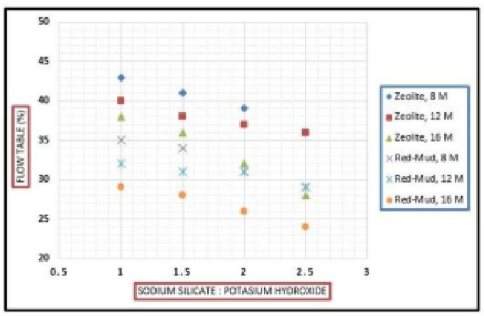

Fig. 10: Effect of the KOH molarity with different Na_2SiO_3/KOH ratios on flowability

Increasing of the NaOH or KOH molarity resulted in reducing of the mortar flowability. Increasing of the Na_2SiO_3/NaOH ratios also, resulted in reducing of the mortar flowability. Also, using KOH solution as an alkaline activator showed workability lower than NaOH solution in different geopolymer mortar mixtures. Fig. 9 and Fig. 10 show the effect of the NaOH and KOH molarity respectively with different Na_2SiO_3/NaOH, KOH ratios on workability.

3.3 Initial and Final Setting Time

The setting time of different zeolite or red-mud geopolymer paste mixtures was measured using Vicat Needle's apparatus under room temperature and according to ***ECP – 203/2007 [15] and Limits of Egyptian specifications 2007/1-4756 [16].***

The results of the initial and the final setting time are listed in Table 7 and shown in Fig. 12 and Fig. 13. The initial setting time for the different zeolite and red-mud geopolymer paste mixtures ranged from 95 - 170 minutes, where initial setting time for OPC and LCFA were (130 min and 155 min.). The final setting time ranged from 260 - 455 minutes, where final setting time for OPC and LCFA were (235 min and 290 min.).

Compared to the OPC which have initial setting time not less than 75 min and have final setting time not greater than 10 hours (600 min), geopolymer materials (Zeolite or Red-Mud) can offer flexible and acceptable ranges of initial and final setting time.

The effect of the NaOH solution on the setting time is shown in Fig. 10 which shows that the initial setting time and the final setting time was increased by increasing of the NaOH solution molarity.

Table 7: Initial and final setting time for the different zeolite and Red-Mud geopolymer paste mixtures

setting time	NaOH (M)	8 M				12 M				16 M			
	(Na_2SiO_3 / NaOH)	1	1.5	2	2.5	1	1.5	2	2.5	1	1.5	2	2.5
Zeolite	Initial (min.)	95	100	110	130	105	110	120	130	110	125	140	155
	Final (min.)	365	380	375	400	380	395	405	420	395	410	425	440
Red-Mud	Initial (min.)	65	75	85	100	80	90	100	100	90	100	110	120
	Final (min.)	260	270	265	275	275	290	300	310	290	305	320	330

setting time	KOH (M)	8 M				12 M				16 M			
	(Na_2SiO_3 / KOH)	1	1.5	2	2.5	1	1.5	2	2.5	1	1.5	2	2.5
Zeolite	Initial (min.)	110	125	125	145	120	125	135	145	125	140	155	170
	Final (min.)	380	395	390	420	395	410	420	440	410	425	440	455
Red-Mud	Initial (min.)	80	90	100	115	95	105	115	115	105	115	125	135
	Final (min.)	275	285	280	290	290	305	315	325	305	320	335	345

In addition, and based on previous studies [15 and 16]; the NaOH solution molarity has a higher effect on the initial setting time more than the final setting time where percentage of increasing for initial setting time is about (10% ± 2) with same ratio of $Na_2SiO_3/NaOH$, while; percentage of increasing for final setting time is about (6% ± 2) with same ratio of $Na_2SiO_3/NaOH$. Also, Increasing the $Na_2SiO_3/NaOH$ ratio has increased the initial and final setting times. This could be related to the higher viscosity of the alkali solution besides the higher Si/Al ratio. It can be considering that the Na content is the main factor affecting the setting time. This may be attributed to the fact that the Na cations work as a reaction catalyst [15].

The higher content of Si will motivate the geopolymerization reactions and hinders the calcium hydration reaction (calcium is already is small amounts in both zeolite and red-mud), which will increase the setting time.

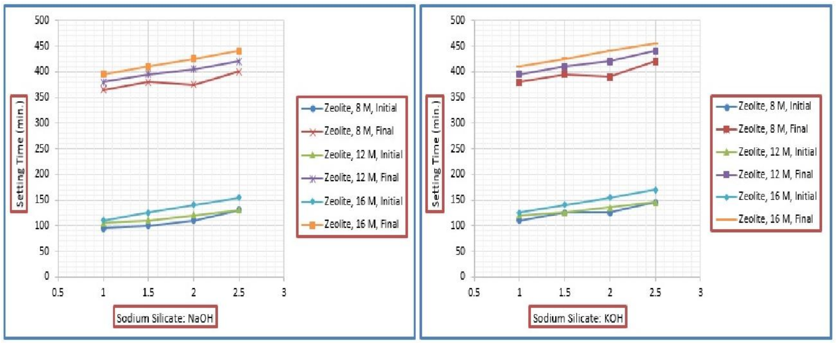

Fig. 12: Effect of the NaOH molarity with different $Na_2SiO_3/NaOH$ ratios and KOH molarity with different Na_2SiO_3/KOH ratios on the setting time of zeolite geopolymer pastes.

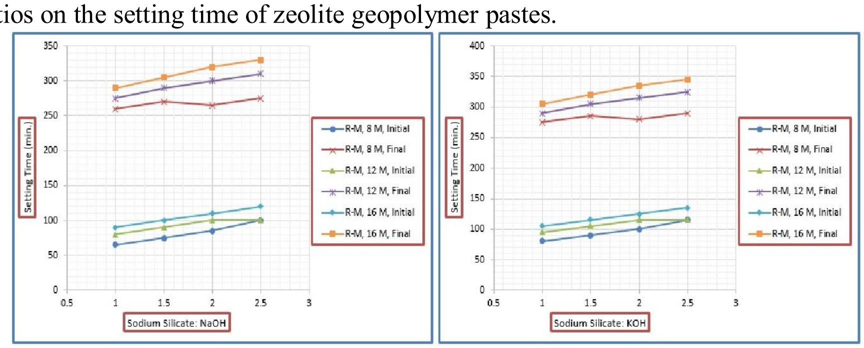

Fig. 13: Effect of the NaOH molarity with different $Na_2SiO_3/NaOH$ ratios and KOH molarity with different Na_2SiO_3/KOH ratios on the setting time of Red-Mud geopolymer pastes.

Also, according to ***ASTM C807 – 08*** [14] the setting time of Geopolymer ***mortar*** mixtures can be calculated to the nearest one minute as follows eq. No. (2)

$$\left(\left(\frac{(H-E)}{(C-D)}\right) \times (C-10)\right) + E$$

Where:

E = time in minutes of last penetration greater than 10 mm,

H = time in minutes of first penetration less than 10 mm,

C = penetration reading at Time E, and

D = penetration reading at Time H.

The results of the setting time for the different zeolite and red-mud geopolymer mortar mixtures are listed in Table 8 and shown in Fig. 14 and Fig. 15.

Table 8: Setting time for the different zeolite and Red-Mud geopolymer morter mixtures

setting time	*NaOH (M)*	*8 M*				*12 M*				*16 M*			
	(Na_2SiO_3 / NaOH)	*1*	*1.5*	*2*	*2.5*	*1*	*1.5*	*2*	*2.5*	*1*	*1.5*	*2*	*2.5*
Zeolite	*Setting time (min.)*	73	73	95	101	74	82	95	104	82	99	113	122
Red-Mud	*Setting time (min.)*	48	50	72	82	57	51	82	86	72	86	105	106

setting time	*KOH (M)*	*8 M*				*12 M*				*16 M*			
	(Na_2SiO_3 / KOH)	*1*	*1.5*	*2*	*2.5*	*1*	*1.5*	*2*	*2.5*	*1*	*1.5*	*2*	*2.5*
Zeolite	*Setting time (min.)*	102	102	133	141	104	115	133	146	115	139	158	171
Red-Mud	*Setting time (min.)*	63	66	95	108	75	67.3	108	114	95	114	139	140

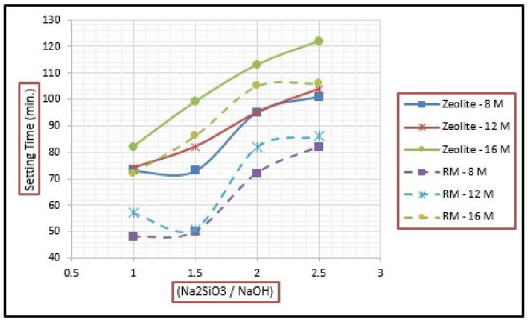

Fig. 14: Effect of the NaOH molarity with different Na_2SiO_3/NaOH ratios on the setting time of zeolite and Red-Mud geopolymer mortar.

Figures 14 and 15 displays that setting time was increased by increasing of the NaOH solution molarity. It can be concluded that the Na content is the main factor which affect on setting time.

At lower NaOH molarity, the geopolymer setting was controlled by leaching of the calcium ions, which is directly available for the reaction compared to the silicon and aluminum ions that are controlled by the dissolution processes.

The comparison between tabulated and based on previous study [16], results showed that, NaOH performed better than KOH as an alkali activator. In general it can be affirmed that the OH– ions act as a reaction catalyst, and the alkaline metal cation acts as a structure forming element.

It is reported that more silicate and aluminate monomers are formed in the presence of NaOH. This may be due to differences in the size of Na+ and K+ ions. It is already reported that K+ ions favor the formation of larger silicate oligomers, and this will play an increasingly significant role when higher silicate activating solutions are used. It is also reported that the Na cations have better zeolitization capabilities in geopolymer forming systems, possibly because they are smaller than K cations and therefore able to migrate easily through the moist gel network.

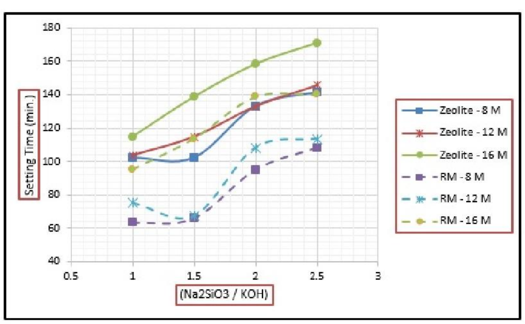

Fig. 15: Effect of the KOH molarity with different Na_2SiO_3/KOH ratios on the setting time of zeolite and Red-Mud geopolymer mortar.

3.4 Mortar bar expansion "Accelerated mortar bar test (AMBT)"

The initial length of mortar bars specimens of 25 x 25 x 285 mm were measured as the zero reading with an equipment (Digital dial gauge). Until the next reading, samples remain in 1M NaOH for a period of time which can be 14 days according to ***ASTM C1260-07*** standard.

The non-mandatory appendix in ***ASTM C1260*** provides guidance as shown in Table 9.

Table 9: ASTM C1260-07 Mortar bar Expansion in 1M NaOH (80°C)

ASTM C1260	
Interpretation	14 days
Innocuous	< 0.10%
Uncertain	0.10 to 0.20%
Potential deleterious	≥ 0.2*%

Expansion values were measured for all the one hundred and forty (140) geopolymer mortars mixtures of this study after 14 days of immersion and also, for each cement, LCFA mortars. Expansion have been measured and tabulated in Table 10.

It can be seen that, the expansion increased gradually with smaller rates with further increases in the molarity of NaOH and Na_2SiO_3/NaOH ratio. On the other hand, the expansion of the specimens with KOH as alkaline activator, increased at relatively smaller rates than NaOH mixtures with further increases in the molarity of KOH and Na_2SiO_3/KOH ratio.

OPC and LCFA mortars with mortar bar expansion 0.002% and 0.016% shows lower expansion than zeolite or red-mud geopolymer mortars, this may refer to the finding of the NaOH, KOH and Na_2SiO_3 alkaline solutions used in different geopolymer mixtures which may react chemicaly with the solution of 1M NaOH (Accelarated heat treatment).

As shown in Fig. 14 and Fig. 15, Zeolite mixturs with NaOH as alkaline activator has a higher effect on AMBT where percentage of increasing for expansion is about (47.6%, 28% and 73.17%) for (8M, 12M and 16M) respectibely. Also, Increasing the Na_2SiO_3/NaOH ratio has increased the mortar bar expansion. Red-Mud mixturs with NaOH as alkaline activator has a higher effect on AMBT where percentage of increasing for expansion is about (58%, 75% and 59%) for (8M, 12M and 16M) respectibely. Also, Increasing the Na_2SiO_3/NaOH ratio has increased the mortar bar expansion. Zeolite mixturs with KOH as alkaline activator has a deacrasing effect on AMBT with increasing of KOH molarity. Where percentage of expansion is about (71%, 30% and 13%) for (8M, 12M and 16M) respectibely. Also, Increasing the Na_2SiO_3/KOH ratio has increased the mortar bar expansion. Red-Mud mixturs with KOH or NaOH as alkaline activator has a same effect on AMBT where percentage of expansion is increasing untill 12M and then start to deacresing to 16M, where percentage of expansion is about (57%, 78% and 61%) for (8M, 12M and 16M) respectibely. Also, Increasing the Na_2SiO_3/KOH ratio has increased the mortar bar expansion.

Table 10: ASTM C1260 Mortar bar Expansion in 1M NaOH (80°C), after 14 days [%]

Expansion	NaOH (M)	8 M				12 M				16 M			
	(Na_2SiO_3 / NaOH)	1	1.5	2	2.5	1	1.5	2	2.5	1	1.5	2	2.5
Zeolite	Expansion %	-0.01	0	0.007	0.021	0.014	0.028	0.049	0.05	0.09	0.119	0.11	0.123
	ASTM Classification	I	I	I	I	I	I	I	I	I	U	U	U
Red-Mud	Expansion %	0.053	0.063	0.067	0.091	0.084	0.088	0.105	0.112	0.077	0.095	0.112	0.130
	ASTM Classification	I	I	I	I	I	I	U	U	I	I	U	U

Expansion	KOH (M)	8 M				12 M				16 M			
	(Na_2SiO_3 / KOH)	1	1.5	2	2.5	1	1.5	2	2.5	1	1.5	2	2.5
Zeolite	Expansion %	-0.01	0	0	0.014	0.009	0.018	0.031	0.03	0.01	0.075	0.07	0.077
	ASTM Classification	I	I	I	I	I	I	I	I	I	I	I	I
Red-Mud	Expansion %	0.039	0.047	0.05	0.068	0.063	0.065	0.079	0.08	0.06	0.071	0.08	0.097
	ASTM Classification	I	I	I	I	I	I	I	I	I	I	I	I

Where: (I) means Innocuous, (U) means Uncertain and (P) means Potential deleterious.

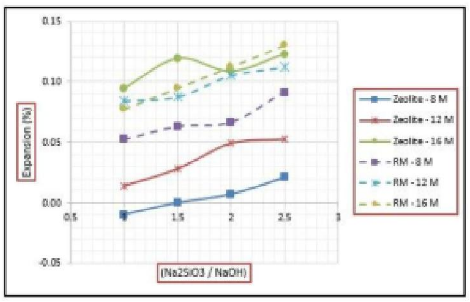

Fig. 14: Effect of the NaOH molarity with different $Na_2SiO_3/NaOH$ ratios on Expansion (%) of zeolite and Red-Mud geopolymer mortar.

The reactivity classification according to Standard ASTM C1260-07 [8] is also listed in Table 10 in order to compare with the AMBT results for different mixtures obtained in this study. Each mixture classified as Innocuous (I), Uncertain (U) or Potential deleterious (P) by using the limits given in Table 9 are shown in Table 10.

Appropriate measures are required to reduce the expansion which classified as uncertain or potential deleterious if reactive aggregates are to be used in concrete.

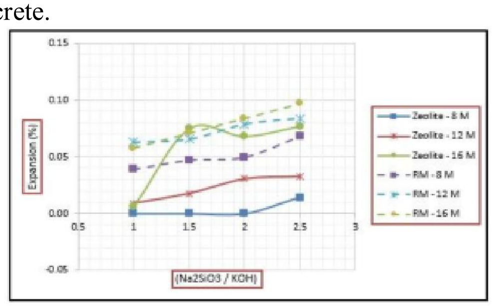

Fig. 15: Effect of the KOH molarity with different Na_2SiO_3/KOH ratios on Expansion (%) of zeolite and Red-Mud geopolymer mortar.

4. Conclusion:

Based on the experimental results the following conclusions could be drawn:

1. The OPC, LCFA mortars show higher workability than geopolymer binder mortars refering to the higher viscosity of the liquids used in geopolymer production.

2. Increasing the NaOH, KOH and Na_2SiO_3 molarity in zeolite or red-mud mixtures geopolymer mortar decreases the workability.

3. The NaOH solution molarity has a higher effect on the initial setting time more than the final setting time.

4. Increasing the Na_2SiO_3/ (NaOH-KOH) ratio has increased the initial and final setting times. This could be related to the higher viscosity of the alkali solution besides the higher Si/Al ratio. It can be considering that the Na content is the main factor affecting the setting time. This may be attributed to the fact that the Na cations work as a reaction catalyst.

5. The higher content of Si will motivate the geopolymerization reactions and hinders the calcium hydration reaction (calcium is already is small amounts in both zeolite, red-mud and LCFA), which will increase the setting time.

6. High specific gravity, high coefficient of viscosity and low water content of the soluble silicate solution are extremely important to exclude unsuitable activator, where means that NaOH is better than KOH as alkaline activator.

7. At AMBT, the NaOH and KOH solution with (8 and 12) M was classified as Innocuous according to Standard ASTM C1260-07.

8. The results showed that changing of the alkaline solution proportions and concentration could provide a geopolymer mixture with a wide range of properties in terms of the workability, setting time, and compressive strength.

9. The NaOH and KOH concentration and the Na_2SiO_3/ (NaOH – KOH) ratio have a similar effect on the workability and setting time of the geopolymers mixes, where increasing these ratios resulted in lower workability and longer setting times.

10. From results, we can considering that NaOH is better than KOH as alkaline activator according to its effect on workability, initial and final setting time and AMBT.

11. Zeolite and Red-Mud can be classified as an acceptable geopolymer material according to results which shown.

References:

1. Jean Noël Yankwa Djobo, Antoine Elimbi, Hervé Kouamo Tchakouté and Sanjay Kumar. "Mechanical properties and durability of volcanic ash based geopolymer mortars" Construction and Building Materials 124 (2016) 606–614.
2. M. Logesh Kumar and V. Revathi "Metakaolin bottom ash blend geopolymer mortar – A feasibility study", Construction and Building Materials 114 (2016) 1–5 .
3. Ahmad B. Malkawia, Muhd Fadhil Nuruddina, Amir Fauzia, Hashem Almattarnehb and Bashar S. Mohammeda "Effects of Alkaline Solution on Properties of the HCFA Geopolymer Mortars" Procedia Engineering 148 (2016) 710 – 717.
4. Davidovits, J., "Geopolymer Chemistry and Applications". 1st. (1979) and 3ed. (2011), Saint-Quentin, France: Institut Géopolymère.
5. C.D. Atis, E.B. Görür, O. Karahan, C. Bilim, S. Ilkentapar and E. Luga "Very high strength (120 MPa) class F fly ash geopolymer mortar activated at different Na OH amount, heat curing temperature and heat curing duration" Construction and Building Materials 96 (2015) 673–678.
6. Amr Ibrahim Ibrahim Helmy "Intermittent curing of fly ash geopolymer mortar" Construction and Building Materials 110 (2016) 54–64.
7. Azizul Islam, U. Johnson Alengaram, Mohd Zamin Jumaat and Iftekhair Ibnul Bashar "The development of compressive strength of ground granulated blast furnace slag-palm oil fuel ash-fly ash based geopolymer mortar". Materials and Design 56 (2014) 833–841.
8. ASTM C1260-07, "Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)".
9. Pouhet Raphaelle and Cyr Martin. "Influence of test conditions on alkali-aggregate reaction in metakaolin-based geopolymer mortar". IJRET: International Journal of Research in Engineering and Technology eISSN: 2319-1163 | pISSN: 2321-7308.
10. Paul Rocker, James Mohammadi, Vute Sirivivatnanon, Warren South and Holcim Australia "Linking New Australian Alkali Silica Reactivity Tests to World-Wide Performance Data". (2016).
11. M. Cyr, R. Pouhet "Resistance to alkali-aggregate reaction (AAR) of alkali-activated cement-based binders", Université de Toulouse, Toulouse, France, Handbook of Alkali-activated Cements, Mortars and Concretes (2015). http://dx.doi.org/10.1533/9781782422884.3.397
12. Ashish Kumer Saha and Prabir Kumar Sarker "Expansion due to alkali-silica reaction of ferronickel slag fine aggregate in OPC and blended cement mortars", Construction and Building Materials 123 (2016) 135–142.
13. ASTM C230 / C230M-14, Standard Specification for Flow Table for Use in Tests of Hydraulic Cement, ASTM International, West Conshohocken, PA, 2014, www.astm.org.
14. ASTM C807-13, Standard Test Method for Time of Setting of Hydraulic Cement Mortar by Modified Vicat Needle, ASTM International, West Conshohocken, PA, 2013, www.astm.org.
15. Ahmad B. Malkawia, Muhd Fadhil Nuruddina, Amir Fauzia, Hashem Almattarnehb, Bashar S. Mohammeda. "Effects of Alkaline Solution on Properties of the HCFA Geopolymer Mortars" Procedia Engineering 148 (2016) 710 – 717.
16. F.N. Okoye a, J. Durgaprasad a, N.B. Singh. "Mechanical properties of alkali activated flyash/Kaolin based geopolymer concrete" Construction and Building Materials 98 (2015) 685–691.

4/3/2018