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Influence of Calcination Temperatures on Microstructures of Alum Sludge and Its Pozzolanic Properties

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ABSTRACT

Background: Pozzolanic activity index of alum sludge is a very important type of material used in the construction industry**. Objective:** The strength development tests based on ASTM C311 are implemented to evaluate the pozzolanic activity index (PAI) of the Treated Alum Sludge (TAS). Nine different mixtures of TAS are selected from calcining temperature that ranges from 100°C to 950°C respectively. Various methods such as Particle Size Distribution (PSD), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF), and thermogravimetric (TGA) techniques are used to run tests on raw and clacined alum sludge. **Results:** The results obtained revealed that after 28 days the PAI of the TAS with ordinary Portland cement performed excellently with it recorded a performance of 75% which is higher than the minimum values specified by ASTM C618**. Conclusion:** It is found that the pozzolanic activity of AS, that has undergone same processing at 750 ºC for 2hours is higher than the pozzolanic activity of other samples.

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INTRODUCTION

Malaysia is one of the many countries where large amounts of alum sludge are easily available. Alum sludge is waste materials generated from treatment plants of drinking water where aluminum salt is used as a coagulant. All water treatment plants do not only produce drinking water but they also generate solid wastes. Large quantities of alum sludge are generated each year from all water treatment plants in Malaysia.

Presently as many as 462 water treatments plants (WTPs) in Malaysia produce up to 11,536 million liters of treated water daily. And many water treatment plants in Malaysia use Aluminium Sulphate and Polyaluminium Chloride as coagulants. An estimated of over 2.0 million tons of water treatment sludge or residue (WTS) is produced annually by the water operators throughout Malaysia(Industry *et al*. 2010). Pozzolanic materials such as fly ash, limestone powder, natural pozzolan, slag, silica fume and alum sludge are used in concrete mixtures to reduce the impact of these materials to the environment and to offset higher consumption of cement (Pourkhorshidi *et al*. 2010), (Colak 2002), (Pourkhorshidi *et al*. 2010) (Shannag and Yeginobali 1995) (Kaid *et al*. 2009)(Donatello, Tyrer, and Cheeseman 2010). Also the application of alum sludge without appropriate management might have adverse impact on human health. ASTM C125 (Specification 2001) defined a pozzolana as “a siliceous and aluminous material which, in itself, possesses little or no cementitious value. But when it appears in finely divided form the presence of moisture, it reacts chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties”. Cement is finely ground powder that, when mixed with water, sets to a hard mass. When the major chemical compounds in cement; C_3S (Tricalcium Silicate, $3CaOSiO_2$), C_2S (Dicalcium Silicate, $2CaOSiO_2$), C_3A (Tricalcium Aluminate, $3CaOAl_2O_3$) and C_4AF (Tetra calcium Aluminate Ferrite, $4CaOAl_2O_3Fe_2O_3$) undergo hydration, the setting and hardening of cement take place. Meanwhile C_3S and C_2S are known to react with

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water (Neville 1995). This reaction forms approximately 70% C-S-H, 20% $Ca(OH)_2$, 7% sulfoaluminate, and 3% in secondary phases. Thus C_3S and C_2S are responsible for the strength of hydrated cement paste. The valuation of natural pozzolan is based on the strength activity index, which is outlined in ASTM C311 (Aggregates 2008) and specified by ASTM C618 (Astm 2010). According to the ASTM C618 specification , the AS mixture should show 75% strength of the control at 7 or 28 days.

In the ASTM C311-2002 test method, the 7 days and 28 days compressive strengths of a mortar involves a 20 % AS mass substitution for cement .This mortar is compared to a control mortar for PAI. The control mortar is prepared with a water-to-cement ratio of 0.484by mass, while the water content of the test mixture is adjusted so that there is an equivalent flow to that measurement for the control mortar. An important factor for consideration is the silica content of the pozzolanic. When any ash from by-products like alum sludge is added to the cement, there is the formation of additional C-S-H is in the hydrated cement matrix that is due to the reaction of silica with $Ca(OH)_2$.however, this additional product increases the density of the matrix and the same time improves the pore structure (Ganesan, Rajagopal, and Thangavel 2007) (Zhang, Lastra, and Malhotra 1996).

Material and Experimental Program:

Ordinary Portland cement (OPC):

The type of cement used in all mortars mixtures is ordinary Portland cement type I (OPC) which conforms to requirements of ASTM C-150 (Specification 2011). table 1 tabulates the physical properties and chemical compositions of this type of cement

Table 1: Chemical composition and physical properties of the cement

Chemical Analysis (%)									Physical Tests	
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	LF	LOI	Specific gravity	Fineness m^2/kg
67.17	20.99	4.60	4.44	2.53	2.98	0.03	0.91	0.63	3.1	328

Alum Sludge (AS):

Raw alum sludge was brought from ABASS plant in Putrajaya, Malaysia. Figure 1 shows the preparation process of RAS and TAS. The dried AS and TAS were grounded using Cross Beater (Rotor Mill SK 100) that is fixed with 14 different aperture sizes ranging from 80 µm to 10mm and a Los Angeles abrasion test machine (LAAT) for obtaining the necessary fineness. It is important that the size of the particle be reduced as this can improve reactivity. It is also necessary to remove unburned organic materials present in AS to avoid the potential negative effects of hydration. Therefore, to take out these adverse substances, drying by oven with105ºC was done for 24 hours. Calcined treatment is used to improve the pozzolanic reactivity. In this process, the AS is heated at a low of temperature of 950 ºC in an electric furnace to avoid glassy phase crystallization and particle agglomeration. The pozzolanic properties might be affected by these two side effects after consumption.

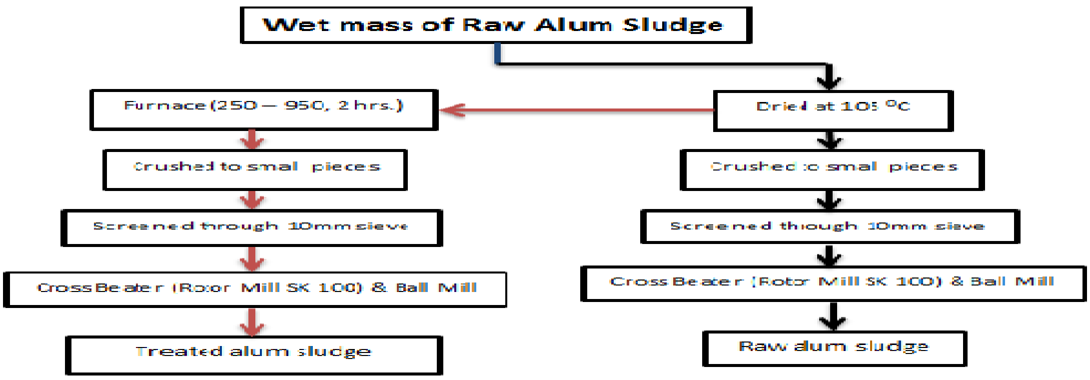


Fig. 1: Preparation process of raw alum sludge (RAS) and treated alum sludge (TAS).

Fig. 2: Picture showing the dried AS and TAS was grounded using Cross Beater (Rotor Mill SK 100) and a Los Angeles abrasion test machine (LAAT) to get the necessary fineness.

Figure 3 shows that the colour of the treated AS after undergoing clacined action. The colour of alum sludge converted from light brown to light orange.

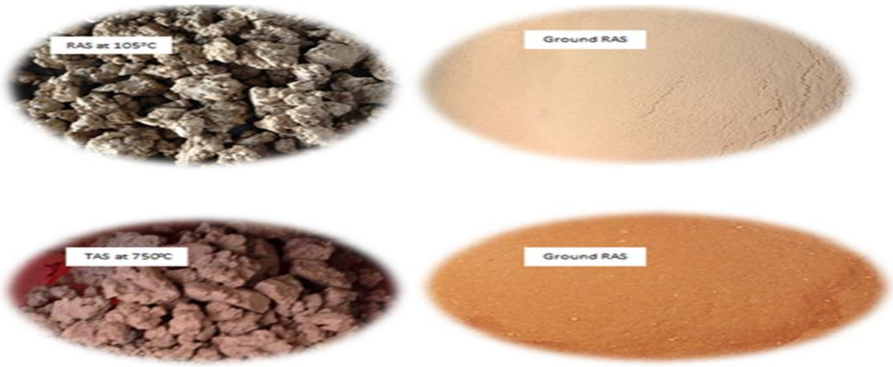


Fig. 3: Picture showing the alum sludge with treatment

Pozzolanic activity Index (PAI):

The implementation of the PA of the AS is centered on the compressive strength developed by the specification of ASTM C311. In this method, the formulae of pozzolanic activity used are: (1) the total amount of main components from silica, alumina and iron oxides (2) the PAI which refers to the compressive strength of a mortar replaced of cement with %20 of pozzolan by weight to the compressive strength of a control mortar as a ratio. For the control mortar, the water to binder ratio is 0.485 by mass (w/b), and water in the control mortar is altered to provide the same flow as the control mortar. Tests are carried out for the mortar with 20 % AS that has partially replaced the OPC. The control mixture is arranged by 500 g of OPC, 1375 g of graded sand and 242 g of water(1:2.75, w/b=0.485). The test mixture is prepared with 400 g of OPC, 100 g of AS, 1375 g of graded sand and the necessary amount of water to get a slump of 105±5% of the control mixture. The mortar paste is then re-mixed for 30 seconds and cast into molds with size of (50 x 50) mm by using vibration table.

Table 2 shows the details of mixtures of this study. Fifty-four cubes are molded. The specimens are maintained at 23(or ± 2ºC) for 24 hours. Then the cube samples are demoulded from their own moulds. (See figure 4). The cubes are then located and kept in soaked lime-water. This is suggested in ASTM procedure that induces for placing the cubes into lime-water bath. The obtained compressive strength is recorded from the average of the three specimens at the specific ages of test. The universal testing machine is used for testing (Model UH-F1000kNI) with1000 KN capacity loading frame. A constant loading rate of 21 MPa/min is used.

Table 2: the details of mixtures used in PAI of treated alum sludge

NO.	*DETAILES OF MIXTURES*	*OPC (g)*	*Mortar sand (g)*	*Pozzolanic (g)*	*Water (g)*
1	CONTROL MIXTURE	500	1375	0	242
2	80% CEMENT + 20% ALUM SLUDGE WITH 100 ^{O}C	400	1375	*100*	*256*
3	80% CEMENT + 20% ALUM SLUDGE WITH 250 ^{O}C	400	1375	100	*255*
4	80% CEMENT + 20% ALUM SLUDGE WITH 350 ^{O}C	400	1375	100	*254*

5	80% CEMENT + 20% ALUM SLUDGE WITH 450 ^{O}C	400	1375	100	*249*
6	80% CEMENT + 20% ALUM SLUDGE WITH 550 ^{O}C	400	1375	100	*245*
7	80% CEMENT + 20% ALUM SLUDGE WITH 650 ^{O}C	400	1375	100	*245*
8	80% CEMENT + 20% ALUM SLUDGE WITH 750 ^{O}C	400	1375	100	*245*
9	80% CEMENT + 20% ALUM SLUDGE WITH 850 ^{O}C	400	1375	100	*245*
10	80% CEMENT + 20% ALUM SLUDGE WITH 950 ^{O}C	400	1375	100	*246*

(SAI) refers to the result of compressive strength of alum sludge specimen divided by result of compressive strength of the control mortar as ratio at specific ages test.

$$SAI = (A/B) \times 100 \quad (1)$$

Where: A is compressive strength of the test alum sludge specimen (MPa): B is compressive strength of the control mortar (MPa).

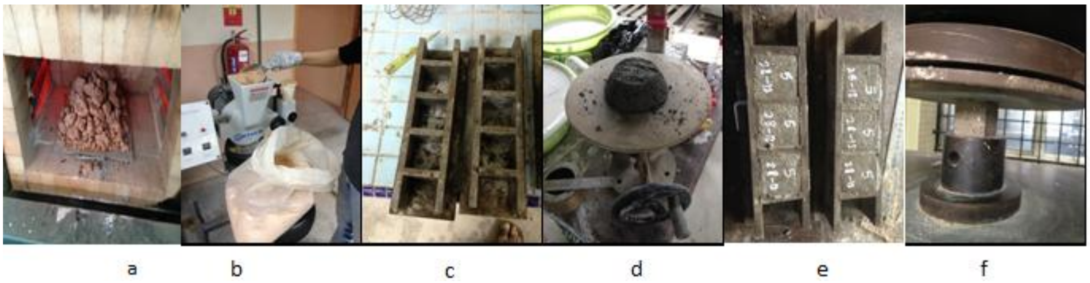


Fig. 4: pictures of preparation procedure of cubes to test

RESULTS AND DISCUSSION

A chemical analysis of calcined AS is conducted using XRF (X-Ray Fluorescence). Table 3 presents the outcomes of experiments. The results revealed the entire fraction of SiO2, Al_2O_3 and Fe2O3 of calcined (AS at 100 ºC), calcined (AS at 250 ºC), calcined (AS at 350 ºC), calcined (AS at 450 ºC), calcined (AS at 550 ºC),calcined(AS at 650 ºC)calcined (AS at 750 ºC) , calcined (AS at 850 ºC)and calcined (AS at 950) ºC are 81%, 85.24%, 83.47%, 90.17% ,78.2%, 93.54%,82.72% and 79.78%, respectively. The X-ray fluorescence was conducted to determine the oxide content. The main component of the treated alum sludge is SiO_2, along with the presence of kaolinite and mica. Figure 5 tabulates the results of XRD of raw alum sludge and treated alum sludge at 750^{0}C. The findings are similar to the other studies on alum sludge (Awab *et al*. 2012) (Tantawy 2015) (Justice 2005) (Cabrera and Rojas 2001) (Sabir, Wild, and Bai 2001).

The distribution of the particle size of the treated alum sludge at 750 ^{0}C is evaluated using Distribution Particle Analyzer (PSD). The specific surface area of TAS is revealed at 1100m^{2}/kg which is higher than the specific area of raw AS which is revealed at (702m^{2}/kg). The calcining process at 750 ^{0}C causes the reduction size of AS particle. The median of the particle size (d50) of TAS is recorded at 11.775um, whereas that of raw alum sludge is recorded at 31.713 um.

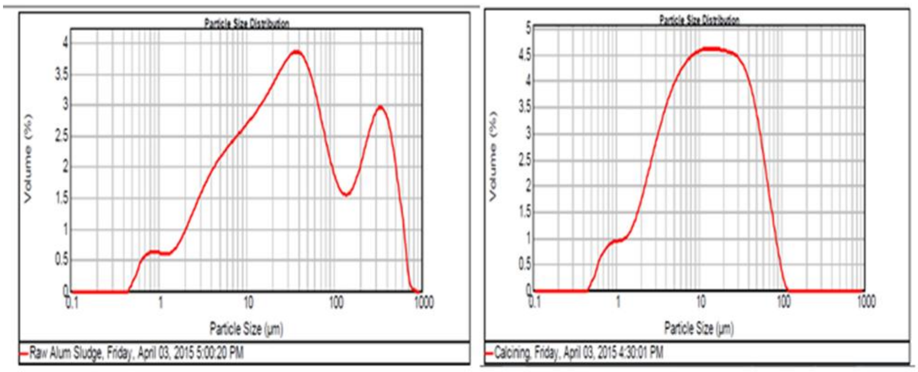


Fig. 6: PSD of raw alum sludge and treated alum sludge by the calcing at 750^{0}C

All the chemical compositions of calcined Alum Sludge wholly obey with the ASTM C618-03 with silica, alumina and iron oxide that are greater than 70%.

Table 3: chemical composition of the treated alum sludge

Oxides%	*Alum Sludge Thermal Curing By 100^{0}C*	*Alum Sludge Thermal Curing By 350^{0}C*	*Alum Sludge Thermal Curing By 450^{0}C*	*Alum Sludge Thermal Curing By 550^{0}C*	*Alum Sludge Thermal Curing By 650^{0}C*	*Alum Sludge Thermal Curing By 750^{0}C*	*Alum Sludge Thermal Curing By 850^{0}C*	*Alum Sludge Thermal Curing By 950^{0}C*
SiO2	*43.29*	45.16%	*43.75*	*47.23*	*41.01*	*48.82*	*42.50*	*41.60*
Al_2O_3	*32.19*	34.65%	*34.14*	*37.68*	*31.40*	*39.42*	*34.72*	*32.54*
Fe_2O_3	*5.52*	5.43%	*5.58*	*5.26*	*5.79*	*5.30*	*5.50*	*5.64*
CaO	*0.17*	*0.17*	*0.17*	*0.18*	*0.20*	*0.22*	*0.17*	*0.19*
MgO	*0.33*	*0.37*	*0,35*	*0.39*	*0.33*	*0.44*	*0.36*	*0.33*
SO_3	*0.22*	*0.07*	*0.24*	*0.18*	*0.17*	*0.09*	*0.10*	*0.12*
Na_2O	*0.10*	*0.07*	*0.07*	-	-		-	-
K_2O	*2.08*	*2.13*	*2.10*	*2.14*	*1.94*	*2.17*	*1.90*	*1.94*
P_2O_5	*0.49*	*0.43*	*0.58*	*0.46*	*0.54*	*0.49*	*0.56*	*0.49*

The scanning electron microscopy (SEM) which produces images is used to investigate the composition of Pozzolan. The SEM recorded at images that are magnifications of 5.00 KX. Figures 7 and 8 show that the particles of raw alum sludge are irregular in shape and non-homogeneous with a porous texture, cement particles and the bond of mortar matrix of control and AS paste. The results show the particle size of the sample alum sludge before and after treatment. The findings indicate no agglomeration of AS particles before the heat treatment.

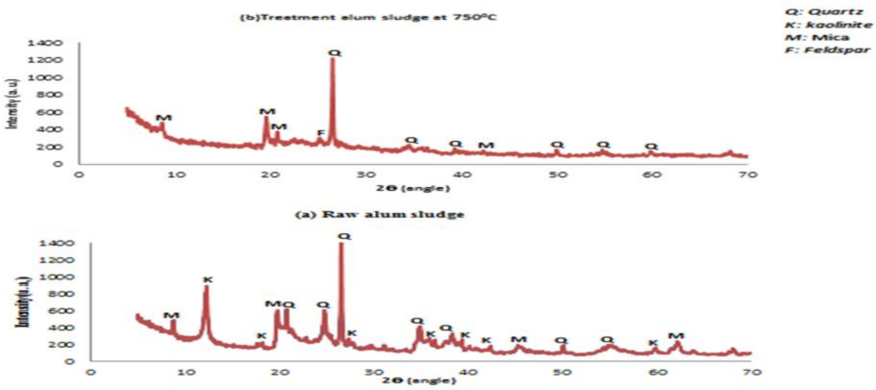


Fig. 7: XRD patterns of (a) raw alum sludge and (b) treatment alum sludge at 750^{0}C

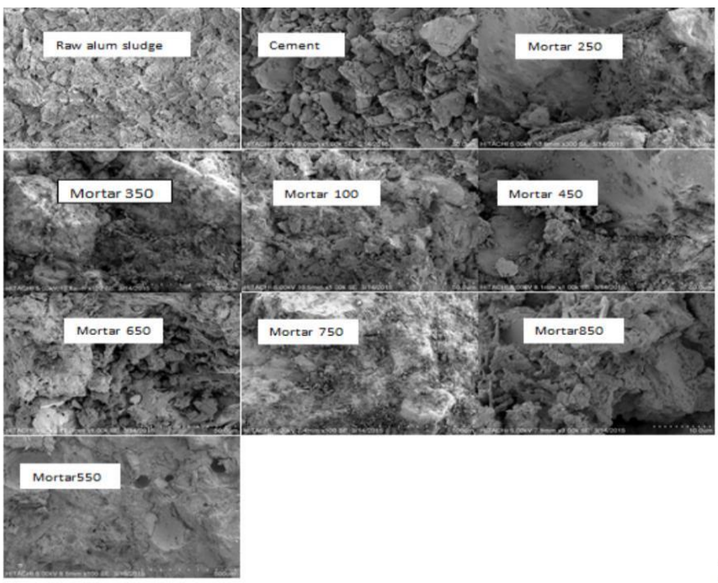
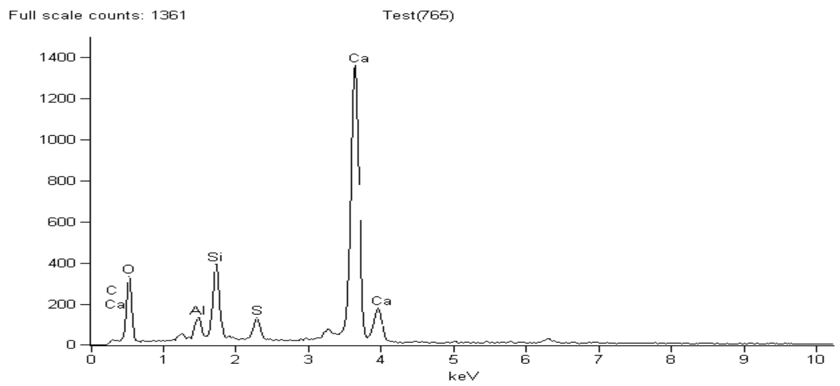
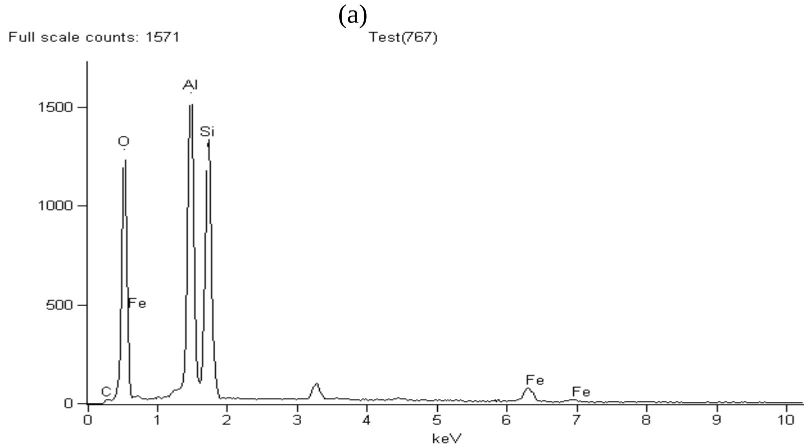


Fig. 8: SEM micrographs of mortar with alum sludge calcined at (100–950) ˚C for 2 hours.



(a)



(b)

Fig. 9: Plot of SEM/EDX results for (a) cement (b) alum sludge

The PAI refers to the ratio of the strength of the AS-cement mortar to the strength of the reference (cement mortar) at each specific ages test. The degree of strength improvement of cement mortar depends mainly on its hydration rate. Meanwhile, the other researchers state that hydration rate depends on the cement hydration and rehydration caused by the pozzolanic reactivity of AS in AS-cement mortar. Figure 11shows that the pozzolanic activity indices at 7and28 days are higher than the index for the minimum requirement of 75% as specified in ASTM C 618. The strength activity indices of the control cement of 7 days curing period are 76.17% , 76.50%, 76.87%, 80.00%, 81.42%, 82.09%, 84.49%, 84.22%, and 83.76%. The pozzolanic activity indices of the control of 28 days curing period are 86.13%,86.31%, 86.65%, 89.90%, 90.60%, 91.57%, 92.06%, 92.02%, and 91.98. The findings indicate a reduction in the compressive strength of OPC that has been replaced with20% alum sludge of 7 days curing period in comparison with the compressive strength of the control mortar. The reason for this finding could be attributed to the mitigation effect and tardy on set of pozzolanic reaction of AS with $Ca(OH)_2$.

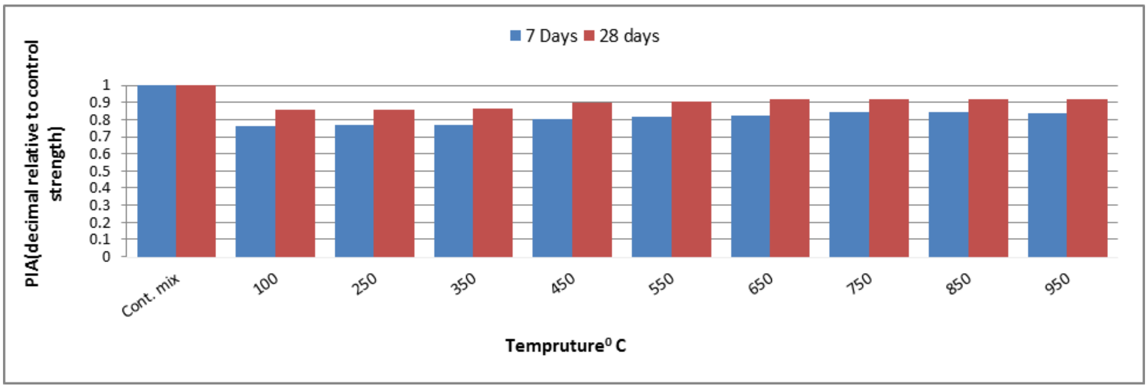


Fig. 10: Result of Strength Pozzolanic Activity Index of Alum Sludge

Thermal gravimetric analysis (TGA) is a method Conducts for conducting continuous measurement to the analysis the sample mass that is exposed to regular change in temperature. The TGA method is for conducting two types of interactions, namely Reactant(s) = Product(s) + Gas and Gas + Reactant(s) = Product(s). In the first interaction weight loss occurs whilst, in the second interaction the reverse take place, this way is appropriate for these two types of interactions only. In addition, TGA is more suitable for the studying of hydration or pozzolanic reaction that takes place at the later stages. The findings are plotted on a graph known as gravimetric thermal TGA. Figure 12 shows the curves of DTA and TGA. The finding in Figure 12 reveal that removal of moisture and decomposmon readions are indicated by the lower weight changes up to about 500^0 C and between 500^0 C and 950 °C on TGA curve and a strong endothermic peak that occurs up to about 200 that may correspond the decomposition of the hydroxide.

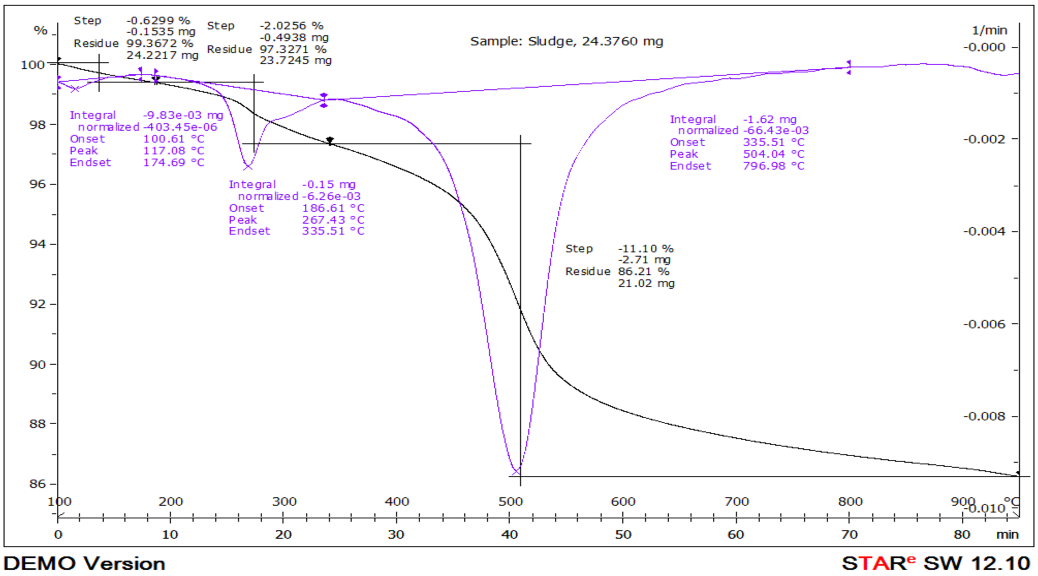


Fig. 11: Thermogravimetry Analysis Results

The differences in particle size of raw AS and TAS is due to the drying process. Raw AS is dried in an oven for 24 hours, then in furnace for 2hours at 750°C. Then the dried AS is used to run PSD test. Finally the ground alum sludge is soluble in alkaline solution (in presence of $Ca(OH_2)$) to produce soluble silica, which provides to the pozzolanic reaction.

Discussion:

The use of alum sludge by-product from water treatment plants as partial replacement in concrete is has attracted mud interest among researches in recent years. This use of alum sludge with pozzolanic properties could contribute the increasing of resource of pozzolanic materials that is used in concrete consumption with time.

Conclusions:

Based on the experimental work, the resulting conclusions can be drawn:

- Ground AS obtained by calcining at 750ºC for 2 hours has resulted in significantly higher reaction pozzolanic than that of the untreated alum sludge and TAS at other temperatures. This is because the treated AS is free from organic matter. In addition, the treatment process has yielded alum sludge with high specific surface area, thus preserving the amorphous characteristic related to pozzolanic activity of alum sludge and making it free from particle agglomeration.
- The optimum temperature a calcining of RAS must be maintained at 750^{0}C to preserve the pozzolanic activity of the resultant ash.
- The PAI for mixtures of 28 days of curing period rises to more than 80% due to the pozzolanic reaction of alum sludge with $Ca(OH)_2$,that produces C-S-H, hence increases the strength.
- The pozzolanic activity index of AS /C mortar obey the requirements of pozzolanic materials according to ASTM C618-05, this means that the compressive strength test confirms the actual behaviour of alum sludge mortar. It is suggested that up to 20% substitution of OPC with AS can produce good results in the strength with regards to pure cement mortar.
- Thermal gravimetric analysis (TGA) is the method that processes the loss in weight of sample as a function of temperature. By tracking the sample mass can observe there is weight loss during thermal curing up to 500^{0}C and Stabilized later.
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