

Effect of Particle Size of Alum Waste Addition on properties of Ordinary Portland Cement Mortar

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Abstract

One problem associated with the manufacture of alum (aluminum sulfate) by leaching calcined kaolin with sulfuric acid is the production of large quantities of dealuminated kaolin waste. This is discharged as very fine particles causing environmental problems on its disposal by dump-filling.

This waste was first screened into four different size fractions to be used in the preparation of cement mortars. The effect of percent waste addition (up to 10% by weight) and particle size on the properties of the formed mortars was investigated. These properties include the fluidity of mortar, the initial and final setting and the compressive strength at 28 days.

Key words: Alum waste, particle size, consistency, initial and final setting, compressive strength.

INTRODUCTION

Egypt is among few countries producing aluminum sulfate (alum) for water purification from domestic kaolin (35% Al_2O_3) as bauxite, the conventional raw material for the production of alum, is not locally available [1 – 4]. Kaolin is first calcined above 600°C to produce m-kaolin which is then treated with sulfuric acid to produce aluminum sulfate solution, commercialized as alum, according to the reaction:



The solid residue remaining, designated as dealuminated kaolin, contains very fine silica as main component [5]. This has incited some research aiming at using that residue as additive to cement [5, 6]. In this respect, the rheological properties of a fresh cement paste play an important role in determining the workability of concrete. The water requirement for flow, hydration behavior and properties of the hardened state largely depends upon the degree of dispersion of cement in water. Properties such as fineness, particle size distribution, and mixing intensity are important in determining the rheological properties of cement paste [7]. The effect of using dealuminated kaolin residue on the workability of fresh cement paste proved to be insignificant [6].

In the present work, the effect of addition of alum waste (up to 10%) of different size fractions on consistency, initial and final setting of cement and compressive strength of cement mortar at 28 days was investigated.

EXPERIMENTAL TECHNIQUES

Raw Materials

Sand

Natural sand was used as fine aggregate in this study. The sand was graded so as to pass from sieve 850µm and be retained on 600 µm. [8]

Water

Tap water was used for mixing and cement curing for all specimens.

Ordinary Portland cement (OPC)

OPC produced by Suez Cement Company was used. Testing of cement was carried out according to the Egyptian Standard ESS4756-1/2009, where the percent retained on sieve 170 was less than 10%. Table 1 shows the physical properties OPC while Table 2 illustrates its chemical composition .

Table 1: Physical properties of OPC

Property	Value	Limits
Specific Gravity	2.63	2.5 – 2.75
Bulk density, kg.m ⁻³	1780	-
% Clay and fine dust content by volume	0.85	< 3

Table 2: Chemical composition of OPC

Compound	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Cl	LOI
% by weight	21.16	5.32	3.52	63.8	1.32	2.01	0.2	0.13	0.02	2.52

Alum Waste

Alum waste obtained from the Aluminum Sulfate Company of Egypt was first dried at 110°C overnight. The dried waste was then screened to four fractions; under 75 micron, 75-150 micron, 150-300 micron, and over 300 micron. The four fractions were analyzed by XRF using AXIOS, analytical 2005, Wavelength Dispersive (WD-XRF) Sequential

Spectrometer. The chemical analysis of the four fractions is shown in Table 3.

Table 3: Chemical Analysis of Alum waste fractions

Main Constituents (wt.%)	As received	Under 75 micron	75-150 micron	150-300 micron	Over 300 micron
SiO ₂	74.66	71.46	75.65	76.32	76.63
TiO ₂	2.85	2.68	2.64	2.69	2.86
Al ₂ O ₃	7.48	10.89	7.12	6.03	5.29
Fe ₂ O ₃ ^{tot.}	0.51	0.79	0.51	0.40	0.42
MgO	0.03	0.03	0.02	0.02	0.04
CaO	0.31	0.72	0.20	0.12	0.15
Na ₂ O	0.08	0.08	0.05	0.06	0.07
K ₂ O	0.08	0.06	0.04	0.03	0.05
P ₂ O ₅	0.05	0.06	0.05	0.05	0.04
SO ₃	5.18	5.25	4.67	4.50	4.60
Cl	0.02	0.03	0.03	0.03	0.02
ZrO ₂	0.15	0.155	0.137	0.141	0.150
LOI	8.4	7.69	8.79	9.50	9.55
Total	99.8	99.9	99.91	99.89	99.87

On the other hand, alum waste was subjected to XRD analysis using a Burker D₈ Advanced Computerized X-Ray Diffractometer apparatus to disclose its constituting phases. The results revealed that its main crystalline phases are quartz and Anatase (TiO₂). The presence of alumina and sulfur oxide in the XRF analysis (Table 3) suggests the presence of aluminum sulfate presumably in amorphous state as no characteristic lines showed up in the XRD pattern. Stoichiometric calculations based on the XRF results have been performed. They show that most of the alumina in the waste is present as part of the unreacted metakolin and only a minor portion (about 10%) is present as aluminum sulfate. Assuming that metakaolin has the chemical symbol Al₂O₃.2SiO₂. This results in having about 8% of the available silica present in combined metakaolin form. Since the total silica is about 74%, then the percent free silica should then be about 66%. This was actually confirmed by determining the free silica present in a sample of waste by a traditional technique used for refractory materials [9]. This method yielded percent free silica of 66.4%.

Mixing and curing

This was determined by the consistency test described by IS 4031-Part4 [10]. Alum waste was used as an addition of 0%, 2.5%, 5%, 7.5%, 10%, 15% and 20% of cement by weight as shown in Table 4 to substitute sand. The ratio of cement to the sand + waste mixture was kept at 1:2.75 by weight in all mixes.

Table 4: Composition of cement – waste mixes by weight

Mix designation	OPC, g	Alum waste, g
A 0	100	0
A 2.5	100	2.5
A 5	100	5
A 7.5	100	7.5
A 10.0	100	10
A 15.0	100	15
A20.0	100	20

Mixing was done in a standard drum type mixer; fine aggregate, cement and alum waste were mixed in dry state until the mixture becomes homogenous, then water was added to the dry mixture and was mixed for 10 minutes.

Determination of mix properties

Flowability

The test used to that aim is the flow table test performed in accordance with ASTM C230 / C230M – 14 [11]. In this test, a layer of mortar of about 25 mm thickness is tamped 20 times in a flow mold that is placed at the center of the table. After one minute, the mold is carefully lifted and the flow table lifted up 40mm and then dropped 15 times, causing the paste to flow. The flowability is measured as the ratio between the diameter of the resulting mass and that of the original mix:

$$\text{Flowability} = \frac{D_f - D_i}{D_i} \times 100\% \quad (1)$$

Where,

D_f = final diameter (mm)

D_i = initial diameter (mm)

Initial and final setting

This standard test was performed as described by IS 4031-Part5 [12]. It involves using the standard Vicat needle in assessing its penetration in a fresh cement mix. Three specimens were tested each time and the average value was taken.

Compressive strength

Compressive tests at 28 days were carried out on 70.7×70.7×70.7 mm cubes. The test specimens were immersed in water in curing tanks after 24 hours for 28 days. The test was carried out according to Egyptian standard ESS 1658-1991 [13]. Three specimens were tested each time and the average value was taken.

RESULTS AND DISCUSSIONS

Effect of alum waste on flow properties

The previously described flowability test necessitates the use of cement mortars. In Table 5 the compositions of the mortars obtained by substituting waste for sand in levels reaching 20% are shown.

Table 5: Composition of hydraulic cement mortar

Waste (%)	Cement (g)	Waste (g)	Sand (g)	Water (g)
0%	170	0.00	467.50	110.5
2.5%	170	4.25	463.25	110.5
5%	170	8.5	459	110.5
7.5%	170	12.75	454.75	110.5
10%	170	17	450.5	110.5
15%	170	25.5	442	110.5
20%	170	34	433.5	110.5

Figure (1) illustrates the results obtained on adding up to 20% waste to cement

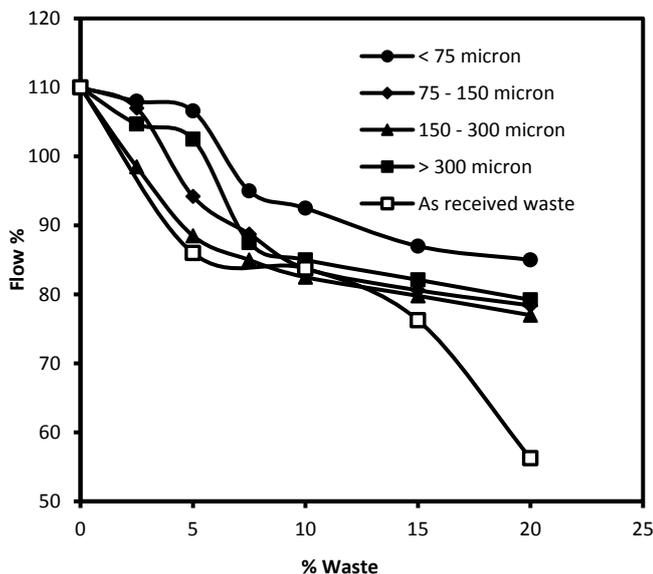


Figure 1: Effect of alum waste addition on the flowability of cement mortars

This curve indicates a regular decrease in flowability of the mixes on adding the waste as it was substituted for sand. This is probably due to the enhancement of the reaction between the fine silica present in the waste and calcium hydroxide beginning to form owing to early hydration of alite (C_3S) producing $C_3S_2 \cdot xH_2O$ crystals. This reaction produces more alite which subsequently hydrates thus contributing to decreased flowability. This result would mean that any

addition that would cause the above reaction should lead to decreasing the flowability. Actually, this result was found to be not necessarily true in case of adding extremely fine fly ash ($<10 \mu m$) to cement [14].

It can also be seen that as the size of waste increases the flowability decreases, except for the coarsest fraction where a slight increase in that property has been observed. Actually, this result agrees with the findings of Hu and Wang [15]. They found out that for sand particles exceeding $150 \mu m$, the flowability steadily increased. They did not provide, however, any explanation for that behavior. The relative effect of waste substitution for sand and average particle size is presented in Table 6 where correlation coefficients between flowability and both parameters are shown. This table reveals the modest contribution of the variability in particle size to flow properties compared to the effect of waste substitution for sand.

Table 6: Correlation coefficients for flowability

	Particle size	% waste	Flow.
Particle size	1		
% waste	0	1	
Flow.	-0.1180	-0.8801	1

Effect of alum waste addition on consistency and setting time

This property does not require any mortar preparation as the tests are performed on pure cement water mixes. The alum waste was added each time to 300 g cement in proportions ranging from 0% to 10%.

Fig 2 shows that the consistency as determined by the water to cement ratio (expressed as percentage) steadily increases with waste addition. Also, finer waste fractions tend to require more water to reach standard consistency. Actually, the correlation coefficients as evidenced by the values in Table 7, reveal that both factors affect the property although the effect of waste addition is more pronounced. The result can be interpreted in view of the fact that the increase in water of consistency is due to a lowering of paste flowability. Also finer particles will enhance the pozzolanic reaction leading to alite and subsequent hydrate formation, thus requiring more water.

Table 7: Correlation coefficients for water of consistency

	Particle size	% waste	%W/C
Particle size	1		
% waste	0	1	
%W/C	-0.338	0.842	1

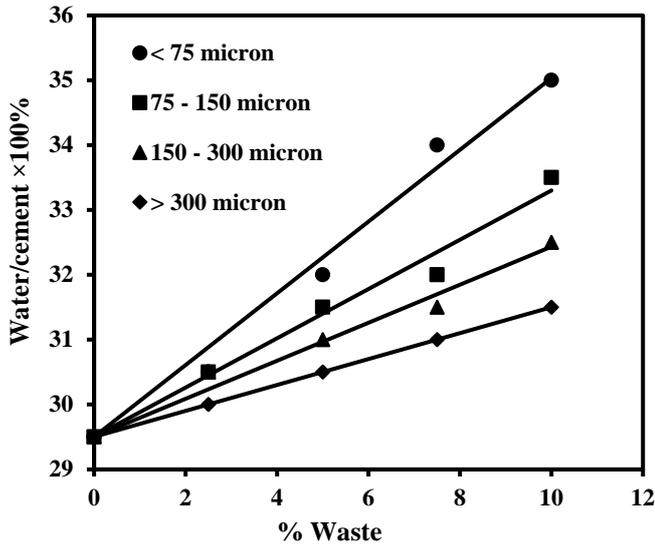


Figure 2: Effect of alum waste addition on water of consistency of cement paste

On the other hand, Fig 3 and 4 reveal similar trends for the dependence of both initial and final setting times on waste addition and to great extent, particle size.

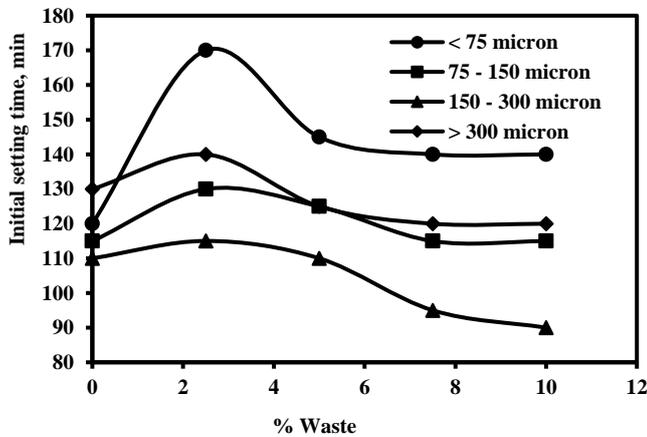


Figure 3: Effect of alum waste addition on initial setting time of cement paste

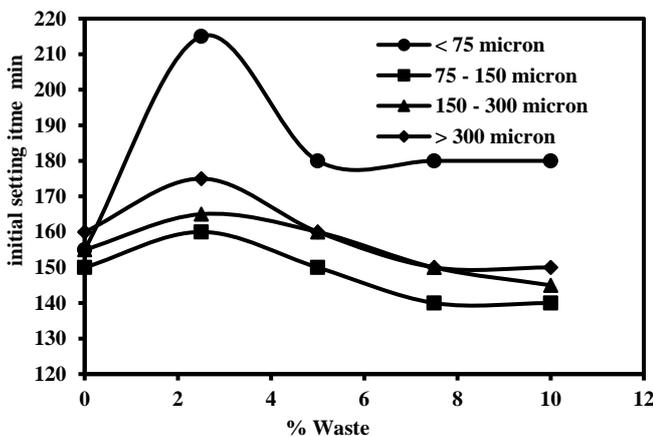


Figure 4: Effect of alum waste addition on final setting time of cement paste

It appears from these figures that the setting time is at its highest value when the finest fraction of waste is incorporated into the mortar mix. Upon increasing the particle size, the setting time decreases to reach a minimum value followed by an increase when the coarsest fraction is used.

It is also apparent that on using plain cement with no waste in the mortar, the values of initial setting times were at their minimum. This is presumably related to the porous character of waste which assists in water being sucked by capillary action in pores therefore decreasing the effective amount of water available for hydration. This has for effect to retard the hydration reactions responsible for setting. Actually, a fixed amount of waste will provide more pores if its particle size is smaller. The following simple analysis explains the dependence of setting time on particle size.

Consider a fixed volume of waste material V_w consisting of n particles of average diameter D . Hence:

$$V_w = n \cdot \Phi \pi D^3 / 6 \quad (2)$$

Where, Φ is some shape factor to account for the non-sphericity of particles.

Hence the number of particles is:

$$n = 6V_w / \Phi \pi D^3 \quad (3)$$

Since open pores are available at the surface of the particles then their number N_p will be proportional to the surface area of the particles.

$$N_p = k \cdot n \cdot \pi D^2 \quad (4)$$

Where, k is proportionality constant.

From equations (3) and (4), one gets:

$$N_p = 6kV_w \frac{\pi D^2}{\Phi \pi D^3} \quad (5)$$

$$N_p = \frac{6kV_w}{\Phi D} \quad (6)$$

This simple analysis indicates that the number of surface pores increases for a fixed volume of waste added with decreased particle size of waste. This explains the high values of setting times obtained when the finest particles of waste were used. As the particle size was increased, this was associated with a decrease in the number of surface pores resulting in lower setting times. However, upon highly increasing the particle size, interparticle porosity will increase requiring more time for hydration reactions as more water will be sucked into these pores. Also, a moderate decrease in initial setting time was observed on increasing the amount of waste from 2% to 10%. This may be due to the increase in the amount of alumina present in the waste that may have enhanced the formation of more tricalcium aluminate by hydrothermal reaction with any free lime available in the cement used. This effect almost ceases as the percent substituted sand reaches 7.5% presumably due to the exhaustion of any available free lime.

Effect of alum waste on compressive strength

Fig 5 shows the results obtained on substituting waste for sand at different percentages for 28 days compressive strength for different particle fractions of alum waste.

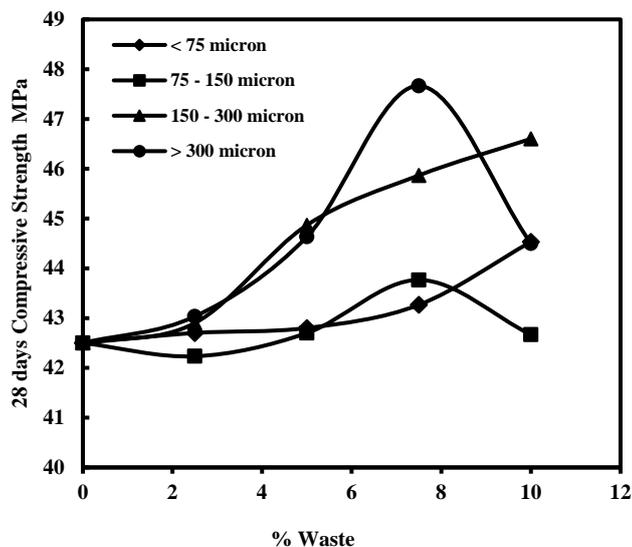


Figure 5: Effect of alum waste addition on 28-days strength of cement mortars

As can be seen from the results, there is a regular increase in strength following an increase in waste addition to values reaching about 12% over that of the control sample (0% addition). This occurred for mixes containing coarse waste particles that reached maximum strength at about 7.5% sand replacement. It is believed that this level of addition is sufficient to neutralize calcium hydroxide present in the pores of the mortar to produce $C_3S_2 \cdot xH_2O$ crystals and any further addition will only act as inert filler decreasing rather than increasing the strength. These results despite being promising are not as good as those obtained on using silica fume as additive [16]. However, the elevated cost of silica fume (minimum \$100/ton) cannot compete with the priceless cost of alum waste. In addition, the maximum percent waste added (10%) would introduce about 0.5% SO_3 and almost zero chlorides (Table 3), which designates this waste as potential additive in reinforced concrete works [17]

CONCLUSIONS

The effect of adding dealuminated kaolin waste of different particle sizes, a residue from the alum industry, on the properties of cement pastes and mortars was determined. The following results were obtained:

- The addition of alum waste results in a decrease in flow properties particularly when the finest size fraction was used. This was interpreted in the light of accelerated pozzolanic reactions on using finer size.
- The rapid production of hydrates following waste addition, particularly the fine fraction, resulted in an

increase in water demand to reach standard paste consistency.

- Both initial and final setting times were more or less unaffected by waste addition except for the finest fraction which produced a maximum setting time at about 2% addition. This was explained by a simple model taking into account the formation of pores and their closure on hydrate crystals formation.
- In general, the 28 days compressive strength increased for all particle size fractions upon increasing sand substitution by waste. This shows that alum waste can be economically used to partly substitute sand in concrete works.

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