

Fly Ash High-Strength Geopolymers: Effect of Grinding and Extra Water Content

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Fluidized bed boiler fly ash, previously calcined at 650 °C (FAT), was used to obtain geopolymers, after treatment with 8 M, and 10 M NaOH, as well with sodium silicate (silicate modulus $MS = 2.5$). The volume ratio of alkaline activating solution/FAT = 0.38 L/kg was kept constant; whereas that the molar ratios $SiO_2/Na_2O = 1.18-1.50$, and $H_2O/Na_2O = 14.7-20.4$, was used. The addition of extra water to the geopolymeric paste was done in two ways, in order to determine the effect on the dissolution rate of aluminosilicates and the strength development of the geopolymers obtained. By pre-grinding the FAT, controlling the mixing time, the H_2O/Na_2O ratio = 14.7 and thermal activation at 80 °C for 24 h, it was possible to obtain geopolymers with high strengths

1. Introduction

Geopolymers are defined as mineral polymers with an empirical formula of $Mn \{-(SiO_2)_z - AlO_2-\}n \cdot wH_2O$, where z is the Si/Al mole ratio, M is a cation (Na^+ , K^+ , Ca^{2+}) to balance the negative charge of $Al(OH)_4^{1-}$ being its stoichiometry $M/Al = 1$ and n is the degree of polymerization (Matsimbe et al., 2022). Geopolymers have good resistance to fire, chemical corrosion and develop high mechanical resistance, making them suitable substitutes for ordinary Portland cement (OPC), with the advantage that its production causes low CO_2 emissions than OPC. Geopolymers are produced by the reaction of a highly alkaline solution with powdered aluminosilicate, forming a network of gel pores containing water. Some of the water is lost as evaporable water, which comes out through the micropores, while another part forms a constituent part of the empirical formula of the geopolymer. Water enters the geopolymeric mixture through three sources: with the NaOH solution, the sodium silicate, and as extra water, which is added to regulate the workability of the mixture. The addition of extra water can affect the physical and mechanical properties of the geopolymer since it increases the liquid phase to solids ratio, generating greater porosity in the geopolymers, reducing the compaction of their structures, and decreasing the compressive strength (Fu et al., 2020). Several research studies have reported on the influence of Si/Al, Na/Al, and H_2O/Na_2O ratios on the mechanical properties of metakaolin-based geopolymers (Castillo et al., 2021). However, if fly ash (FA) is used as a precursor, which has diverse origins and is composed of crystalline and amorphous phases, the mixture design requires greater care to ensure a homogeneously consistent product, particularly with the dosage of the alkaline activator (Hadi et al., 2018).

Fly ash with a high percentage of unburned can serve as raw material to obtain zeolites, as demonstrated in a previous study. Now, this same raw material is used to produce FA-based geopolymers with the aim of determining the effect of dosing and the mechanism of extra water entry in the formation of geopolymeric paste, associated with the mixture time and grinding of the FA, to obtain high-strength geopolymers.

2. Instrumental

2.1 Materials

Fly ash from a fluidized bed boiler was supplied by cardboard company in Peru. The ashes come from anthracite coal and their chemical composition is Class F according to ASTM C 618-03 (Table 1). The ashes were calcined for 3 h at 650 °C (FAT) to eliminate the unburned (LOI). Sodium silicate $MS = 2.5$ ($SiO_2 = 32.5\%$, $Na_2O = 13.1\%$, $H_2O = 54.4\%$) was used to obtain two kinds of alkaline activating (AA) solutions, one mixed with 8 M NaOH

and another mixed with 10 M NaOH. With these activating solutions, seven types of test tubes were prepared, whose dosages are shown in Table 2. The ratio of AA volume to ash was kept as a $V(\text{AA})/\text{FAT} = 0.38 \text{ L/kg}$.

Table 1. Chemical composition of fly ash batch 10375 (YURA Cement Laboratory, Arequipa, Perú)

Component	SiO ₂	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	TiO ₂	Other oxides	LOI	Amorphous phases
wt. %	44.50	27.38	1.87	1.63	1.44	2.35	20.82	42.7

2.2. Preparation of geopolymer pastes

Once the mass of FAT to be treated was weighed, the volumes of sodium silicate and NaOH (AA solution), were defined by the ratio $V(\text{AA})/\text{FAT} = 0.38 \text{ L/kg}$ and by the ratio $V\text{Na}_2\text{SiO}_3/V\text{NaOH}$. The AA was mixed in a closed plastic container with magnetic stirring for 30 min at 500 rpm. It was then added to the FAT, which was previously weighed and placed in a mortar mixer, stirring at 139 rpm. When spherical lumps were formed by the reaction of the AA on the ashes, the addition of extra water, in two modes was supplied. In Mode A, it was added gradually to keep the mixture fluid and homogeneous during the mixing time. In Mode B, all the extra water was added at once. When the paste achieved fluidity, the agitation was increased to 591 rpm. After a mixing time (*tm*) of 18 to 45 min, the pastes were placed in 50x50x50 mm molds, tapped and compacted on a vibrating table for 3 min to eliminate air bubbles. The specimens were then sealed with a polypropylene film and thermally activated. Triplicate specimens of each group were prepared to obtain the average strength values (Table 2).

Table 2 Dosages for the groups of test tube under study ($V(\text{AA})/\text{FAT} = 0.38 \text{ L/kg}$)

Test tube	[NaOH], mole/L	Activation temp.(°C)	Activation time (h)	$V\text{Na}_2\text{SiO}_3/V\text{NaOH}$	SiO ₂ /Na ₂ O (*)	H ₂ O/Na ₂ O (*)	Mode of extra H ₂ O
P-08	8	60, 70, 80	24, 48, 72	65/35	1.51	20.4	A
P2-088024	8	80	24	65/35	1.51	18.2	B
P-10	10	60, 70, 80	24, 48, 72	65/35	1.38	18.3–17.1	A
S1, S2, S3, S4	10	80	24	69/31	1.51	17.1	A
S5	10	80	24	69/31	1.51	17.1	B
S6 (**)	10	80	24	65/35	1.18	15.3	B
SM1	10	80	24	69/31	1.50	14.7	B

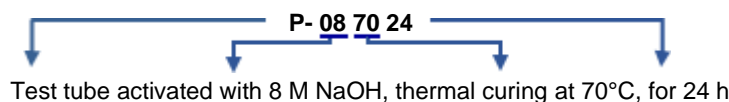
(*) molar ratio. (**) with sodium silicate, MS = 2.0 (SiO₂ = 29.25%; Na₂O = 14.65%; H₂O = 56.1%)

2.2.1. NaOH concentration

To study the effect of NaOH concentration on the compressive strength, test tubes P-08, P2-088024 and P-10 were made with the activation conditions shown in the Table 2. Soluble SiO₂ was provided by sodium silicate, and the total Na₂O was obtained from the sum of NaOH solution and sodium silicate. Likewise, the total H₂O was determined from the sum of the water in the NaOH solution, the sodium silicate and the extra water added during the mixing process.

2.2.2. Thermal activation temperature and time

All samples were preheated in an oven at 30 °C for 24 h and then at the maximum activation temperature of 80 °C for 24 h. However, the samples P-08 and P-10 (Table 2) were activated at 60, 70 and 80 °C, using three activation times of 24, 48 and 72 h. These samples were identified with the following code:



All the specimens, after thermal activation, were demolded to determine their compressive strength at 7, 14, 21 or 28 days of curing at room temperature.

2.2.3. Extra water addition

Extra water was added (in Mode A and Mode B, see 2.2) to geopolymeric paste to regulate its workability and viscosity, allowing for longer mixing time (*tm*). The amount of the water added was as a part of the H₂O/Na₂O

ratio, as described in section 2.2.1 (Table 2). However, the water excess can decrease the compression resistance of the cement paste and concrete.

2.2.4. The mixing time (tm) and mode of extra water adding

The effect of mixing time (tm) was studied based on the behavior of test tubes S1, S2, S3 and S4 (Table 2). The extra water addition in Mode A was used to manipulate the tm , which ranged from 18 min to 45 min. Part of the specimens tested for compression resistance were pulverized and their XRD and FTIR analysis were carried out. On the other hand, to study the effect of the extra water addition in Mode B, test tubes S5 and S6 were prepared (Table 2). For S5 specimens, a sodium silicate $MS = 2$ was used.

2.2.5. The fly ash (FAT) grinding

The FAT precursor was grinded in a porcelain mill, using 12 balls of 3 cm in diameter and 10 balls of 2 cm in diameter for each 150 g of FAT, for 2 h at 120 rpm. With the grinded ashes, the geopolymeric paste was prepared following the procedure described in 2.2 and identifying the sample as SM1, which activation conditions are shown in Table 2.

2.3. Geopolymer characterization

For compressive strength resistance measurement, the tests were performed according to the practice of the ELE International, ADR 2000 equipment, applying a loading speed of 0.9 kN/s, under ASTM C-39 and AASHTO T-22 specifications. The X ray analysis of the samples was performed by X-ray diffractometer (Rigaku, Miniflex 600), with a Cu-K1 radiation source of $\lambda = 1.540 \text{ \AA}$. The analysis of the IR spectra was achieved by ThermoFisher spectrophotometer (Nicolet iS50R FT-IR).

3. Results and discussion

3.1 Effect of NaOH, temperature, thermal activation time and H_2O/Na_2O ratio on the compressive strength

The compressive strength average values of the P-08, P-10 and P2-088024 fly ash geopolymer specimens after 28 days of curing are shown in Figure 1. The test tubes P-0860, P-0870 and P-0880, each of them activated for 24, 48 and 72 h, have the same ratio of $H_2O/Na_2O = 20.4$. Their strength oscillated between 27 MPa and 34 MPa, showing a random behavior, which did not allow to establish any correlation, neither with the temperature nor with the time of thermal activation. The P-08 specimens presented an excessive fluidity, because of the excess of extra water, which fact allowed a mixing time (tm) of 30 min. On the other hand, the test tube specimen P2-088024 (Table 2), elaborated with less extra water, reduced their total amount of water, at $H_2O/Na_2O = 18.2$ ratio, and tm at 25 min. The strength for this specimen group ($76.8 \pm 3.01 \text{ MPa}$) was twice higher than that of any specimen of the P-08 group. The decrease in total water content allowed to elaborate denser paste and stronger geopolymers, because their structures were more compact and less porous (Cui et al., 2019). This fact explains the larger difference in strength values, between P-0880 and P2-088024 specimens.

Figure 1 includes the strength values of P-10 geopolymers, for which H_2O/Na_2O ratios of 17.1–18.3 were used

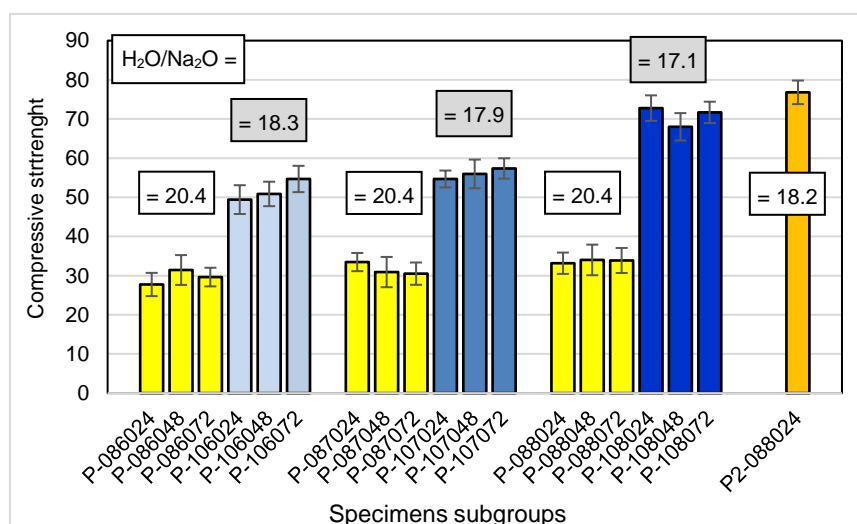


Figure 1. Average 28-day compressive strengths values of geopolymers specimens, from FAT activated with 8 and 10 M NaOH. All samples P-08 have the same H_2O/Na_2O ratio = 20.4

the increase in NaOH concentration, thermal activation temperature and time, and the decrease in the H_2O/Na_2O ratio, which caused a higher dissolution of aluminosilicates, accompanied by a higher dissolution rate of amorphous phases and higher polycondensation, which allowed to form more compact structures, giving higher compressive strength (Mishra et al., 2022). The results (Figure 1) indicated that the specimens of P-108048 and P-108072 had lower strength values than P-108024, indicating that at 80°C, the strength decreased after the activation time of 24 h, and this is due to the fact that at high temperatures, long curing times can break the granular structure of the geopolymer, increasing its volumetric shrinkage and dehydration rate, causing compressive strength decay (Khale and Chaudhary, 2007); consequently, the activation at 80 °C should not be more than 24 h.

Figure 2 compares the XRD spectra of the fly ash grinded (FAT) and those of P-10, P2 and P-08 geopolymer specimens (Table 2) activated at 80 °C for 24 h. The characteristic peaks of quartz, SiO_2 , are preserved in all spectra, indicating that it was inert to the alkali treatment. However, the peaks of the crystalline phase of *fluorannite* and talco-2M, observed in the range of $2\theta = 15^\circ - 19^\circ$, no longer appeared in the geopolymers, indicating the dissolution of these phases or that they were converted to amorphous phase as a part of the geopolymers. Similar fact occurred with both crystalline phases of TiO_2 (*anatase* and *rutile*).

The Figure 3 presents the ATR-FTIR spectra of the FAT and the three geopolymer groups. In the FAT, the band at 1024 cm^{-1} is attributed to the asymmetric stretching of the Si-O-T (T: Si o Al) bond in its tetrahedral structure (Yu et al., 1999). This band is descending to 1012 cm^{-1} in P-088024 specimen, to 1007 cm^{-1} in P-108024 and to 989 cm^{-1} in P2-088024, indicating that the aluminosilicate gel is increasingly richer in Al, occurring the partial replacement of SiO_4 by the tetrahedral AlO_4 , while increasing the degree of geopolymerization (Hajimohammadi et al., 2010), which fact is considered for the specimen P2-088024. The spectra of Figure 3 allowed to consider that P2-088024 specimen had a higher degree of geopolymerization, due to the higher SiO_2/Na_2O ratio (Mishra et al., 2022) and/or due to the addition of extra water in Mode B.

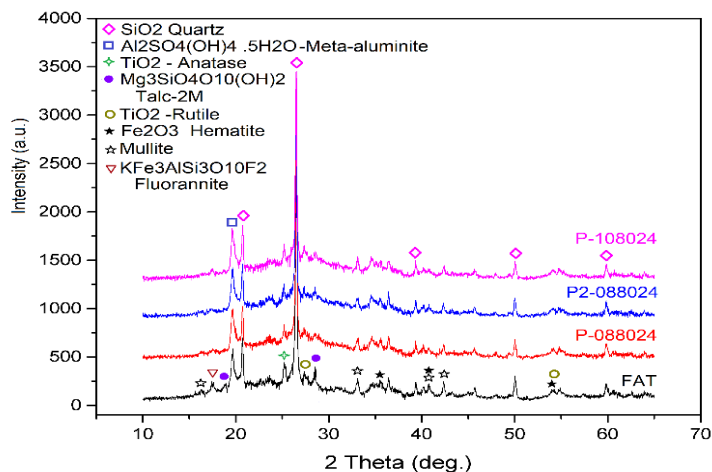


Figure 2. XRD spectra of FAT and geopolymers P-088024, P2-088024, P-108024

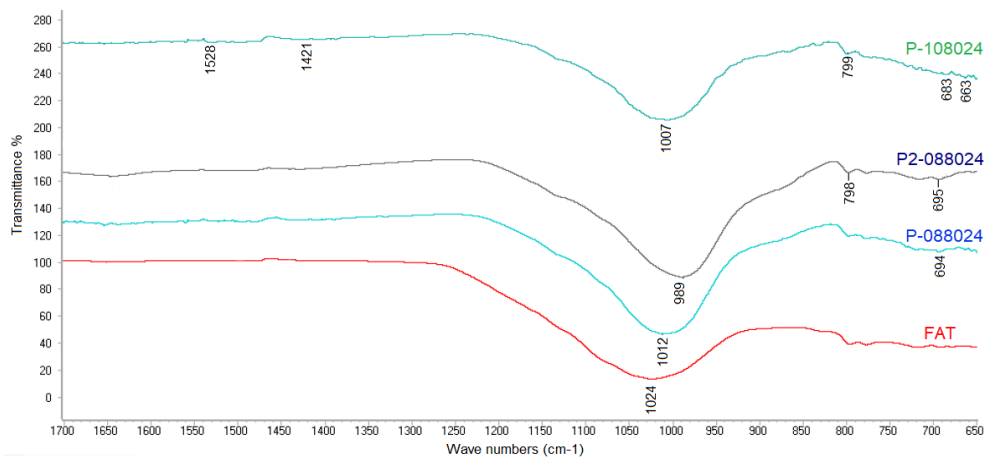


Figure 3. ATR-FTIR spectra of FAT and P-088024, P2-088024, P-108024 geopolymers

3.2. Effect of mixing time (tm) and the mode of extra water adding on the compressive strength

The beginning of geopolymerization occurs with the precise contact of the amorphous phases of the precursor and the OH^- ions of the alkaline activator. The breaking of the covalent bonds T-O- (T: Si or Al) occurs by the ionic strength of the OH^- , forming complexes of $\equiv\text{Si-O}^-$ and $\text{Al}(\text{OH})_4^-$, which pass into solution (Provis and van Deventer, 2009). However, when the precursor is a heterogeneous material such as a fly ash (FA), the chemical reaction is complicated by the existence of inert crystalline phases that hinder the dissolution and polycondensation stages (Ranjbar et al., 2020). Therefore, the longer mixing times (tm) helps the dissolution process, polycondensation and subsequent geopolymerization stages, which result in the strength progress. As shown in Figure 4, samples S4, S3, S2 and S1 (Table 2), being chemically similar, their compressive strengths increase with the respective tm increment. The specimens S5 and S6 (Table 2), which received the extra water in Mode B, present strength of 98.7 MPa and 92.7, respectively, at 28 days, comparable to that of the specimen S1, with a higher tm of 45 min. The entry of all the extra water in the initial stage of paste formation favoured the dissolution rate of the Si-O-Si and Al-O-Al compounds, since the initial volume of the alkaline activating solution increased with the added water, homogenizing the dissolving action of the OH^- ions, increasing the polycondensation and the bonds of water molecules in the inorganic lattice of aluminium tetrahedra, silicon and sodium ions (Kobera et al., 2011). On the other hand, the S5 specimens showed higher strengths than S6, due to the longer mixing time and the higher $\text{SiO}_2/\text{Na}_2\text{O}$ ratio (Table 2).

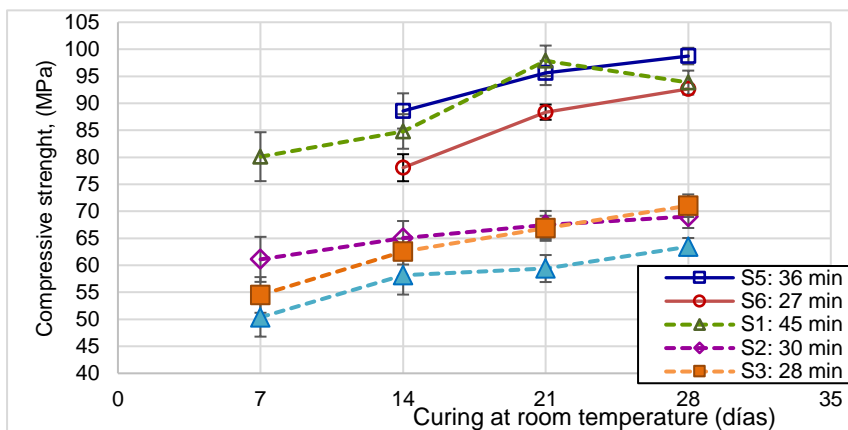


Figure 4. Compressive strengths of fly ash geopolymers, elaborated with pastes of different mixing time (tm)

3.3. Effect of FAT grinding on the compressive strength

The chemically similar samples SM1, S1 and S5 showed similar compressive strength values (Figure 5a) at 28 days of curing, exceeding the maximum value of 83 MPa, stipulated for high-strength concretes using fly ash (ACI 211.4R, 2008). However, the strength progress of SM1 is almost linear during the curing time. Another different aspect of SM1 is its higher hardening rate, since it reaches a strength of 99 MPa in only 7 days of curing. The reduction of the particle size may increase the dissolution rate, decrease the degree of crystallinity, and reduce the water demand, since a ratio of $\text{H}_2\text{O}/\text{Na}_2\text{O} = 14.7$ was achieved for SM1, compared to 17.1 ratio for the specimens S1 and S5 (Table 2). The lower water level may maintain a higher NaOH concentration, promoting the dissolution of more amorphous phases, as well as leaving more alumina available for the

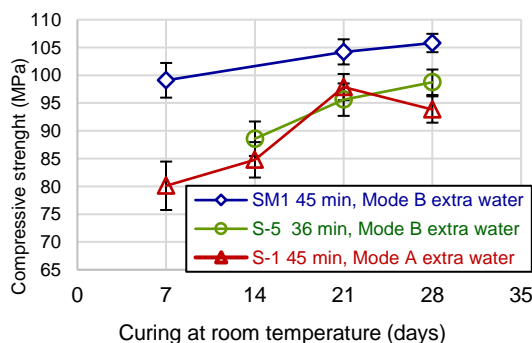


Figure 5a. Average compressive strength vs. curing time of SM1, S1 and S5 geopolymers

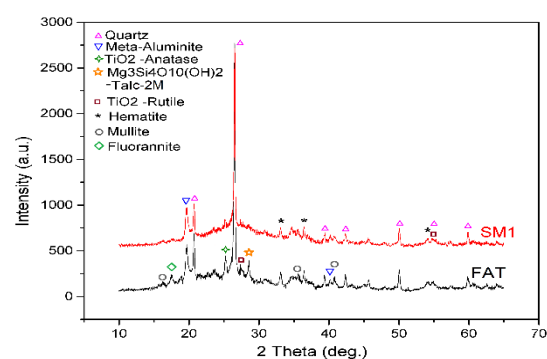


Figure 5b. XRD spectra of SM1 and FAT samples.

formation of a more homogeneous geopolymer gel (Marjanovic et al., 2014), hence, the almost linear behavior of the strength progress of SM1 specimens with curing time. Figure 5b presents the XRD spectra of the SM1 geopolymer, and of its precursor, the FAT. The hump of the baseline of 2θ , between 25° and 30° , is more uniform than that for P-088024, P2-088024 and P-10-08 (Figure 2), indicating that FAT grinding caused a higher solubility of the talc, TiO_2 and a part of the crystalline phases mullite and hematite, deduced by the attenuation of their respective peaks. The increase of the homogeneous amorphous phase improves the mechanical properties of the geopolymer making them similar to those of ordinary Portland cement (Ge et al., 2022)

4. Conclusions

High-strength geopolymers based on precalcined fly ash (FAT) at 650°C to eliminate unburned material, were obtained. In the preparation of the pastes, the alkaline activator was added to the FAT, and immediately, the extra water, extending the mixing times to the maximum possible before the setting of the mixture, to favor the development of compressive strength. The extra water added improved the workability of the pastes, but an excess of water can decrease the compressive strength of the geopolymers, being the $\text{H}_2\text{O}/\text{Na}_2\text{O} = 14.7\text{-}18.0$ ratio, as acceptable in the study conditions. The FAT milling gave a lower demand for extra water, thus maintaining the high alkali concentration, and a decrease of the crystalline phases, with a higher reactivity of the precursor to the alkaline activating solution, factors that increased the initial compressive strength. High-strength geopolymers of 100 MPa may be achieved by FAT grinding, using an activating solution/FAT ratio = 0.38 L/kg, a $\text{VNa}_2\text{SiO}_3/\text{VNaOH}$ ratio = 69/31, as well as molar ratios of $\text{SiO}_2/\text{Na}_2\text{O} = 1.50$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 14.7$, and with thermal activation at 80°C for 24 h.

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