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Effect of Curing conditions on the Compressive Strength of Spent Fluid Catalytic Cracking Catalyst (SFCCC)-based Geopolymers

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Abstract. This research evaluates the effect of the curing conditions on the mechanical properties of geopolymers containing spent fluid catalytic cracking catalyst (SFCCC) generated as a waste by the Peruvian oil-refinery industry. For this purpose, two curing conditions were evaluated: i) sample sealing during oven curing to avoid water loss, and ii) the time before curing (pre-curing time or delay time, before heating). The curing temperature was varied from 25°C up to 100°C. The performance of samples was assessed measuring the compressive strengths and the bulk densities. The results reveal that there are optimal curing conditions associated with the higher compressive strength of the SFCCC-based geopolymers. This optimal condition occurred when water loss was reduced by sealing, and samples were allowed to rest before curing (pre-curing). These two conditions assured not only a higher compressive strength but also a denser and more homogeneous product. The results indicate that the higher compressive strengths (up to 34.5 MPa) and bulk densities (up to 1.6 g/cm^3) were obtained when the specimens were sealed with plastic bags during the curing process to avoid moisture loss and when they were subjected to a pre-curing period of 24 hours before heating in an oven at 50°C for 1 day followed by curing at room temperature for 6 days.

1. Introduction

Geopolymers and alkali-activated binders are developed as a friendly environmental alternative of Ordinary Portland Cement (OPC) [1] due to its reduced CO_2 emissions compared to the cement industry [2] and other properties [1,3]. Geopolymers are inorganic polymers synthesized by alkaline activation from materials rich in silica and alumina at slightly elevated temperatures [1,3,4]. The aluminosilicate material is used as a solid precursor and mixed with an activating solution to produce a paste-like OPC's.

Besides an optimum composition of the activating solution required for an adequate reaction of the precursor [5,6], generally, geopolymers require heat to achieve better mechanical properties [7]. In this concern, curing conditions can be defined by temperature and time to promote the geopolymerization reactions and the protection system used to avoid water loss.

However, the effect of curing on compressive strength is still unclear [8,9]. Heating is necessary for geopolymerization for the proper dissolution and to favor the polymerization process [8,10,11], but an excess of temperature or an excessive time at these conditions can affect adversely the mechanical properties of the product [7,8,12–14]. In general, it is recognized as an optimum temperature the one that produces the highest compressive strength of the geopolymer [8,12,14]. Temperature is also related to the appearance of cracks and micro-cracks in the samples. Al Bakri Abdullah et al. found that a curing temperature of 60 °C produced denser samples without micro-cracks when compared to samples cured at room temperature for fly ash foamed geopolymers [15]. Similarly, it has been observed that prolonged curing at high temperatures can result in the breakdown of the granular structure of the geopolymer mixture. This can result in fast dehydration and excessive shrinkage due to the contraction of the gel, which does not transform into a more semi-crystalline form [12]. In addition, it has been mentioned that temperature and curing time can result in an increase of the compressive strength but only if enough water is present in the environment during the reaction [10]. Another important parameter in the pre-curing time at room temperature; it has been found to be beneficial for strength development [8]. It is thought that pre-curing, this is, the time before application of heat, induces dissolution of silica and alumina from the solid precursor and the formation of a continuous matrix phase, increasing, therefore, the homogeneity of the geopolymer materials [8,12,16]. All these conditions need to be determined by experimentation.

Spent fluid catalytic cracking catalyst (SFCCC) is a by-product from the petroleum industry used to improve the efficiency of the process [17]. The total amount of SFCCC generated worldwide is estimated to be about 170 000 t/year [17] causing waste disposal problems [18]. An oil refinery in Piura, northern Perú, discards up to 4 ton of SFCCC daily as solid wastes. Moreover, the SFCCC is considered a hazardous waste material due to its content of heavy metals (Mo, Co, Ni, V, S) and other contaminants as coke and residual oil [17]. However, this catalyst is a highly reactive aluminosilicate with excellent pozzolanic properties [19–22] and thus, the investigation of its use as a raw material to produce alkaline-activated composites is very attractive. In this line, stable geopolymer binders and mortars and alkali-activated mortars have been developed with this SFCCC by [6,18,22]. Tashima et al. have synthesized stable geopolymer binders and mortars with compressive strengths in the range of 8.52–68.34 MPa using SFCCC [6]. Alkali-activated mortars with up to 80 MPa of compressive strength have been also developed using SFCCC wastes [22]. In both studies, sodium silicate and sodium hydroxide were used to synthesize the SFCCC-based binders. These results were obtained applying 65 °C curing temperature during 3 days in samples protected with plastic bags.

The aim of this paper is to investigate the effects of several curing regimes on the compressive strength and bulk density of the SFCCC-based geopolymers. The use of this waste material could bring a reduction in cement used as a construction material and also help reduce the need for hazardous waste disposal, being both aspects of great environmental impact in the construction industry.

2. Experimental program

2.1. Materials

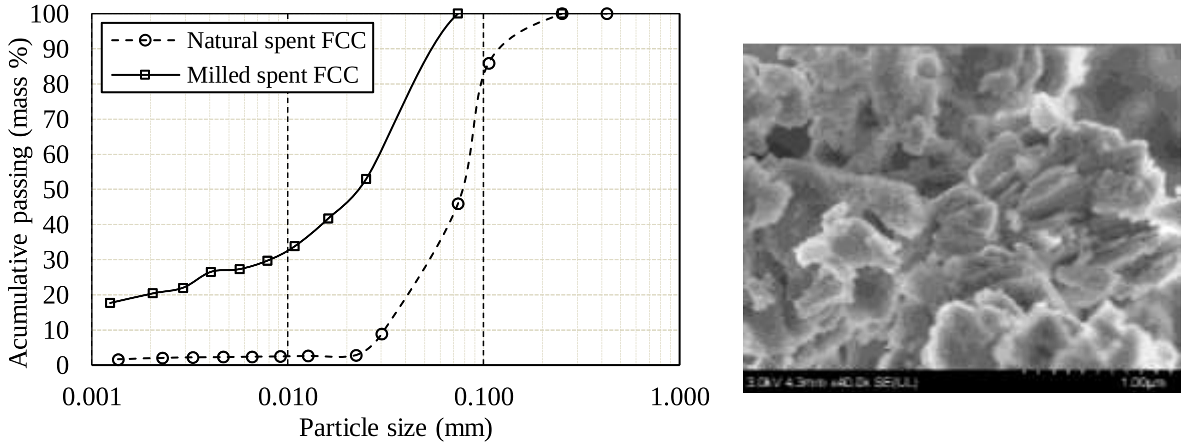
The SFCCC was obtained as a solid powder residue from a local oil refinery in Piura, northern Perú. The chemical composition analysis of SFCCC by X-ray fluorescence (Table 1) revealed that it has slightly more SiO_2 and less Al_2O_3 than similar materials previously reported [6,18,22] and a SiO_2/Al_2O_3 ratio greater than one. Lanthanum and vanadium oxides were identified as contaminants present in the zeolite structure during the catalyst synthesis [18]. The mineralogical information obtained from powder X-ray diffraction (XRD) analysis showed the presence of several crystalline phases together with an important quantity of amorphous components. Area analysis performed with Bruker TOPAS 5 indicated that the total amorphous components are approximately 64 - 66% (w/w). The crystalline phases were identified as a partially dealuminated Y-zeolite (PDF file 79-1479), mullite (79-1457), a silicate with the ZSM-5 zeolite structure (PDF file 44-0002) and quartz (PDF 86-2237). Rietveld fit with Bruker TOPAS 5 indicated that Y-zeolite dominated the crystalline phases (roughly 85% w/w) with minor amounts of other minerals (mullite 8-9%; ZSM-5 zeolite and quarts being below 3% each) The chemical composition is in agreement with the presence of these minerals. Its specific gravity was 2.6 g/cm^3.

The SFCCC was subjected to a milling process to reduce its particle size and increase its reactivity [9,12,14,21] using a laboratory ring pulverizing mill. Particle size analysis was determined by sedimentation process. The particle size range was 1.2-52 µm with a mean particle diameter of about 22 µm, which is slightly larger compared to what has been reported in previous studies [6,18,22]. The particle shape of SFCCC before and after milling were examined by SEM microscopy observation. Before milling, particles are spherical and have a roughness texture and after milling, particles are angular and laminated. The distribution of the particle size of the SFCCC and shape of the particles after milling are presented in Figure 1.

Table 1. Chemical composition on an oxide basis of SFCCC from X-ray fluorescence analysis (wt%).

Oxide	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	La_2O_3	V_2O_5	P_2O_5	LOI	Others
SFCCC	49.61	46.23	0.70	0.19	0.09	0.70	0.06	0.72	2.93	0.91	0.20	1.01	0.47
[18]	46.94	48.40	0.59	0.17	0.11	0.31	0.02	1.20	1.36	0.01	0.01	0.50	0.38
[6,22]	46.04	47.47	0.58	0.17	0.11	0.30	0.02	--	--	--	-	--	5.31

An activating solution (AS) based on a mixture of sodium silicate (SS) and sodium hydroxide (NaOH) solutions were used as suggested by Tashima et al. [22]. Sodium hydroxide pellets (99% purity) were dissolved in deionized water and a commercial sodium silicate solution (water glass, 28% SiO_2; 8% Na_2O: 64% H_2O) was used as provided.



(a) (b)

Figure 1. Particle size distribution and shape of the spent FCC. (a) Particle size distribution comparing in natural and after milled using the laboratory ring mill. (b) Laminar particles of SFCCC after milled.

2.2. *Specimens preparation*

Based on previous reports [6,18,22], the mixture was prepared using a 15 M NaOH solution and SS in a proportion of 1.25 in weight (Ms=0.85) and AS to SFCCC weight ratio of 1.20 (Na_2O 18.8%, SiO_2 15.6%, H_2O/SFCCC mass ratio of 0.74, H_2O/total solids mass ratio of 0.52). Geopolymer samples were prepared by mixing dry SFCCC powder with AS at approximately 25 °C for 10 minutes. The fresh paste was cast immediately in forged bronze cubic moulds (5 cm) that meet recommendations for testing the compressive strength of hydraulic cement mortars of ASTM C109 standard [23] and were subjected to vibration for 1 minute to remove air voids. Bulk density and compressive strengths of cubic samples were determined after 7 days. The reported values were the average of three samples.

2.3. *Experimental program for curing conditions*

To evaluate the curing conditions, two factors were considered as the curing regime: use of covering protection for the samples to avoid loss of water and a pre-curing period at room temperature for 24 hours. In this way, two conditions for protection against water loss were evaluated, covered (C) and uncovered (U) samples. Covered samples were sealed with plastic bags. Uncovered samples were let in the moulds without covering during curing inside the oven or at ambient conditions. The pre-curing consisted of letting the samples sit at room temperature for 1 day after been poured into the mould before heating. A curing temperature in a range of 25 °C to 100 °C for 24 hours was then applied for all cases. Ambient conditions were in the range of 25±2°C and 55% of humidity. Samples cured at high temperatures were stored in a ventilated oven with no humidity control.

The samples were subjected to three different regimes of curing conditions as a combination of the two factors mentioned before, as follows:

(1) Uncovered condition without pre-curing regime (UT). The demoulded samples were put in the oven without any protection. For temperatures higher than 25 °C, samples were placed in the oven immediately after being poured in the moulds for 1 day. After this time, the samples were taken out from the oven and let cool down to room temperature (25±2°C) until the time of testing.

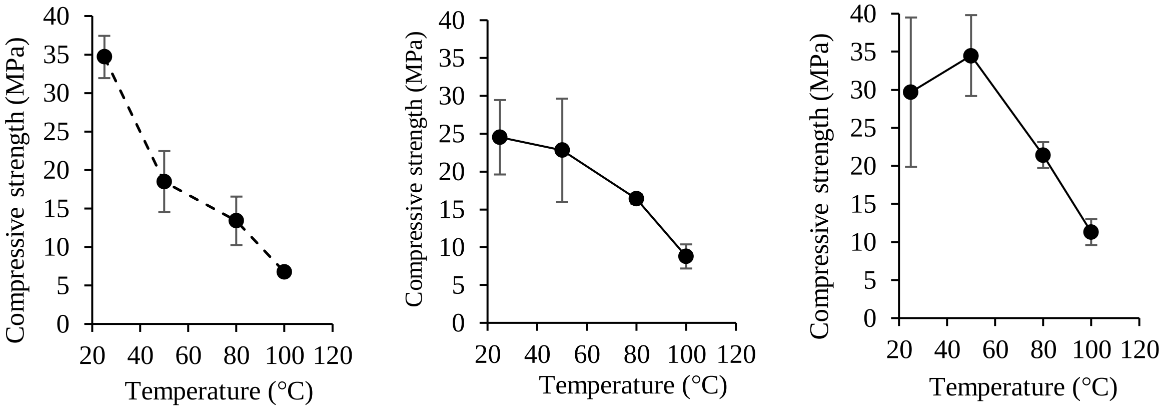
(2) Covered condition without pre-curing regime (CT). The samples were covered with plastic bags immediately after being poured in the moulds and heat was applied immediately after for 1 day. After this time, samples were taken out from the oven and let cool down to room temperature (25±2°C) until testing.

(3) Covered condition with pre-curing regime (CPT). The samples were let to sit at room temperature (25±2°C) in the moulds without covering for 1 day. After that, samples were demoulded, sealed with plastic bags and cured. In this case, covered protection was applied for 6 days. The curing temperature was applied for 1 day after which samples were taken out from the oven and allowed to cool down to room temperature (25±2°C) until testing.

3. Results and discussion

3.1. Effects of curing regime on the compressive strength

The results of the compressive strengths of geopolymer binders are shown in Figure 2. For UT regimen, the temperature in an oven application seems to have an adverse effect on the compressive strength when covering protection is not applied. All the samples presented cracking after curing, even though at room temperature. At room temperature, cracks had a depth of about 0.1 mm and oriented the failure pattern during the compressive test. On the exterior of this depth, the material was dense and had a shiny appearance; inside, the matrix had a white and powdering texture. This result can be attributed to an accelerated process of polymerization of the sample from the outside to the inside. This also produces a high strength layer on the exterior but reduces the homogeneity of the material. Despite the cracks, the compressive strength of the samples cured at room temperature was considerable compared to the samples cured at higher temperatures. The humidity in the environment during polymerization might have been responsible for the increase in the strength. For higher temperatures, the material presented a lower compressive strength but a more ductile fracture than the sample exposed to room temperature. This indicates that a better evolution of the polymerization process occurs. This behavior is consistent with the drying process and can be attributed to the lack of water when the temperature of the oven is increased. In this case, the samples had a more homogeneous texture, inside and outside, than that obtained at room temperature. However, samples cured at 100 °C presented a reduced compressive strength unless the homogeneous texture. This indicates a poor geopolymerization process of the samples by an excess of temperature and explains the low compressive strength measured. So, considering the integrity and homogeneity of the material, an optimal temperature near 50 °C can be considered for this regimen, at which the compressive strength reaches an acceptable level.



UT regime CT regime CPT regime

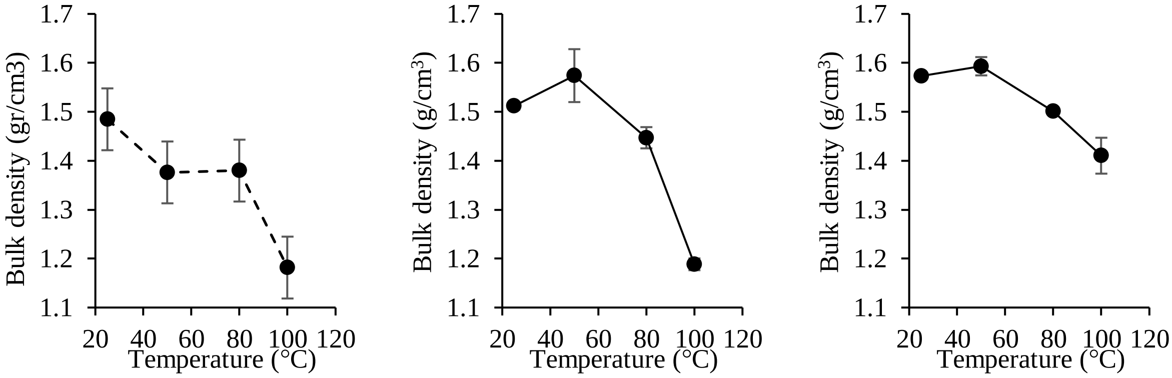
Figure 2. Effect of covering protection, pre-curing application and curing temperature on the compressive strength. (UT) Uncovered condition without pre-curing regime. (CT) Covered condition without pre-curing regime. (CPT) Covered condition with pre-curing regime.

In the CT regime, the samples were covered with plastic bags the whole time, right after moulding and until testing. In this case, a significant increase in the compressive strength was observed for temperatures above 25 °C. At room temperature, a reduction of the compressive strength is observed, when compared to the previous regime (UT). For this condition, the use of plastic bags reduces the compressive strength. This may occur because, at low temperatures, the excess of water inside the bag reduces the velocity of the polymerization, reducing the compressive strength compared to the uncovered condition (UT), since the reaction is an equilibrium process which needs to be displaced by water removal. But at higher temperatures, heating compensates this excess of water, accelerating the reactions and increasing the strength. This confirms that heating can be unfavorable to the final properties of geopolymers even at high humidity conditions [24] and the reduction of the loss of water results in a denser and more homogeneous material. For this regime, room temperature can be considered the optimal temperature.

Pre-curing, which is the time before the application of heat, was also evaluated (CPT). An optimal temperature was identified in this regime for the compressive strength. It is clear that pre-curing has no influence in the compressive strength at elevated temperatures, but it is of great consideration at the optimal temperature. These results confirmed the importance of pre-curing before application of heat as Nazari, Bagheri, and Riahi concluded [12]. This previous time is required to allow the dissolution of silica and alumina in the solid precursor without an excessive acceleration of polymerization. Compared to the previous two curing regimes, an increase of the compressive strength was observed when pre-curing was applied in addition to water loss protection. This increase was observed in all the samples with respect to CT regimen, although this increment is not significative for higher temperatures.

3.2. Influence of curing conditions on bulk density

For technological applications, it is often important to get the value of the apparent density of the finished product. The bulk densities of the samples versus the temperature of curing for the curing regimen are presented in Figure 3. It can be observed a severe reduction of the bulk density when no plastic bags were used (UT) compared to the other two regimens (CT and CPT). This can be attributed to the loss of water at the beginning of the geopolymerization, avoiding its incorporation at the framework structure. The water lost also includes the water required to form the OH^- ions needed for the synthesis of the geopolymer compounds [10]. This explains the reduction of the compressive strength observed in this condition. The same effect is observed when high temperatures are applied even if the sealed bags are used (CT and CPT).

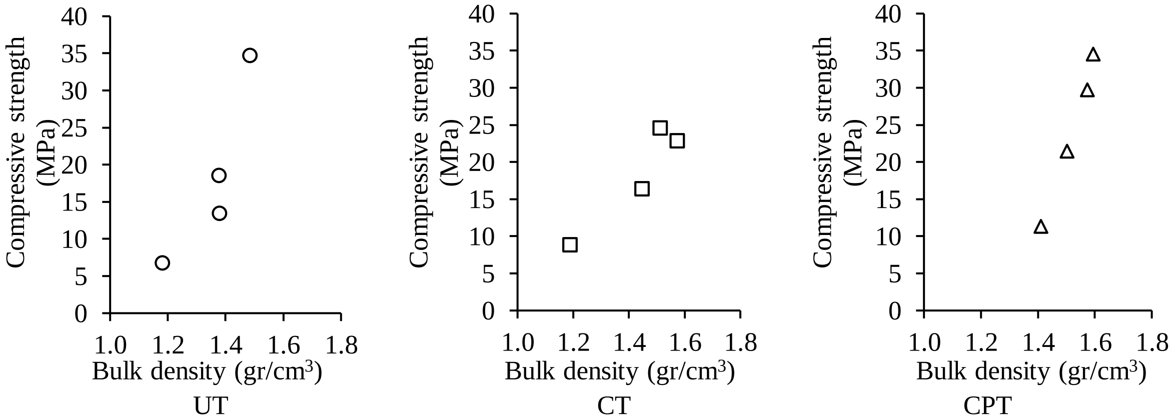


UT regime CT regime CPT regime

Figure 3. Effect of covering protection, pre-curing application and curing temperature on bulk density. (UT) Uncovered condition without pre-curing regime. (CT) Covered condition without pre-curing regime. (CPT) Covered condition with pre-curing regime.

Using sealed bags (CT and CPT), an optimal temperature for a maximum bulk density was observed and match to the temperature for the maximum compressive strength. At low temperatures, the excess of water cannot be eliminated quickly and remains in the material during solidification, creating microporous in the material which results in a slight reduction of its density but does not affect its compressive strength. At higher temperatures, the velocity of the reaction is higher than the velocity needed to eliminate the excess of water, increasing the microporosity of the matrix and reducing its density. Cracking development on the material needs to be taken into consideration as a factor for the reduction of the compressive strength. While porous and homogeneity of the material influence the density, the presence of cracks determines the compressive strength, reducing it. However, this process is different if a pre-curing period is applied. This can be explained because the amount of water remaining after pre-curing is lower, making the velocity of the reaction similar to the velocity needed to eliminate the water, improving the homogeneity of the material and its bulk density.

Individual values of the compressive strength and their corresponding bulk densities are plotted in Figure 4. A tendency to increase the compressive strength with the bulk density is observed. Even though the mechanical properties of geopolymers do not depend on the bulk density of the materials [24], curing conditions and pre-curing regimes influence the geopolymerization process and the framework structure of the matrix, promoting a denser and more homogeneous material. The homogeneity of the material can contribute to a higher compressive strength.



UT CT CPT

Figure 4. Relationship between bulk density and the compressive strength in SFCCC based geopolymer binders evaluated in this research: (UT) Uncovered condition without pre-curing regime. (CT) Covered condition without pre-curing regime. (CPT) Covered condition with pre-curing regime.

4. Conclusions

The temperature of curing, the pre-curing regime and the covering protection are key factors that determine the final compressive strength of the SFCCC based geopolymers. No covering protection of the samples can contribute to a higher compressive strength upon certain curing temperatures but cannot assure the homogeneity of the material nor the cracking of the sample.

The use of sealed plastic bags helps to reduce the loss of water and helps to control the cracking of the samples, producing a denser and more homogeneous material. In consequence, it is an efficient system to improve the homogeneity when heat is applied and to increase the compressive strength at room temperature.

Pre-curing before heating is of great importance to assure the correct geo-polymerization process. Nevertheless, it has no influence in the compressive strength at elevated temperatures.

Optimal temperature for curing in order to get a maximum compressive strength is only possible when pre-curing is applied together with a convenient water loss protection. The optimization is not possible if no covering or no pre-curing is used.

The curing regime has a significant effect on bulk density. The higher values for the bulk density are associated with a homogeneous material and can be increased if sealed plastic bags and a pre-curing regime are applied. This denser and more homogeneous matrix results in a higher compressive strength material.

For SFCCC-based geopolymers, the highest compressive strength (about 34 MPa) can be obtained with a 24 hours pre-curing period at room temperature followed by curing at 50 °C for one day in sealed bags. However, at 25 °C, the same pre-curing period and water protection system, an acceptable compressive strength of 29.7 MPa can be reached for practical purposes.

Finally, it can be concluded that SFCCC can be used effectively to produce geopolymer binders and, in this way, contribute to reduce the environmental impact of its disposal.

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