Chemical and mechanical properties of geopolymer concrete incorporated with cigarette filters

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Abstract. Smoking epidemics have increased the number of smokers around the globe. Moreover, the world urbanization steadily increases. As a result, environmental problems are exacerbated by the proliferation of combustible and electronic cigarettes and the cement invasion of permeable spaces. Therefore, sustainable construction/building materials that use recycled ingredients like cigarette filters are worth considering. This paper assesses and compares, for the first time in the literature, the chemical and mechanical properties of geopolymer concrete substituted by 0, 10, 15, and 20% by weight of cigarette filters. Results have shown that the higher the amount of cigarette filters, the lower the mechanical strength. However, the results also indicate that the geopolymerization reaction is still in progress as the compressive strength of all aged samples is still increasing.

1. Introduction
These Population and economic growth promote urbanization, which has led to a rapid shrinkage of permeable farmland. Sustainable construction materials and incorporation of recycled components therein could compensate for this phenomenon, as green buildings mitigate the impact on the environment and reduce the level of pollution [1]. Due to the production process of Portland cement, which is used in the vast majority of structural applications, carbon dioxide gas (CO₂) is emitted. For instance, to produce 1,000 kg of cement, 800 kg of CO₂ are released into the air, which represents around 7% of global CO₂ emissions [2]. To decrease the emissions generated from the production of Portland cement, a new alternative has been recently developed: geopolymer concrete. Indeed, the use of geopolymer concrete can reduces the CO₂ emissions rate [3]. The CO₂ emitted by geopolymer concrete is only due to the production of the alkaline solution [4]. This is reflected by the fact that only 200 kg of CO₂ are released into the air, to produce 1,000 kg of cement. This is 78% less than the CO₂ emissions generated by the production process of Portland cement [1]. Therefore, geopolymers can be
a viable solution to mitigate the CO$_2$ emissions rate. Although geopolymer technology is considered new, it potentially has ancient roots; being postulated as the building material used in the construction of the pyramids in Giza as well as other ancient constructions [5]. The process of forming the metakaolin-based geopolymer system is split into three main stages. At first, the continuous dissolution of the aluminosilicate precursors by breaking SiO$_4$Si or SiO$_4$Al bonds of the metakaolin particles to form free SiO$_4$ and AlO$_4$ tetrahedral units under the complex action of hydroxide ions [6]. Secondly, partial orientation and internal restructuring of precursors and alkaline polyciliate, the tetrahedral units SiO$_4$ and AlO$_4$ are linked alternately to yield amorphous geopolymers. The final step is reprecipitation where the whole system sets into a crosslinked inorganic three-dimensional network [7]. Geopolymers have a wide variety of properties and characteristics that rely on the raw materials used and the processing conditions. The characteristics of geopolymer include high compressive strength, low shrinkage, fast or low setting, acid resistance, fire resistance, and low thermal conductivity. With these advantages, geopolymers are considered to be suitable for a broad range of engineering applications [5,8].

Additional to the above, smoking epidemics is also leading to an increase in the number of smokers. According to the World Health Organization (WHO), smokers around the globe consume nearly 18 billion combustible cigarettes every day [9]. Trillions of cigarette filters – also known as butts – are thrown into the environment every year [10]. Only two-thirds of them reach the trash can. The rest is dumped on the street or outside the window. Generally, one waste cigarette butt consists of three parts: the filter tip, the remnant tobacco, and the paper wrappers [8].

While most cigarette entrails and paper wrappers disintegrate when being smoked, and cigarette filters are made of cellulose acetate, throwing cigarettes into the environment will not only drench them in plastic, but will also release nicotine, heavy metals, and many other chemicals into the surrounding environment [11, 12]. Due to their poor biodegradability, combustible cigarette butts greatly reduce plant growth, reach waterways and eventually the oceans, and can take many years to decompose [13]. As a result, the disposal and littering of cigarette filters is a serious environmental problem. In recent years, this environmental problem has been exacerbated by the proliferation of electronic cigarettes, which are largely made of plastic. E-cigarette use is prevalent. Nearly 6.9 million adults in the United States are using e-cigarettes [14] and usage rates are continuing to increase [15], especially among young adults [16].

As far as the authors are aware, an investigation aiming to assess the benefit of geopolymer concrete embedded with recyclable combustible cigarette filters is not available in the literature. It is essential to point out that geopolymer concrete was manufactured with combustible cigarette filters at 10%, 15%, and 20% by weight, then tested and compared to “reference” geopolymer concrete (with 0% combustible cigarette filters by weight).

2. Material and methods

2.1. Preparation of potassium-based geopolymer

To produce geopolymers, metakaolin has to be used as the main source of silicon dioxide (SiO$_2$) and aluminum oxide (Al$_2$O$_3$). The metakaolin used for this research purposes of this article were sourced in Lebanon and France. The industrial French metakaolin was purchased from Imerys [17]. Their particle size distribution curves were determined by laser diffraction. The sand used was normalized sand having the same properties as the standard sand used in concrete and mortar mixes (particles size, voids ratio etc...). Since geopolymers are formed by reacting aluminosilicate minerals (i.e., metakaolin) and silica, aqueous alkaline (MOH) solutions, where M is an alkali cation, our choice was to produce the following mortars by using an alkali metal cation (K$^+$). The alkali aluminosilicate geopolymers of the composition K$_2$O·Al$_2$O$_3$·4SiO$_2$·6H$_2$O will react to form high-strength monoliths, to form the mortars used as structural cement. The highly alkaline solutes KOH have been used as alkaline activators [18], with the mass ratio of activator liquid to the source material in the range of 0.6. The preparation of potassium-based geopolymer with the mole ratio of SiO$_2$/Al$_2$O$_3$ = 3, K$_2$O/SiO$_2$...
= 0.6, and H$_2$O/K$_2$O = 6.8 was obtained by mixing metakaolin with a potassium silicate solution. These mass and molar ratios showed optimal mechanical properties as reported in the literature [19]. The potassium silicate solution was prepared by dissolving potassium silicate and KOH. The solution was matured for 24 h to completely dissolve the silica and avoid any exothermic reaction [20].

In parallel to the preparation of the geopolymer material, the remains of smoked cigarettes were collected to partially replace metakaolin. In the laboratories of the Faculty of Engineering of the University of Balamand, tobacco and paper wrappers were thoroughly removed from the collected remains of smoked cigarettes, to obtain cigarette filters (CF) as displayed in Figure 1. Afterward, filters were blended and sieved to understand their particle size distribution. Similarly, since geopolymer mortars require the use of aggregates i.e., normalized sand, a granulometry analysis was carried out for the same purpose.

Four blends of MK/CF were investigated: 100/0, 90/10, 75/15, and 80/20, where numbers refer to the mass percentage of metakaolin and cigarette filters in each ratio. Geopolymer samples were prepared by mechanically mixing stoichiometric amounts of metakaolin and alkaline silicate solution to give K$_2$O/Al$_2$O$_3$ = 2.1, forming a homogenous slurry. The normalized sand was added considering a mass ratio of Sand/Metakaolin =3. After 5 minutes of mechanical mixing, the metakaolin, cigarette filters, and normalized sand the liquid activator was added gradually and mixed at low and high speeds for 15 minutes in the mixer to obtain the desired geopolymer mortar [20]. The potassium-based geopolymer mixes were then transferred to molds and vibrated for a further minute to remove entrained air before being heated at 60°C for the first 24 hours. Samples were then transferred from molds into sealed storage vessels cured in the laboratory at temperature ±25°C until the day of testing.

2.2. Chemical and mechanical characterization
To provide the general chemical compositions of the raw material, chemical characterization was performed. Table 1 summarizes the general chemical compositions of the Lebanese and the industrial French metakaolin. This characterization will underline the rate of the geopolymerization reaction and assess the raw materials. The data indicate that SiO$_2$ and Al$_2$O$_3$ were the major components determined for the different sources of metakaolin. As for the cigarette filters, the main component obtained from 2,826 types of non-burned cigarette filters indicated that the main component is cellulose acetate with an average value of 105.8 mg [21].

| Table 1. Chemical composition of Metakaolin (weight %). |
|----------------------------------|
|       | Al$_2$O$_3$ | CaO | SiO$_2$ | Fe$_2$O$_3$ | K$_2$O | MgO | Na$_2$O | P$_2$O$_5$ | TiO$_2$ | Lol  |
| Lebanese Metakaolin            | 31.21  | 0.07 | 45.21   | 2.26       | 0.12   | -   | 0.49    | 0.04     | -       | 13.96 |
| French Metakaolin              | 39.00  | 0.35 | 54.80   | 1.80       | 2.70   | 0.25| 0.10    | 1.50     | 1.10    |      |
The mechanical characteristics of the prepared samples were also assessed. The compressive strength (f’c) was determined according to the ASTM C39 (ASTM C39 / C39M-21) and using a universal testing machine (U test machine) with a pacing rate of 2.4 KN/s. Six samples from each mix were tested to achieve representative results.

### Table 2. Sieving and Specific Granulometry of Material used in the GP Mixes.

|                     | Sand   | Cigarette Filters | French Metakaolin |
|---------------------|--------|-------------------|-------------------|
| Median particle size, d50 (µm) | 24.7   | 2.5               | 6.1               |
| Specific Gravity (SG)    | 2.65   | 1.18              | 2.2               |

### 3. Results and discussion

The design of the geopolymer mortars requires selection and correct proportions of the alkali-activated solution, binder, etc... Each ingredient may improve a property while adversely affecting others. The following sections examine and discuss the effects of mixed parameters on the compressive strength of the potassium-based geopolymers with cigarette filters incorporated at different mass substitution rates.

#### 3.1. Elemental Analysis

The properties of geopolymer binder greatly depend on the chemical composition of source materials and activator solutions. Metakaolin from various sources has different mineralogy and reactivity that influence the reaction rate and the reaction product. Metakaolin with the high content of glass phase and finer particles could increase the degree of geopolymerization reaction and consequently increase compressive strength. In both metakaolin chemical characterization seen in Table 1, both types contained high levels of SiO\(_2\), nevertheless, the French industrial metakaolin contained higher levels of silicate. For this reason, it was selected to produce the final mixes. This approach was necessary since cigarette filters do not contain the required material for the geopolymerization reaction and contained cellulose acetate in great amounts. The formulations produced with the different mass rate substitution of cigarette filters have shown different consistent classes ranging from the different amount of silica present that will react to produce the geopolymer mortars. This affects mechanical performance. The findings could be explained by the interface between the aggregates (sand/cigarettes) and the binder exhibiting good adhesion.

#### 3.2. Sieving and specific granulometry

Sieve analyses were conducted for all solid minerals to check their specification (Table 2). The particles sizes conformed with the grading requirements. The metakaolin sieving analysis of the two different sources seen in Figure 2, indicates that the French metakaolin contains finer particle size that will thereby increase the rate of the geopolymerization reaction, thus confirming their use as well. The results of the grain size distribution of the cigarette filters indicated that the fineness modulus is a very fine graded material. Specific gravity (SG) is an important concept to know if mixtures are immiscible since it is related to particle size and morphology and therefore can have a fundamental influence on the characteristics and performance of the geopolymer mortars produced. The specific gravity of the fine materials was 2.65 for the normalized sand, 1.18 for CF, and 2.2 for the French metakaolin indicating that the cigarette filters have the lowest SG.
3.3. Scanning Electron Microscopy (SEM)

Pore Structure Characterization is important to determine the pore sizes. To compare the microstructure of metakaolin with the cigarette filters SEM (Scanning Electron Microscope) was performed and are presented in Figure 3.a and 3.b. The samples were cured at ambient temperature (23-25°C) and investigated for general microstructural features using SEM. As seen in Figure 3.a the microstructural size of the metakaolin powder showed a more uniform and bigger grain size than the cigarette filters. This observation is crucial to observe how the binder gel will form and bind around the MK and CF. The larger cenosphere can be seen in Figure 3.a that will act as a micro-filler in the matrix (geopolymer matrix). Comparing the microstructure of metakaolin with that of CF, it is clear that, the CF is smaller and varies in size and shape. The partial replacement of metakaolin with CF will thereby affect how the CF particles will bind in the paste. While the paste has a higher portion of CF, the mortars will reveal some un-reacted or partially reacted binder particles due to their very small size and the possibility of disseminating through the reaction process.

3.4. Mechanical Analysis

The early-age compressive strength of the synthesized alkali-activated geopolymer pastes (with different substitution rates 10, 15, and 20%) was measured after sealed curing for 3, 7, 28, and 90 days as per ASTM C39 [22] on 2.3x4.6 mm cylindrical samples. The purpose of testing the samples at different curing stages is to observe the rate of geopolymerization reaction of the potassium-based geopolymers depending on substitution with cigarette filters by mass. Figure 4 shows the variations in compressive strength for the four types produced tested. The results plotted in Figure 4 are the average of 6 tested samples to have a good consistency and repeatability in results. The compressive strength of the mixtures ranged from 2.25 MPa (20% mass substitution of CF) to slightly more than 10.21 MPa (100 % geopolymer paste) after 90 days. Since all the mixtures were designed with a constant amount of alkaline activator, the results indicate the effect of adding cigarette filters in different portions to the mixes with aging. The properties of source materials of geopolymer play a crucial role in the reaction mechanism of geopolymerization. The concentration and chemical composition of the alkaline activator (potassium-based) had a significant influence on the nature of the reacting products. As observed in Figure 4, the strength of the geopolymer mortars is affected by the amount of cigarette filters incorporated in the mixes. It has been noticed that the 100% potassium-based geopolymers gained higher strength from an early age. This is primarily related to the amount of silicates in the metakaolin that will be reacting with the potassium silicate solution. The presence of
soluble silica in the activator solution reduces the reaction kinetics and prompts the formation of more Si-rich gels [23]. It also affects the rate of crystallization and improves the degree of condensation and hence increases the compressive strength. Compared to the mortars containing 10, 15, and 20% mass substitution of cigarette filters, a loss of mechanical properties was observed. The higher the amount of cigarette filter included, the lower the mechanical strength developed. This is primarily due to the presence of free OH in the alkali-activated matrix, which could change the structure of the geopolymer. However, the geopolymerization reaction was still occurring since with aging, the samples containing different ratios of cigarette filters demonstrated an increase in compressive strength. The activation of cigarette filters by the alkali activator affected the strength due to the lesser degree of reaction in addition to the relatively smaller morphology of the cigarette filters.

Figure 3. SEM observation (a) Metakaolin Powder and (b) Cigarette Filters.

The properties of the resulting four types of geopolymer mortars can be drastically affected by minor changes in the available Si and Al concentrations during synthesis and with aging. Moreover, the partial insertion of the cigarette filters widely variates the proportion of the reacted silica and alumina that will later affect the compressive strength of the mortars produced. When comparing the geopolymer mortars with concrete mortars, it can be concluded that samples made with geopolymers indicated higher compressive strength values. For instance, according to Mohajerani A. et al, concrete mortar samples with 7.5 % mass substitution of cigarette filters showed a compressive strength of 6.5 MPa at day 28 and remained constant from this age on. Whereas, for geopolymers, it was seen that compressive strength kept continuous variation after day 28 and reached stable values with an asymptotic behavior around 9 MPa as of day 90 for samples with 10% mass substitution. In addition, it was visible that the geopolymerization reaction took place since day 1 like in previous studies and was seen as the main reason for early mechanical strength [18-20]. Another key factor was that was seen to affect in this research as well as in several studies was the increase in drying temperature within the first 24 hours of production (60°C). This rise in temperature improved considerably the compressive strength before exposing the samples, after day 1, to normal curing temperature 25±3 °C.
4. Conclusion and perspectives
Chemical and mechanical characterizations of the produced geopolymer concrete (0% combustible cigarette filters by weight) and geopolymer concrete with 10%, 15%, and 20% of CF by weight was performed. The aim of this study is evaluating whether modified geopolymers are superior to reference geopolymer concrete from a mechanical perspective. As indicated by the results, mortars containing 10, 15, and 20% by weight of CF are mechanically weaker. The higher the amount of CF, the lower the mechanical strength. It is worth mentioning that the geopolymerization reaction is still in progress as the compressive strength of all aged samples is still increasing.

Future research could focus on evaluating the thermal and mechanical properties of geopolymers with a lower CF weight percent (e.g., 2.5, 5.0, and 7.0%). As well as the evaluation of the environmental footprint of geopolymers throughout a Life Cycle Assessment (LCA) including the use and the end-of-life phases.

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