Concretes of low environmental impact obtained by geopolymerization of Metakaolin

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Abstract. This work shows results of partial replacement of Portland Type I cement®, by geopolymers obtained through alkaline activation of Metakaolin, in concrete mixtures. Replacement was made with 10%, 20% and 30% of geopolymers at 7, 14, 28 and 90 days of setting. Cement samples was mechanical and electrically tested. Mechanical resistance to compression assay shows that the best percentage of replacement is 10% for every setting time; highest value is 26.75 MPa at 90 days. Nyquist diagrams at different times of immersion exhibit same trend: decreasing of electrical resistance as time of assay goes by.

1. Introduction
In concretes, cement is one of the most important elements because of its properties of setting, expansion, and resistance to compression. Nevertheless, in the production cement process, there are huge emission of CO₂, due to calcination of clay and limestone, which in turn, produces clinker. Calcination temperature is so high and to reach it requires uses of petroleum fuels. In last decades, research has been focus on development of new cementitious materials, which production can be environmental friendly. Geopolymerization is a chemical process that can be carried out at room temperature and with reasonable CO₂ emission. Geopolymers are obtained by alkaline agent acting on an aluminosilicate source, these materials have had good cementitious properties [1-4]. This paper shows substitution of cement in concrete mixtures by geopolymers obtained from alkaline activation of Metakaolin [5]. Replacement percentages was 10%, 20% and 30% for setting times of 7, 14, 28 and 90 days. New material formed was tested mechanical and electrically.

2. Experimental
Synthesis of geopolymer started with Metakaolin (Mek) (thermical transformation of commercial Kaolin Faraon), sand, aluminum oxide Al₂O₃ and aluminum silicate Na₂SO₃, mixed until homogeneity. Reaction was performed during 20h with continuous stirring at temperature between 60 °C and 120 °C. The mixture is solidified and dried at 60 °C. Geopolymer (GP Mek) was then crushed according to ASTM C136 [6] to get a particle size of 4.75mm. New GP Mek, was studied by XRD to find that it is amorphous material with some crystalline phases: muscovite, anatase, microcline and quartz from kaolin starting material.

Concrete specimens were prepared at 10%, 20% and 30% of replacement of Portland by GP Mek and 7, 14, 28 and 90 setting days. Concrete specimens for mechanical strength resistance test had dimensions of 7.5cm diameter, 15cm high, according to NTC 673 [7]. Specimens for electrical
test of 3.0 cm diameter and 6.0 cm high, working electrode (steel) and reference electrode (graphite), were submerged in a 2% sodium chloride solution with bubbling oxygen. Design of mixture of concrete followed NTC 3752 specifications [8].

3. Result and discussion

3.1. Mechanical analysis

Results of mechanical assay are shown in Table 1. In this, it can be observed that the specimens with 10% replacement of geopolymer had higher resistances to strength than those for specimens with 20% and 30% for all setting times. In Figure 1, the tendency of the compression resistance values for both the reference specimens and the 10% substitution with geopolymer is shown. Here it can be seen that for 14 and 28 days of setting the resistance values of the specimens with geopolymer substitution are higher than for the reference ones, and even for higher times, the values are very close [9,10].

| Age of specimen (setting days) | GP Mek (%) | Compressive strength (MPa) |
|-------------------------------|------------|--------------------------|
| 0                            | 0          | 10.32                    |
|                               | 10         | 14.76                    |
|                               | 20         | 7.66                     |
|                               | 30         | 5.99                     |
| 7                             |            |                          |
|                               | 0          | 16.32                    |
|                               | 10         | 17.54                    |
|                               | 20         | 14.10                    |
|                               | 30         | 13.21                    |
| 14                            |            |                          |
|                               | 0          | 26.19                    |
|                               | 10         | 26.08                    |
|                               | 20         | 23.97                    |
|                               | 30         | 18.76                    |
| 28                            |            |                          |
|                               | 0          | 27.41                    |
|                               | 10         | 26.75                    |
|                               | 20         | 24.08                    |
|                               | 30         | 19.65                    |

Figure 1. Value of resistance to compression of 10% GP Mek and standard specimen as a function of setting days (The line that joins the points is to see the trend).
3.2. Electrochemical impedance spectroscopy (EIS)

The corrosion behavior of specimens of 90 setting days, with 10% and 20% was studied utilizing electrochemical impedance spectroscopy (IES) technique [11,12]. Specimens with 10% of GP Mek replacement showed highest impedance. Thus it could be more resistant to corrosion.

Figures 2 and 3 shows Nyquist plots for specimens with 10% of GP Mek and standard specimen (0% GP Mek) respectively, at different setting days. As times of study goes by, both plots show increasing impedance. With these diagrams and Bode plots (not shown here), resistance to corrosion ($R_\Omega$), resistance to polarization ($R_P$) and capacitance ($C_p$) were calculated (Table 2).

![Figure 2. Nyquist plot for 10% GP Mek specimens at different days (show in color).](image)

The values of $R_\Omega$ and $R_P$ are high at first day of assay, for both specimens (standard and 10% GP Mek), corroborating thus that there was no corrosion before. For 2 and 11 days of assay, $R_\Omega$ and $R_P$ diminish for both kind of specimens, but at second day, 10% GP Mek were lower than the standard specimen resistances. On the eleventh day, the behavior is the opposite. However, on that day, $C_p$ for standard is very low compared to 10% GP Mek, so it is assumed that in the 10% GP Mek, a protective oxide layer has been formed on the steel surface. This oxide decreases the exchange of ions of the solution to the material.

![Figure 3. Nyquist plots for standard specimens (0% GP Mek).](image)
Table 2. Values for the simple circuit of some samples evaluates on days 1, 2 and 11.

| GP Mek | Day | $R_\Omega$ (Ω$^a$cm$^2$) | $R_p$ (Ω$^a$cm$^2$) | $C_p$ (µF) |
|--------|-----|--------------------------|----------------------|------------|
| 10%    | 1   | 1720.00                  | 3.60x10$^{10}$       | 2.12x10$^{-11}$ |
| 11     | 2   | 132.10                   | 3052.1               | 252.94     |
| 11     | 11  | 128.30                   | 2514.1               | 307.08     |
| 0%     | 2   | 8001.00                  | 4.17x10$^{10}$       | 1.85x10$^{-11}$ |
| 11     | 11  | -19.48                   | 3432.8               | 224.89     |
| 11     | 11  | -19.48                   | 3432.8               | 224.89     |

4. Conclusions
Concrete mixture with replacement of 10% Portland Type I cement by GP Mek, exhibits appropriate mechanical behavior for shorts setting times, thus in the first seven days, it has higher values than those for standard. For large setting times (90 days) mechanical resistance has a slight decrease.

In electrical resistance study, it was found that specimen with 10% of GP Mek has high $R_p$ values, which means a corrosion rate close to zero. With two days of immersion in corrosive medium, $R_p$ is $3052.1\Omega \times cm^2$ and $3432.4\Omega \times cm^2$ for 10% GP Mek and standard, respectively, so rate of corrosion would be lowest for specimen without replacement. Nevertheless, with eleven days, $R_p$ for specimen with replacement is very high yet, which can be due to appearance of protective layer of oxide, according to elevated $C_p$ value found.

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