Pozzolanic Effects of Meta-Halloysite and Micro-Silica on Mechanical Strength and **Durability of Concrete**

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1-Introduction

The present study extracted residual halloysite soil from Shahr-e Babak area, Kerman, Iran. The soil was genetically formed by the degradation of quartzo-feldspathic rocks under hydrothermal processes. Halloysite, a natural mineral belonging to the aluminum-silicate hydrated group containing tetrahedral and octahedral Al layers, forms tubes in a nano scale with dramatic properties which have contributed to its widespread industrial applications. When it crystallizes with two water molecules in formula, it is structural called "endellite" $[Al_2Si_2O_5(OH)_4].$ Endellite originates from hydrothermal alteration of rhyolitic and granitic rocks, and changed into halloysite by hot fluids at 400 °C. Chemically, the outer surface of the halloysite tubes has properties similar to SiO₂ while the inner cylinder core is related to Al₂O₃ which together may improve the cement matrix [1-2]. When the structure of halloysite experiences a state of disorder, it can contribute to pozzolanic reactions. On the basis of X-ray diffraction (XRD) and X-ray Fluorescence (XRF) data (Figure 1 & Table 1), the selected halloysite is a chemically-appropriate additive for developing strength in concrete.

2-Materials and Methods

The selected halloysite was milled by the Los Angeles machine. To attain the fine powder of halloysite, a 38-µm sieve mesh size No. 400 (ASTM-E11& ISO 565/3310-1) was used in dry sieving, resulting in extending the surface area. The fine powder was gently calcined at 750 °C (ASTM C311) and remained in kiln at the same temperature for three hours. This process carried out by Iranian Mineral Processing Center, Karaj, Tehran. To compare the pozzolanic activity of meta-halloysite and obtain high strength concrete, the commonly used micro silica (SF) was employed in mix designs with 7% of the proportion. Meta-halloysite was added in 10 and 20% of replacement. For the present investigation, 8 mix designs were performed based on the water/cementitious materials (W/C) of 0.40 and 0.45; all samples were cured until the ages of 14, 28 and 90 days.



Figure 1. XRD analysis for meta-hallosite.

Table 1. XRF data for meta-halloysite.	
Major oxides	Wt%
SiO_2	46.29
Al ₂ O ₃	17.51
Fe ₂ O ₃	6.94
MgO	5.67
CaO	11.27
K ₂ O	3.17
Na ₂ O	1.04
P_2O_5	0.30
TiO_2	0.97
SO_3	1.22
SrO	0.07
Cl	0.62
Loss On Ignition (LOI)	4.92
Total	99.99

3- Discussion

The optimum amount of replacement OPC by adding pozzolanic materials includes 7 and 10% for SF and meta-halloysite, respectively. By increasing the age, all samples commonly show an increase in compressive strength (Fig. 2). A reverse trending is observed by increasing the W/C ratio from 0.40 to 0.45 which means that the high surface areas of additives (meta-halloysite and SF) prevented further water consumption in the concrete production. The compressive strengths of hardened concretes do not show a considerable increase at the ages of 14 and 28 days. This is related to pozzolanic reactions caused by SF (mostly until 14 days) and meta-

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halloysite (mostly until 28 days). After 28 days, the progressive improvement in compressive strength is observed in all mixing designs, indicating a new performance for the replacement of OPC by metahalloysite which is related to its long-term contribution in cement clinker reactions. This suggests that meta-halloysite contributes to both pozzolanic and long-term cement reactions. In other words, industrial additives (e.g. SF) mostly perform pozzolanic reactions which occur in the early stages of concrete hardening while natural additives, particularly calcined clays (e.g. meta-halloysite) perform early and late stages of strengthening concretes made with OPC.

The modulus of rupture was determined following the ASTM C78-02 on prismatic samples. For all the samples containing SF and meta-halloysite, the obtained flextural strengths are higher than control sample, indicating filler effects and low porosity in the cement gel. They could be associated with the high surface area of additives and low level of W/C ratio.

The durability of hardened concretes was determined by ultrasonic velocity (UV). After 28 days, for all mix designs, the UV results show higher speeds. In particular, samples made with 7% of SF and 10% of meta-halloysite at a low W/C ratio show a better performance indicating the condensation of the paste at early stages. Therefore, such concretes are durable in aggressive environment.



Figure 2. Compressive strength at different ages.

4-Conclusion

The results of this study clearly suggest that the combination of meta-halloysite and micro-silica for both W/C ratios— particularly in the case of the lower water ratio (0.40) when the mixes were made with 10% meta-halloysite—yields a significant

increase (89%) in the compressive strength (from 25.3 to 47.7 MPa). Also, the highest flexural strength (6.18 MPa) resulted in a lower W/C ratio (0.40). It is noteworthy that increases in W/C ratios for all mix designs do not show a considerable decrease in flexural strengths. Notably, the ultrasonic velocity (UV) for all mixes in the lower W/C ratio (0.40) shows a considerable increase, particularly in 10% of meta-halloysite compared with control samples. The aforementioned findings are indicative of better improvement of concrete strengths by natural pozzolan (meta-hallovsite) when compared with industrial pozzolan (SF). Taken overall, the novel findings for meta-halloysite include its significant development in pozzolanic reactions as opposed to SF, its long-term enhancement in mechanical strengths and durability indices as well as improved performance in low water contents in comparison with OPC and SF.