THE EFFECT OF SILICA FUME ON DIELECTRIC CONSTANT OF ORDINARY PORTLAND CEMENT AND HIGH ALUMINA CEMENT PASTE

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ABSTRACT

AC-Impedance Spectroscopy has been applied for the study of the dielectric properties of High Alumina Cement (HAC), Ordinary Portland Cement (OPC) and Silica Fume (SF) admixture in the frequency region from 10 Hz to 10 MHz. The real and imaginary dielectric constant ($\varepsilon$) has been computed for the cement paste containing Pure 100%HAC, 85%HAC+10%OPC+5%SF, 80%HAC+10%OPC+10%SF, 75%HAC+10%OPC+15%SF and 70% HAC + 10% OPC + 20% SF using GW in a W/C of 0.4. The dielectric constant ($\varepsilon$) value increases non-linearly and the compressive strength values reversibility up to 6.4 Mpa, although the reversibility is not complete. It is observed that an increase in HAC substitution by silica fume in the OPC-HAC blend decreases the aggressive attack of sulphate ions. The values of dielectric constant at a constant temperature of – 30º C, were dominated by properties of C-S-H gel percolation threshold at a volume fraction of approximately 15% - 20%. It is also evidenced that increasing the aluminium content beyond the percolation threshold decreases the relative dielectric constant. The dielectric properties of concrete can be used to characterize the development of the microstructure of the cement paste. During hydration the microstructure changes and so does the amount of water in the pore structure.

Keywords: OPC; HAC; SF; Characterization; AC-Impedance Spectroscopy; Dielectric Constant.

INTRODUCTION

Impedance spectroscopy (IS) is an electrical technique that has been used to characterize the microstructure of cement paste, providing useful information about the relationships between microstructure and chemical processes during the hydration of cement paste. Due to the presence of ionic bonding and moisture in cement, electric dipoles are present and dielectric constant has been measured for the purpose of fundamental understanding of cement based materials [1]. The dielectric measurement is a non-destructive and it can be performed
irrespective of the state of the sample (fluid slurry or solid). Hence the hydration reaction and structural changes can be monitored over an extended period after initial mixing. The hydration reaction of HAC produces $\text{CAH}_{10}$ and $\text{C}_2\text{AH}_8$. However the stable phases are $\text{C}_3\text{AH}_6$ and $\text{AH}_3$ and the other phases will inevitably convert to this [2].

Conversion reaction are shown schematically below

\[
\begin{align*}
3\text{CAH}_{10} & \rightarrow \text{C}_3\text{AH}_6 + 2\text{AH}_3 + 18\text{H} \quad \text{------- (1)} \\
3\text{C}_2\text{AH}_8 & \rightarrow 2\text{C}_3\text{AH}_6 + \text{AH}_3 + 9\text{H} \quad \text{------- (2)}
\end{align*}
\]

High early strength is one of the major advantages of HAC over OPC. This high early strength may mislead designers into ignoring the conversion effect during its service life.

The use of a siliceous material in this combination with a HAC and OPC was recently reported to be more effective than the siliceous material alone in promoting formation of stratlingite instead of hydro garnet. Siliceous materials including natural zeolites, fly ash, slag and silica fume were effective in inhibiting hydro garnet formation and preventing strength reduction in HAC and OPC. SF is preferred because it is highly pozzolanic due its particle nature and improves the properties of paste/concrete in fresh as well as hardened state. Generally the additions of SF increase the strength and improve the resistance to sulfate attack [3,4].

In the present investigation it has been planned to mix the proportions of HAC, OPC and SF in different combination. A particular permutation and combination of this blend is expected to bring a maximum strength development. The dielectric measurement using microwave technique in the AC impedance may give some useful information regarding the state of hardening of the cement paste and mortars at different time intervals since mixing. The present work explains the results and measurements of change in the dielectric constant and conductivity of the prepared blended cement paste when mixed with GW for the first 24h of the hydration in the microwave frequency range from 1 MHz to 12 GHz.

**MATERIALS AND METHODS**

High Alumina Cement (HAC), Ordinary Portland Cement (OPC) and Silica Fume (SF) supplied by Coromondal Ltd, Chennai, Ace Refractory, Chennai and Polygon Chemicals Ltd, Mumbai respectively. Chemical composition of raw materials is presented in table 1. The admixture cement pastes were prepared in the w/c ratio of 0.4 being this formulation 85%HAC+10%OPC+5%SF, 80%HAC+10%OPC+10%SF, 75%HAC+10%OPC+15%SF and 70%HAC+10%OPC+20%SF. Ground Water (GW) was used as medium. The prepared samples were analyzed by dielectric measurements used AC Impedance Spectrometer, Novo control technologies, Central Instrumentation Facility Lab at Pondicherry University. In these. Technique input AC 1V, Impedance ranges from 0.1 to 100 Ohm, Capacitance ranges from 0.1PF to 1F and Frequency ranges from 10Hz to 10 MHz.
The Chemical Oxide compositions of the HAC, OPC and SF materials are given in Table – 1.

<table>
<thead>
<tr>
<th>Chemical Oxide Composition (%)</th>
<th>OPC</th>
<th>HAC</th>
<th>Silica Fume</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>64.0</td>
<td>39.8</td>
<td>0.23</td>
</tr>
<tr>
<td>SiO₂</td>
<td>21.1</td>
<td>4.5</td>
<td>95.17</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.9</td>
<td>41.2</td>
<td>0.21</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.0</td>
<td>11.3</td>
<td>0.13</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.1</td>
<td>-</td>
<td>0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>1.6</td>
<td>0.6</td>
<td>0.15</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.78</td>
<td>0.05</td>
<td>0.25</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.18</td>
<td>0.05</td>
<td>0.15</td>
</tr>
<tr>
<td>LOI</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSIONS

For OPC, the dielectric constant decreases within 20 minutes after gauging with water. At 4-5 hours the dielectric constant decreases. At 2 hours the value of dielectric constant is 34. The dielectric constants of HAC are very much different from that of the OPC [5]. Comparing with the OPC, the HAC has a higher initial value of dielectric constant at 2 hours 39 and a much smaller values at 28hours. We noted that for the HAC the slow change period lasts for about 6 hours. At 6 hours the dielectric constant drops dramatically [6]. For the paste containing 100% HAC, the curves are similar to that of the HAC. But the values of dielectric constant are smaller than that of the HAC at 2 hours and greater at 28 hours

Figure 1 Plot of (a) real dielectric constant and (b) Imaginary dielectric constant with frequency for paste prepared 100% HAC using GW
**85% HAC+10% OPC+5% SF**

In addition of 5% SF, the relative dielectric constant (ε) decreases with increasing frequency as expected. In initial stage begins immediately after the cement mixing with water. The initial dissolution of cement grains into water and the formation of CAH$_{10}$, C$_2$ASH$_8$ etc. Make dielectric constant changes quickly. The formation of stratlingite (C$_2$ASH$_8$) is an important consequence of SF addition [7,8].

Using silica fume increases the strength of concrete at all ages, but it is apparent that much of the increase is realized at early ages and the rate of strength development at later ages is similar for silica fume concrete and Portland cement and alumina cement.

The setting of cement is controlled by the formation of a network of partially hydrated cement practices connected by hydration products [9] that can resist a shear force.

![Figure 2](image)

Figure 2 Plot of (a) real dielectric constant and (b) Imaginary dielectric constant with frequency for paste prepared 85% HAC+10% OPC+5% SF using GW.

**80% HAC+10% OPC+10% SF**

In ternary cement pastes, ettringite can be formed in the first few minutes of the hydration mainly through the following reactions

\[
\begin{align*}
\text{CA} + 3\text{CSH}_2 + 2\text{C} + 26\text{H} & \rightarrow \text{C}_6\text{AS}_3\text{H}_{32} \quad \text{(3)} \\
\text{C}_3\text{A} + 3\text{CSH}_2 + 26\text{H} & \rightarrow \text{C}_6\text{AS}_3\text{H}_{32} \quad \text{(4)}
\end{align*}
\]

In this stage, the rapid drop in dielectric constant, changes in both electric parameters slow down. Effects of SF on the rate and amount of heat evolution may be attributed to its physical and chemical effects on the cement hydration process. GRUTZECK et al., observed that the addition of SF underwent rapid dissolution in the calcium hydroxide solution and formed a new phase on the SF particles in a matter of minutes. This new phase is a calcium poor silica rich layer and may serve as a substrate for the formation of conventional CASH gel. In the first few minutes of hydration there is a rapid release of Ca$^{2+}$ and alkali ions from the cement compounds, the reduction in Ca$^{2+}$ in the solution increases the rate of release and amount of heat evolution i.e. hydration at this stage is accelerated by SF [10].
This may be due to the principal reaction between the metakaolin and the calcium hydroxide derived from cement additional, cementations aluminium containing CSH gel together with crystalline products which include calcium aluminate hydrates and alumina silicate hydrates ($C_{2}ASH_8$, $C_4AH_{13}$ and $C_3AH_6$) the formation of CAH and CASH phases increases the compressive strength [11].

Figure 3. Plot of (a) real dielectric constant and (b) Imaginary dielectric constant with frequency for paste prepared 80% HAC+10% OPC+10% SF using GW 75% HAC+10% OPC+15% SF

Fig. shows the addition of 15% SF observes the decrease of the dielectric constant with time can be ascribed to three phenomena; 1. Modification of the chemical nature of the constituents (2) change of the relative amount of individual phases and (3) variation of local topology the first effect seems to be of little importance because the concentration of ionic components in the free water does not change significantly in time and the dielectric constants of clinker and of CSH are substantially similar [12,13]. The 2 and 3 are strictly related to each other. The hydration of cement is accompanied by a decrease of the free water content and an increase of the volume of the solid phase. The downward shift of the spectra of the dielectric constant has also been attributed to the thickening of layers in the CSH [14,15,16]. In general, factors that either increase the porosity (e.g., high W/C ratios) or decrease the thickness of the gel layers (e.g., short hydration times) increases the dielectric constant.
Figure 4. Plot of (a) real dielectric constant and (b) Imaginary dielectric constant with frequency for paste prepared 75% HAC+10% OPC+15% SF using GW.

70% HAC+10% OPC+20% SF

Silica fume adsorbs the calcium ions to its surface and reduces the concentration of Ca\(^{2+}\) in the solution of this effect may accelerate the process of diffusion as shown by the results [17,18]. SF is composed of very small particles which when mixed with water may form agglomerations and are soon covered with a gel-like layer. Water may become enclosed in this layer, which has been suggested as the cause of the rapid water consumption of SF mixtures [19,20].

Chatterji et.al stated that around each cement particle there were approximately 100,000 grains of SF. Clearly this number depends on the size of the cement and SF particles and the percentage of SF in the mixture. Water required for the hydration of the cement grains will have to percolate the rough the layers of SF. The resistance to this water flow would increase with an increase in the thickness of the SF layer with a lowering of the w/c ratio. At higher w/c ratios the voids between particles are originally filled with water and the particles may be fully separated by a water film. In this case SF will dissolve and move into the solution instead of adhering to the cement particle surfaces as both surfaces have a silica rich layer (negative Charge). SF even though it adsorbs some water, does not reduce the amount of water available for cement hydration therefore the retarding effect reduces. The addition of 15% SF develops very low strengths and high levels of porosity. It implies that the formation and interlacing of microcrystal and the agglutinative “gel of alumina” remain incomplete.
Figure 5. Plot of (a) real dielectric constant and (b) imaginary dielectric constant with frequency for paste prepared 70% HAC+10% OPC+20% SF using GW

Conclusion

The combination of silica fume and Portland cement and high alumina cement should result in a number of synergistic effects, some of which are obvious as follows.

- Silica fume increases the long term strength development of cement/concrete.
- To obtain the dielectric capacitance of cement paste free of contributions from the solid sample phase and determined the various frequency and real and imaginary dielectric constants are calculated. It is expected that their study will allow gathering information related to diffusion mechanisms in concrete.
- A higher water-cement ratio promotes greater ion dissolution. The dissolution depends on the water quality and impurities present in the water.
- Increase in pore size or a decrease in product layer thicknesses leads to a higher dielectric constant.
- During the initial period of hydration the water evaporation is higher for higher W/C ratio.
- Dielectric constant decrease with increasing frequency from 100 Hz to 10 KHz and then decreased slowly and become almost constant up to 1 MHz, this is due to the inability of the electric dipoles relaxation.
- The value of dielectric constant is water content dependent.
- Dielectric constant values for hardened Portland cement pastes in the RF range show a rapid decrease in the interval 1 MHz to 100 MHz. They reach relatively constant values at higher frequencies.
- Increase of HAC substitution by silica fume to complete substitution in the 10% OPC 80% HAC 10% SF composite decreases the aggressive attack of sulphate ions on the hardened cement pastes.
The dielectric properties can very well be used to characterize the changes in the microstructure during hydration. The dielectric properties can be linked to the microstructure with the degree of hydration. The degree of hydration, in its turn, is directly related to properties like strength.

References