Investigation on the Electrical Impedance and Microstructure Behavior of Cement Pastes Containing K$_2$SO$_4$

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Abstract: The effect of partial replacement of K$_2$SO$_4$ with ordinary cement in the different concentrations (X) ppm K$_2$SO$_4$ by weight (X=0, 4000, 8000 and 12000 ppm) at Water / Cement (W/C) ratio (25 %) on the electrical impedance. The hydration mechanism was studied in the presence of different concentration (X) of K$_2$SO$_4$ in different samples systems (M$_0$, M$_1$, M$_2$ and M$_3$).

Key words: Electrical properties • Physical properties • Effect of sulfate

INTRODUCTION

The study includes the electrical impedance, phase changes and microstructure by using XRD diffraction and scanning electron microscope (SEM) analysis. The results show a clear change in the measured parameters, with porous correlation to the changes in the pore microstructures, the pore solution chemistry and the dipoles of ions inside the micro pores oriented to follow the alternating signal when an electric field is applied.

Results indicate that the changes in the electrical impedance and the hydrated phases mainly depend on the microstructures changes, occurring during the hydration mechanism. These changes are not constant with the curing time and the concentration (X) of sulfate ions, in the different samples. Also the experimental results show that the minimization variation in the electrical impedance occurs at x=4000 ppm (i.e.) in the system M$_{01}$, that is related to

- The water of hydration is becoming adsorbed and retentionally bound.
- Polar molecules are becoming bound and locked as the gel-like hydration products of cement grains extend to meet each other and interact with sulfate ions.
- The crystallization of the calcium hydroxide (CH) hydrated phase.
- The expansion effect due to the formation of the gypsum and ettringite through the interaction of the sulfate ions with the hydrated phases of the cement material and.
- The loss of strength and mass of the cement material, which caused by the deterioration of the cohesiveness of the cement grain matrix [2, 3].

The effect of the sulfate ions in the cement material is a quite complex and despicable process. This mechanism is mainly depending on a various parameters such as cement type, cement composition, sulfate add, cation type, exposure conditions and pH value of the cement medium [4, 5].

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The electrical properties microstructure analysis of cement pastes and their effect by using different concentrations of sulfate ions were studied to clarify the physical performance during the hydration mechanism and can be used as a tool for assessing the potential deleterious effects of sulfate bearing in cement materials [6].

The objective of this work is to provide information for the durability problem of the actual composition of the hydration products and their variation with the concentration of the sulfate ions in the different cement matrix (M₀, Mᵢ₀, Mᵢ and Mᵢᵢ) through the electrical impedance measurement, X-Ray (XRD) and scanning electron microscopy (SEM) analysis.

MATERIALS AND METHODS

The Experimental Procedures: The materials used in this investigation are composed from the ordinary Portland cement (OPC) (M₀) system mixed with different concentrations (4000, 8000 and 12000 ppm) of ultra pure (Aldrich) of K₂SO₄ to form the other systems (Mᵢ₀, Mᵢ and Mᵢᵢ) by weight at w/c ratio (0.25). The chemical composition analyses of the OPC used to prepare the different systems of (M₀, Mᵢ₀, Mᵢ and Mᵢᵢ) under investigation is represented in the table (1).

The cement pastes were prepared using the standard water of consistency. In the electrical impedance measurements, the test cell of the coaxial type [7], included concentric inner and outer polished electrodes mounted on an insulated based plate. The different samples were placed in the space between the electrodes and the cell was kept in a humidity chamber at room temperature ~ 25°C as well as 100 % relative humidity during the test period ~ 7 hours. The measurement was taken exactly 5 minutes after the first contact with water at 100 kHz. The electrodes were hooked to an automatic RLC bridge [PM-6304 Fluke & PHILIPS] for impedance measurements between the electrodes during the hydration stages of setting and hardening.

RESULTS AND DISCUSSION

The pore microstructure and the pore solution chemistry mainly determine the impedance behavior. The explanation may be as follows, the dipoles of ions inside the micro pores are oriented to follow the alternating signal when an electric field is applied. The time for the orientation of ions or relaxation time appears to be affected by the pores geometry. The surface chemistry of the solid, pore size and pore surface chemistry could limit the oscillation frequencies of the hydrated ions and water molecules, which respond to the applied AC signal [8].

Fig. (1) shows the variation of the impedance within minutes for the different samples of cement paste. The Figure shows that the impedance depends on the concentration of K₂SO₄ in cement paste samples. For all samples the impedance shows a small change with curing time, due to the small numbers of the free ions and the particles are bound to the particle’s surface. At a certain critical time ~ 200 min, the impedance increases with curing time, depending on the concentration of K₂SO₄ in cement pastes. This increment gives the rise of amplification mechanism which related to the existence of many almost pure conducting channels which stretch across the entire length of the system and are blocked off only by very thin barriers. Every channel of this type contributes to an abnormally large capacitance and all of these are connected in parallel [9]. The rate of decrease in the electrical impedance with increasing the concentration of K₂SO₄, have contributed to the decrease in the free ions in different samples with curing time and also decreased the charges, which are not bound to the particle’s surface. Also the increase in the impedance at ~ 300 min. in the sample of concentration 4000 ppm can be regarded as a geometrical random arrangement of material phases which results in effective impedance is much higher than the value of any individual material phase [10].

Figure (2) illustrates the dependence of the impedance with the concentration of K₂SO₄ in the different samples at the curing time ~ 200 min. The impedance increases in the Mᵢ₀ system, but it decreases with the higher concentration in the other systems Mᵢ₀ and Mᵢᵢ. The increase of impedance in the M₀ system is related to the rise of amplification mechanism which related to the existence of many almost pure conducting channels which stretch across the entire length of the system and are blocked off only by very thin barriers, but the decreases in the system Mᵢ₀.

Table 1: Chemical analysis of OPC (mass %).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>H₂O</th>
<th>SO₄₂⁻</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>20.85</td>
<td>0.28</td>
<td>4.7</td>
<td>3.86</td>
<td>0.16</td>
<td>1.6</td>
<td>61.71</td>
<td>0.967</td>
<td>0.25</td>
<td>0.61</td>
<td>0.68</td>
<td>2.9</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig. 1: The dependence of the impedance on the concentration of potassium sulfate in cement paste samples with time.

Fig. 2: The variation of the impedance with the concentration of potassium sulfate in cement paste samples at 200 min.

Fig. 3: The relation dependence of the impedance on the different concentration of potassium sulfate in cement paste samples in the time range up to 30 days.

Fig. 4: The variation of the impedance in the intervals times 30 days with the concentration of potassium sulfate in cement paste samples.

Figure (3) illustrates the variation of the impedance with curing time (days) in the different system M₀, M₀₁, M₀₂ & M₀₃. The impedance is increased gradually during the (14-20) days; this increase is clear in the M₀ and M₀₁ systems only. After this range there is a large peak due to the jump in the values of impedance and becomes a maximum at ~ (24-28) days, this peak is deformed with increasing of K₂SO₄ that is clear in the M₀, M₀₁ & M₀₂ systems. The increase in the impedance through the variation of hydration time (days) in the different samples may be due to the voids in these mortars and the polarization effects or capacitive reactance [1]. The decrease of the electrical impedance after the duration curing time ~ (24-28) days in all systems can be related to the water which is insufficient for complete hydration, some cement remains unhydrate and can never hydrate, since gel which already occupies all spaces is available [12].

Figure (4) represents the variation of maximum impedance value in the different systems, through the hydration interval time (24-28) days. Figure (4) shows maximum values reached with a minimization variation in the M₀₁ (4000 ppm) then accompanied by increasing in the M₀₂ & M₀₃ systems. The decrease in the impedance is due to absorption of free water, then combined into the structure caused by the interaction of sulfate ions with calcium silicate hydrate (CSH) and these leading to the CSH layer collapse [13]. The increase in the impedance with increasing of K₂SO₄ especially in the M₀₂ and M₀₃ systems indicating that the ionic conduction paths through the paste become more tortuous as the cement gel extends, the viscosity of the solution increases and the ionic concentration decreases, because the free ion in the water of hydration finds it more tortuous to drift through the capillary pore in the paste [9].
Figure (5) represents the variation behavior of the maximum impedance in the interval hydration time (22-28) days with the concentration of K$_2$SO$_4$ for the different samples. The behavior of this curve represents the same behavior as in fig. (4) and supported that the minimum variation for this relation is occurring in the M$_0$ (4000 ppm). The decrease of hydration time with increase the sulfate ions in cement paste may be related to the (SO$_4$)$^{2-}$ group, which separates and bits of the gel covering from the underlying crystal and immediately causes the crystal surface to be accessible to the sulfate group ions at such spots and thus permits a rapid reaction during a small interval time [14]. But the increases of hydration time in the M$_0$ and M$_1$ systems are mainly related to the dormant period of reaction of (SO$_4$)$^{2-}$ groups in cement paste and that is depending on the concentration, this dependence could be due to the bleeding or flocculation of these phases contained in cement paste during the interaction of (K$_2$SO$_4$) with these phases [15].

Figures 6(a-d) illustrates the XRD patterns of hydrate cement paste in the different systems at curing time of 28 days. This figure related the free lime content in all systems. This may be due to the increase of the hydration process with curing time [16]. From the figure, one can also notice that the continuous variation in the intensity of CH, β-C$_3$S, CaCO$_3$ tends to the decrease with the increase of (SO$_4$)$^{2-}$ group in the different samples. This result could be attributed to increase the degree of stability of ettringite formed in higher porosity pastes [17].

The peak of C$_3$S phase decreases by increasing the concentration of K$_2$SO$_4$ in cement pastes and it leads to excess of liberation of free lime during the hydration of the different systems. Also, the peak of ettringite tends to decrease with increasing the (SO$_4$)$^{2-}$ groups that could be due to the reaction of K$_2$SO$_4$ with the Ca(OH)$_2$ to form gypsum [18].
The effect of (SO$_4^{2-}$) groups on the microstructure of the different mixes are deposited in Figs. 7(a-d) at curing time of 28 days, where Figure (7a) is for a pure cement M$_0$ system which is appearing as a massive structure and is composed from a nearly amorphous CSH. In addition, there is platly crystal of calcium hydroxide (CH) and minor of both hexagonal lamellar crystals Figure (7d) represents the cement system M$_{10}$ (12000 ppm), which indicates the presence of gypsum and ettringite. This reveals that some deleterious reactions have been taken place between the cement components and sulfate ions. [19]

CONCLUSIONS

The following conclusions can be drawn based on the test results of this study:

- The change in electrical impedance with the concentration (x) of sulfate ions can be taken as a monitor of change in the pore microstructure during drying and rewetting and it is because the dipoles of ions inside the micro pores are oriented to follow the alternating signal of the applied electric field. The time for the orientation of ions or relaxation time appears to be affected by the geometry of the pores.
- The increase in the impedance for all different systems with curing time is attributed to the complex geometry. This gives rise to the amplification mechanism which is related by the possible existence of many pure conducting channels which stretch across the entire length of the system and can be blocked off only by very thin barriers.
- The decrease in the electrical impedance is related to the rate of increasing in the number of free changes that are not bound to the surface and the numbers of bound charges, which are bound to the surface and able to oscillate under the action of the alternating electric field by producing a polarization current.
- At the later age of hydration (22-28) days, the clear variation of the value of maximum impedance and curing time in the system M$_{10}$ (4000 ppm) are mainly related to the microstructure change caused by the interaction of sulfate group (SO$_4^{2-}$) with the calcium silicate hydrate (CSH) and this leads to the CSH layer collapse. With respect to the curing time this is related to (SO$_4^{2-}$) group which separates the gel bits covering from the underlying crystal.
- The rate of variation in the intensity of an anhydrous cement phases C$_3$S and $\beta$-C$_3$S the hydration products interact with (SO$_4^{2-}$) group to form gypsum and ettringite, leading to the water absorption of crystallization ettringite and change in the morphology of the ettringite crystal size. These results are in good agreement with the X-Ray analysis and the SEM micrographs.
REFERENCES


