ABSTRACT: The microstructure of hardened cement paste was investigated by A.C. impedance spectroscopy in range of 50 Hz to 1 MHz. We monitor the hardening process of cement paste with two different water – cement ratios (0.4 and 0.5). The results demonstrate that impedance measurement is very sensitive to changes in hydration kinetics and microstructure development due to water – cement ratios.

KEY WORDS: cement paste, impedance spectroscopy, microstructure

1. INTRODUCTION

Portland cement is the most common type of cement in general usage in many parts of the world, as it is a basic ingredient of concrete and mortar. It is a fine powder produced by grinding Portland cement clinker and gypsum which controls the set time.

When water is mixed with Portland cement, the product – cement paste sets in few hours and hardens over a period of weeks. These processes can vary widely depending upon the mix used and the conditions of curing of the product. The reaction and the reaction products are referred to as hydration and hydrates or hydrate phases, respectively.

Setting and hardening are caused by the formation of a microstructure of hydration products of varying rigidity which fills the water-filled interstitial spaces between the solid particles of the cement paste or mortar. The behavior with time of the setting and hardening therefore depends to a very great extent on the size of the interstitial spaces, i.e. on the water/cement ratio.

After initial mixing, the water originally between the cement particles gradually becomes a highly conductive pore fluid, due to the dissolution of calcium and alkali ions from cement. The main product of reaction is a poorly crystalline or amorphous calcium silicate hydrate commonly referred to as C-S-H (standard cement chemistry notation: \( C = CaO, S = SiO_2, H = H_2O \)), with the hyphens denoting a varying C/S ratio non-stoichiometric compound. This phase is also conductive, because its nanometer-sized pores are filled with conductive pore fluid. Another important product is calcium hydroxide, CH, which forms in crystals. With respect to electrical properties, the only phases of importance are capillary porosity and C-S-H. Other phases are insulators. [1]

Since its initial application as an investigative technique for monitoring hydrating cementitious systems, impedance spectroscopy (IS) is now receiving considerable attention as a potentially powerful method in characterizing microstructural evolution and pore structure development in cement. [2] In IS measurements are made over a range of frequencies and usually presented in a Nyquist plot, showing the imaginary versus real components of the impedance, with generally takes the form of two complete or partial semi-circular arcs. The low-frequency arc is dominated by the polarization resistance of the electrodes, and the high-frequency arc by the behavior of the bulk material. [3] Impedance spectra of cement pastes depend strongly on the amount of porosity present in microstructure, and their changes that accompany hydration are due to changing amounts, distribution, and arrangements of microstructural phases. [1]
2. EXPERIMENTAL

Impedance spectra were monitored on hydrating Portland cement pastes CEM I. The pastes were prepared with two different water – cement ratios: 0.4 and 0.5 (S1 = 0.5, S2 = 0.4). The mixtures of water and cement have been cast into cylindrical modules. IS measurements was used form 50 Hz to 1 MHz with the pairs of Pt electrodes. The equipment employed to obtain the impedance spectra was a RCL Meter PM 6306 Fluke. The experiments were conducted in environmental relative humidity. The samples were investigated at 9, 37 and 135 days.

3. RESULTS

![Graph of S1 impedance vs. frequency for samples 1 and 2]

Fig. 1: Impedance vs. frequency for sample 1

![Graph of S2 impedance vs. frequency for samples 1 and 2]

Fig. 2: Impedance vs. frequency for sample 2
Fig. 3 – 8: Nyquist plots of samples 1 and 2, reacted for 9, 37 and 135 days
The results of the electrical properties of Portland cement pastes are shown in Fig. 1 and Fig. 2. A typical impedance spectrum of the cement paste is shown in Figures 3 – 8, where imaginary versus real component of the impedance is reported (Nyquist plot). For sample S1 and S2 too, appear a single arc in the high - frequency range with a small part of a second arc in relatively low - frequency region.

The high-frequency arc is attributed to the bulk paste impedance behavior and the second low frequency arc is due to the cement paste-electrode surface capacitance contribution. Higher porosity, larger pore size of cement paste and the increase ionic concentration result in smaller high-frequency semicircle (after 9 day). As the hydration process progresses an increase of the high-frequency arc diameter was observed - it increase with decreasing porosity. This behavior is due to that, in fact, in cement - based materials the most relevant contribution to conductivity comes from the presence of capillary aqueous phase, which is consumed in hydration process.

4. CONCLUSIONS

The experimental results demonstrate the possibility of monitor of the hydration process of Portland cement pastes by IS technique.

5. REFERENCES