Effect of Different Micro Metal Powders on the Electrical Resistivity of Cementitious Composites

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Abstract. The electrical resistivity is an essential parameter describing materials' capacity to convey electric current. Normal cementitious materials display high estimation of the electrical resistivity because of their insulating nature. However, the high electrical resistivity of concrete can be reduced by a sufficient amount of electrically conductive admixture. Such an improvement is advantageous in self-sensing or self-heating concrete design. In this study, the effects of metal additives on the electrical resistivity of hardening cement paste were investigated. In the experiments, two different types of metal admixtures; copper powder and iron powder were used. Hybrid composition of copper and iron were also considered for comparisons of the electrical resistivity. A water to binder ratio of 0.35 was used. The metal powders were used in the mixtures by replacing the cement in ratio of 0%, 5%, 10%, 15% and 20% by weight. The total binder content (cement and metal additives) was always the same in the experiments. The measurements were carried out at room temperature by using two-electrode-AC method. The test results indicate that the metal cement composites with 20% of cement weight improved the lower electrical resistivity of the cement paste than plain cement paste. In addition, composites with copper powders had less electrical resistivity than those with iron powders. The reduction of electrical resistivity with an increase of metal content was steady for when of using hybrid composites better than when using metal powders alone. The Different frequency options 1 kHz, 10 kHz and 100 kHz were used to investigate the effect of impedance-frequency and phase angle-frequency of a sample test using the LCR meter. The highest current frequency available on the LCR meter, 100 kHz, was chosen to be used as the applied current frequency in all of the experiments which exhibit much lower phase angle values that can cancel the effect of change in electrical resistivity measurements.

1. Introduction
The electrical resistivity of the concrete is a very important material property that can be defined as the resistance of the concrete against the flow of an electrical current through the concrete. Concrete, which can be classified as a semiconductor material, has an electrical resistivity (around 109 Ω.m) changing considerably depending on a number of variables [1-3].

The electrical current is carried by the broken down charged particles streaming through the pore arrangement in the concrete. In this manner, all the variables such as water-cement ratio (w/c), cement type, pozzolanic admixtures, and the degree of hydration that are influencing the pore structure of the concrete, are moreover influencing the electrical resistivity of the concrete [4]. Environmental conditions such as temperature and moisture contents moreover have a huge effect on the electrical resistivity of the concrete [5].
Recently, many researchers focused on the study of the electrical resistivity of cement-based materials, which is due to the fact that an addition of a relatively small amount of conductive materials leads to a significant decrease of the electrical resistivity [2,6-13]. This alteration opens up modern application ways. Such materials can be utilized as self-sensing sensors [14-19], self-heating components [20-24] or materials utilized for electromagnetic protecting [25]. Different electrically conductive admixtures, such as steel fibres (SF), carbon black (CB), carbon fibres (CF), carbon nanotubes (CNT), graphite powder (GP) or nickel powder (NP) were examined in the past [18] in an effort to achieve aminimize of the electrical resistivity.

The electrical resistivity of concrete can be described as the ability of concrete to resist the exchange of particles subjected to an electrical field. In this setting, resistivity measurement can be utilized to evaluate the estimate and degree of the interconnectivity of pores. Resistivity $\rho$ is an inherent characteristic of a material, and is independent of the geometry of the sample. Equation (1) describes the relationship between the resistivity and resistance:

$$\rho = K \cdot R$$  \hspace{1cm} (1)

where $R$ is the resistance of concrete; and $k$ is a geometrical factor which depends on the size and shape of the sample as well as the distance between the probes on the testing device. In practice, electrical resistance is directly measured by the testing device and resistivity is calculated from Equation (1).

Electrical resistivity estimation of concrete can be made by utilizing the four or two-probe strategy. The previous includes utilizing four electrical contacts - the external two for passing current, the inner two for voltage estimation so that the contact resistance is not included in the measured resistance. The latter mentioned includes utilizing two electrical contacts - each for both current and voltage, so that the contact resistance is included in the measured resistance.

The utilization of mineral admixtures such as silica fume, fly ash and granulated blast furnace slag (i.e. pozzolans) in the concrete generation has picked up noticeable quality in worldwide concrete construction. In 2012, [8] used mineral admixtures (silica fume, fly ash and granulated blast furnace slag) inside cement paste and found that applying electric current can be used for obtaining rapid setting time on the cement paste with high volume mineral admixture.

Recently, Nickel powder has been used by 5, 10, 15, 17, 18, 19, 20 and 23% of cement weight to study the change of electrical resistivity in cement composites [27]. The results showed that the composites filled with adjusted nickel powder illustrated great abrasion-sensing properties, with humidity and temperature self-compensation capacities.

In recent years, numerous studies have been done on the mechanical and electrical properties of cementitious composites blended with different sorts of fillers, and a few of these consider have gotten significant upgrades. However, little or no work has been done on the improving effect of different metal fillers in micro size scales. This work aimed to study the electrical properties of blended cement pastes containing different types of metal admixtures as copper powder and iron powder in ratio of 0.5, 10%, 15% and 20% by weight of the cement.

2. Experiment

2.1. Materials

Portland cement type CEM II/B-M 32,5 R (Aşkale Cement Factory/ Turkey) was used as the cementitious material. Table 1. shows the Physical and chemical properties of OPC. Copper powder with particle sizes (0-50 \(\mu\)m, purity 99.9%) and iron powder with particle sizes (0-50 \(\mu\)m, purity +99%) purchased from (Ege Nanotek Kimya Sanayi Limited Co. Ltd.) were used as electrically conductive components (Figure 1). Hyper plasticizer (Master Glenium T 803) used in ratio 0.5 % of cement weight to improve the workability of cement paste. In addition, copper plate with dimensions of 1×6 cm were used as electrodes.
Figure 1. A view of Ordinary Portland Cement and metal powders

Table 1. Physical and chemical properties of Portland cement type CEM II/B-M 32,5 R.

| Chemical Composition | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | SO₃ | Na₂O | physical properties |
|----------------------|-----|------|-------|-------|-----|-----|------|---------------------|
| Wt.%                 | 56.39 | 16.87 | 4.35  | 3.02  | 1.97 | 2.39 | 0.22 | S. s. Area (cm²/g)  |
|                      |      |      |       |       |     |     |      | Density (g/cm³)     |
|                      |      |      |       |       |     |     |      | Ig. loss (%)        |
|                      | 4801 | 2.91 | 13.61 |

2.2. Specimens preparation
In order to achieve a reasonable electrical resistance in cement paste, the cementitious composites with different content levels of copper and iron powders were fabricated. The content levels of copper and iron powders are 0%, 5%, 10%, 15% and 20% of cement weight, and the hybrid composition (copper and iron) was also same ratios as used in this study. The corresponding mixtures for copper and iron were termed CP5/IR5, CP10/IR10, CP15/IR15 and CP20/IR20, respectively. The hybrid composition was termed IR-CP5, IR-CP10, IR-CP15 and IR-CP20.

Dry materials (cement and metal powders) were mixed together by mixer for about 1 minutes; then this mixture and (70% of water) were mixed in the mixer for 2 minutes. After that the remained (30% of water and the hyper plasticizer) were added to the mixture and mix together in the mixer for another 2 minutes. After pouring the mix into oiled moulds (5x5x5 cm), a vibrator was used to decrease the amount of air bubbles. After vibration, two electrodes made of copper were embedded in the paste in parallel with distance 3 cm between the two electrodes. Three specimens were fabricated for each group, the specimens were demoulded after 1 day, then allowed to cure at room temperature in water for 15 days.

2.3. Measurements
The electrical resistances of metal cement pastes at the curing ages of 3, 7, and 15 days were measured. Specimens after water curing for certain ages were taken out from water and dried with cloth for one day and then measured.

The electrical resistivity of metal cement pastes was measured by using methods of two-electrode-AC. The test results were uniformly referred to “resistance”. The two electrode-AC resistance was measured using digital LCR meter EDC-1630 (at the frequency of 1, 10 and 100 KHz) According to several previous studies [28,29] (Figure 2). In this study, the voltage was set to (200 mV) with an equivalent excitation frequency of (1 kHz, 10 kHz and 100 kHz) to eliminate the influences of polarization and any possible Joule effect on resistivity measurement [30].

According to several previous studies [6,27-30], direct current (DC) increases resistance over time due to the polarization effect. The polarization effect can be explained as follows: the electrical current passing through the cement paste causes hydrogen and oxygen liberated, causing a thin film between the electrodes and the cement paste [31]. Therefore, the electrical current at a given applied voltage is reduced by the thin film formed. For this reason, alternative current (AC) at a frequency of 100 kHz
was used to partially solve the problems of polarization, similar to Banthia's and Chen's studies [6,32], although its stabilization of current is still not clearly validated yet. The electrical resistivity of specimens was calculated according to the equation (2):

\[ \rho = \frac{RA}{L} \]  

(2)

R is the electrical resistance of specimen measured by LCR meter, A is the cross section areas of specimen (5x5 cm) and L is the distance between the two electrodes (3cm).

3. Results and discussion

3.1. Effect of current frequency

Since we are using AC, the current frequency becomes important element to be considered. For a capacitive mechanism, higher frequency leads to lower capacitive reactance and for an inductive mechanism, the lower the frequency, the lower the inductive reactance [33]. Cement based composites are capacitive in nature. The impedance is expressed as follows:

\[ Z = \frac{R_s}{\sqrt{1 + \omega^2 C_s^2 R_s^2}} \]  

(3)

Where Z: impedance in ohms (Ω), Rs: resistance in ohms (Ω), \( \omega = 2\pi \): angular frequency in radians per second (rad/s), Cs: capacitance in farads and f: signal frequency in hertz (Hz).

A series of frequency tests (1,10 and 100kHz) were conducted to investigate the effect of current frequency on the Cement based composites specimens. According to Equation (3), in order to reduce the reactance part of impedance, higher frequencies should be utilized. As example, the samples with metal content 15% by volume at curing time 15 days as well as the hybrid samples exhibit much lower electrical resistivity values especially at frequencies of 100 kHz compare with 1 kHz and 10 kHz. It is observed in Figure 3 that reactance part of impedance can be neglctable with high frequency (100 kHz) as well as much lower negative phase angle values. The highest current frequency available on the LCR meter, 100 kHz, was chosen to be used as the applied current frequency in all of the experiments.
3.2. Effects of material type and curing age on electrical resistivity of cement paste

Figure 4 shows the electrical resistivity of all specimens with age. The electrical resistivity of plain cement paste was considerably decreased by counting metal powders. Higher metal content resulted in lower resistivity, but the contrast was very little at ratio 5 % of metal powders. For example, the electrical resistivity of the pastes with 10 % metal content was 8.87 and 8.69 Ω.m for the iron and copper powders, respectively, at 7 days, approximately 28.6% and 30% smaller than that of the samples made with cement paste only at the identical age. In other hand the hybrid composites (10% of iron and copper) shows 33% of decrease at 7 days.

It is interesting to note that the hybrid composites within 15% of metal content shows good decrease in electrical resistivity (6.18, 7.79 and 11.08 Ω.m) compare with iron alone (10.17, 11.17 and 12.81 Ω.m), copper alone (7.10,9.96 and 11.87 Ω.m) and cement paste (8.55,12.43 and 16.08 Ω.m) at 3,7 and 15 days, respectively (Figure 4 c).

The composites with 20 wt% iron or copper alone and hybrid materials exhibited similar or slightly lower electrical resistivity than the plain cement paste. For example, the decrease in electrical resistivity of the composites with (iron, copper and hybrid) at 15 days was about (42.47,36.5 and 37%, respectively) of the resistivity of the plain paste (Figure 5).

Electrical resistivity increased with age for all test series, as shown in Figure 4. The increment rate of the resistivity was much higher for the plain paste than composites containing metal powders. The fundamental reason why the resistivity increased with age in the plain cement paste is that the nonstop hydration between cement and water diminished the amount of water in the pores of the hardened cement paste over time, causing the empty pores crowded with hydration items [31]. As shown in figure 4. The results confirm one more that in specimens with large content of metal materials, curing time has a much smaller effect on the resistivity values.
Figure 4. Electrical resistivity of specimens while curing

Figure 5. AC electrical resistivity with different dosages of metal powders
4. Conclusions
In this study, the effects of metal materials (iron, copper, and hybrid materials), current Frequency and curing age on the electrical resistivity of cement-based composites were examined. The main findings of the present study can be summarized as follows:

- The electrical resistivity of plain cement paste was considerably decreased by counting metal powders, higher metal content resulted in lower resistivity. Using 20% of metal powders in cement paste can reduce the electrical resistivity up to 47%.
- Current frequency of AC measurement shows significant effect in reduction of measured electrical resistivity of cement composites. High frequencies can reduce the reactance part of impedance. Highest current frequency available on the LCR meter, 100 kHz, was chosen to be used as the applied current frequency in all of the experiments.
- Electrical resistivity increased with age for all test series. The increment rate of the resistivity was much higher for the plain paste than composites containing metal powders.
- The reduction of electrical resistivity with an increase of metal content was steady for when of using hybrid composites better than when using metal powders alone.

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