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The effect of a polynaphthalene sulfonate superplasticizer on the contribution of the interfacial transition zone to the electrical resistivity of mortars containing silica and limestone fine aggregate

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Abstract

The effect of the varying dosages of a polynaphthalene sulfonate superplasticizer on the electrical resistivity and the interfacial transition zone (ITZ) characteristics of mortars containing reactive and non-reactive fine aggregates was investigated, using AC impedance spectroscopy and electrical conductivity models. The water-to-cement (W/C) ratio used was 0.45. The sand-to-cement (S/C) ratios ranged from 0.5 to 2.5. Superplasticizer contents by mass of cement were 0% to 1.5%. The results showed that the effect of the superplasticizer on the ITZ of the mortars was dependent on not only the dosage levels of the superplasticizer, but also W/C ratio, S/C ratio and type of aggregate. The improvement of the interfacial zone due to the presence of superplasticizer in low W/C ratio mortars does not necessarily occur in high W/C ratio mortars due to possible bleeding, segregation and increased water layer thickness around the aggregate. The number of aggregate–paste interfaces may also be a contributing factor. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Electrical properties; Interfacial transition zone; Microstructure; Aggregate; Admixture

1. Introduction

It has been shown [1–6] that the properties of the interfacial transition zone (ITZ) in a Portland cement mortar are affected by the mineralogical nature of the aggregate. For example, the calcareous or limestone aggregate can react chemically with the cement components to form "carboaluminates" or "calcium carbonate–calcium hydroxide" complexes. The surface of the limestone aggregate can be "corroded" or "etched" by the alkaline solution in the cement paste and this is found to increase the paste–aggregate interfacial bond [5,6]. In the case of siliceous aggregates, chemical reactions have not been considered significant at normal temperatures.

Superplasticizers have been increasingly used in the construction industry. The effect of the admixture on the structure of the ITZ has been reported in several recent articles [7–9]. We [8,9] investigated the effect of the addition of varying dosages (0.1–1.5% by mass of cement) of a polynaphthalene sulfonate (PNS) superplasticizer on the transition zone of mortars with a water-to-cement (W/C) ratio of 0.35 and silica sand-to-cement (S/C) ratios of up to 1.5. It was found that all the superplasticized specimens had higher overall electrical resistance and smaller interfacial excess conductance (or interface descriptor described later) values compared to the corresponding control specimens without superplasticizer. This indicates that the superplasticizer had favorably modified the microstructure of the mortars. The improvement may result from the more efficient particle distribution pattern in a superplasticized system. It was, however, observed that the transition zone was more porous at the early stages of hydration for high-dosage mortars that showed a set retardation.

The present work was designed to investigate the effect of the PNS superplasticizer on ITZ in mortars containing reactive and non-reactive aggregates. A W/C ratio of 0.45

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Table 1
Mix proportions

Mixes	Proportion by mass Portland cement (Type 10)	Sand[a]	Superplasticizer	Water
1	1	0.5	0	0.45
2	1	0.5	0.3	0.45
3	1	0.5	0.8	0.45
4	1	0.5	1.5	0.45
5	1	1.0	0	0.45
6	1	1.0	0.3	0.45
7	1	1.0	0.8	0.45
8	1	1.0	1.5	0.45
9	1	1.5	0	0.45
10	1	1.5	0.3	0.45
11	1	1.5	0.8	0.45
12	1	1.5	1.5	0.45
13	1	2.5	0	0.45
14	1	2.5	0.3	0.45
15	1	2.5	0.8	0.45
16	1	2.5	1.5	0.45

[a] Two parallel groups of mixes were manufactured. Each group consisted of 16 mixes with either silica sand or crushed limestone fine aggregate.

was used as opposed to 0.35 in the previous study [8,9]. It was thought that the effect of superplasticizer on the ITZ might be more pronounced at higher W/C ratios.

Techniques such as X-ray diffraction, scanning electronic microscopy, microhardness and mercury intrusion porosimetry are often used in attempts to characterize the microstructure of the transition zone. Recently, AC impedance spectroscopy (ACIS) and the interfacial excess conductance methods have been used/developed [10–12] for such studies. These two techniques were employed in this study.

The Bruggeman's effective media theories [13] have been widely used in the area of applied physics for predicting the effective conductivities of heterogeneous systems consisting of low conductivity grains embedded in a high-conductivity matrix, or vice versa [14–16]. An attempt is also made in the current study to employ the Bruggeman's asymmetrical conductivity equation to compare the theoretical effective electrical conductivities of the mortars, with the experimental data (obtained using the ACIS) in the presence and absence of superplasticizer. The effect of the superplasticizer on the ITZ is inferred from the results.

2. Experimental

2.1. Materials, mix proportions and specimen preparation

The superplasticizer used was a commercially available PNS sodium salt in powder form. Type 10 Portland cement (Lafarge), crushed limestone sand and Ottawa grade 20–30 silica sand were used. The limestone sand was produced by crushing larger pieces and sieving to the required particle sizes. The two types of sand had particle sizes ranging from 600 to 850 μm.

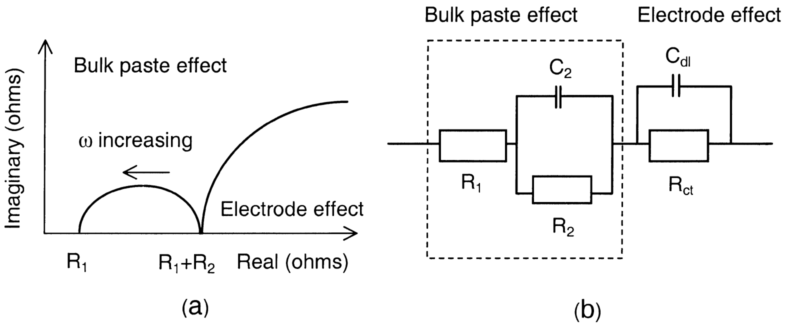
Mortars containing limestone sand and silica sand, respectively, were produced. S/C ratios by mass were 0.5, 1.0, 1.5 and 2.5. PNS superplasticizer dosages by mass of cement for each S/C were 0%, 0.3%, 0.8% and 1.5%. A constant W/C ratio of 0.45 was used throughout the experimental program. Two specimens were used for each of the mixes. Details of the mixes used in the experimental program are shown in Table 1.

The fresh mortar was cast into a plexi-glass electrical conduction cell and compacted by vibration. The cell had an internal dimension of 77 × 77 × 50 mm with the two opposite sides fitted with flat stainless steel electrodes for AC impedance measurements. Particular care was taken in the preparation of electrodes to ensure the best possible contact with the cementitious material. The specimens were cured in a 100% relative humidity room for 24 h and then immersed in saturated limewater for testing at selected hydration times.

2.2. Methods

2.2.1. AC impedance spectroscopy

ACIS is a well-known electrochemical technique of characterizing the electrical properties of cementitious



(a) (b)

Fig. 1. (a) A schematic of an AC impedance spectrum in the real–imaginary complex plane for hardened cement paste. (b) An equivalent electrical circuit model.

materials [10,17–22]. The impedance spectrum contains information that can be used to characterize the microstructure of the hardened cement system. A typical impedance spectrum that is ideal for a hydrating cement paste is plotted in the real–imaginary complex plane, shown in Fig. 1a. It depicts a single arc in the high frequency range, with a small part of the second arc in a relatively low frequency region. It is suggested that the impedance behavior of solid–liquid interfaces in the cementitious system may be modeled as a combination of resistors and capacitors using an electrical equivalent circuit (Fig. 1b) where R_2, the high-frequency arc (HFA) diameter represents the interfacial impedance behavior, and $R_1 + R_2$, the intercept of the HFA with the real axis, represents the overall bulk resistance of the specimen [17–19]. The second arc is due to the cement–electrode interface capacitance effect. A Solatron 1260 Impedance Gain-Phase Analyzer was used for the impedance measurements at selected hydration periods of 5 h, 1, 3, 7, 14, 28 and 56 days. Data were collected at frequencies ranging from 13 MHz to 1 Hz. Spectra for the two specimens from each mix were found to be approximately coincident. The plot points in the figures showing the impedance spectra are actually points taken from a continuous curve obtained by regression analysis programs that are part of the impedance software.

2.2.2. Interfacial excess conductance method

This method was developed by Xie et al. [11,12] and has been used to assess the relative difference in electrical conductance between the interfacial region and the bulk cement paste in a mortar system using the following equation:

$$\theta = \delta(\sigma_t - \sigma_p) \tag{1}$$

where δ is the thickness of transition zone, and σ_t and σ_p are the electrical conductivity of transition zone and bulk paste, respectively. Values of $\sigma_t > \sigma_p$ or $\theta > 0$ indicate a transition zone that is less dense than the bulk paste matrix; $\sigma_t < \sigma_p$ or $\theta < 0$ indicates the opposite. The electrical conductivity of a specimen can be calculated from the following equation:

$$\sigma = \frac{d}{A}\frac{1}{R} \tag{2}$$

where R is the bulk resistance ($R = R_1 + R_2$, Fig. 1a), A is the cross-section area of the specimen and d the specimen thickness or the distance between the electrodes of the cell. For a mortar specimen containing spherical aggregate particles with radii r, the electrical conductivity may also be expressed in Eq. (3):

$$\sigma = k\varphi_a + b \tag{3}$$

where φ_a is the volume fraction of aggregate in the mortar specimen and k and b are constants determined by the $\sigma - \varphi_a$ relationship. This relationship was established for the mortar studied. Xie et al. [11,12] derived the following relationship for θ [Eq. (4)]:

$$\theta = \delta(\sigma_t - \sigma_p) = r\left(\frac{k}{3} + \frac{b}{2}\right) \tag{4}$$

The parameter θ can be readily obtained by substitution of the experimentally determined values of k, b and r (the average radii of the aggregate). A Solatron 1260 Impedance Gain-Phase Analyzer was used for the conductivity measurements. More details of the ACIS and the interfacial excess conductance methods are described in Refs. [10–12].

2.2.3. Bruggeman's asymmetrical effective medium theory

This theory, as it applies to the present work, is briefly described [15]. If a small volume fraction, $d\varphi_m$, is removed from a uniform material (e.g., cement paste) of conductivity (σ) in the form of a sphere, then the resulting change in conductance of the material will be:

$$d\sigma = -\frac{3}{2}d\varphi_m\sigma \tag{5}$$

The successive incremental removal of material results in a volume fraction, V_m, of the original material removed. Thus, the actual volume fraction of the material remaining becomes $(1-V_m)$.

Suppose that the spherical pores of volume fraction V_m are uniformly distributed in the material. If we now take out a volume fraction of $d\varphi_m$ from the material, the change in pore volume fraction will be:

$$dV_m = d\varphi_m(1 - V_m) \tag{6}$$

since part of the spherical pore formed in an earlier removal was also included in the term $d\varphi_m$ in Eq. (6).

Combining Eqs. (5) and (6) yields Eq. (7):

$$\frac{d\sigma}{\sigma} = -\frac{3}{2}\frac{dV_m}{(1 - V_m)} \tag{7}$$

which can be integrated to form the well-known Bruggeman's asymmetrical equation:

$$\sigma_1 = \sigma_0(1 - V_m)^{3/2} \tag{8}$$

where σ_1 is the electrical conductivity of the material with added pore volume of V_m, and σ_0 is the conductivity of the original material with $V_m = 0$. One can fill the added spherical pores in the conductive material (say, cement paste) with non-conductive material (say, sand). Eq. (8) can then be rewritten as:

$$\sigma_m = \sigma_p(1 - V_{f,sand})^{3/2} \tag{9}$$

where σ_m is the electrical conductivity of mortar, σ_p is the conductivity of cement paste and $V_{f,sand}$ is the volume fraction of sand in the mortar.

Eqs. (8) or (9) is derived on the assumption that: (i) the sand grains are spherical and non-conductive; (ii) the sand is

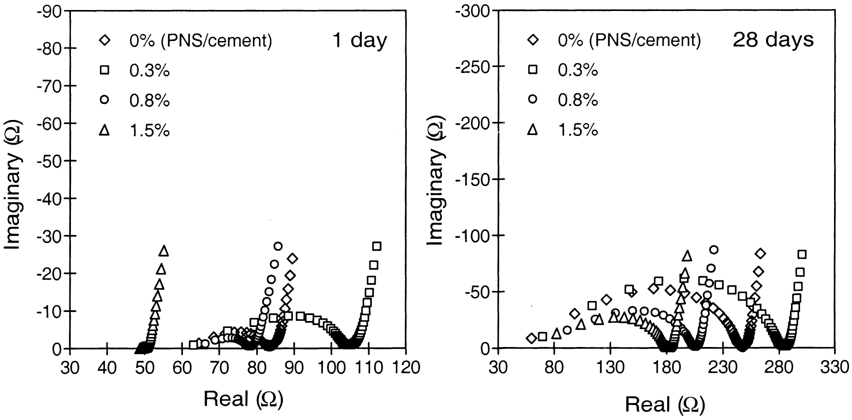


Fig. 2. AC Impedance spectra of silica sand mortars (S/C ratio = 1.5 and W/C ratio = 0.45) in the presence and absence of a PNS superplasticizer at 1 and 28 days (0% to 1.5% are superplasticizer content).

introduced into a continuous conductive cement matrix (that is, there is no sand–sand particle contact); (iii) the conductivity of the cement matrix does not change with the introduction of sand; and (iv) there is no interfacial effect. These assumptions are obviously not completely true for practical mortars.

Nevertheless, it can be shown by plotting σ_m/σ_p, the relative or normalized conductivity of the mortar σ_m to the paste σ_p against $V_{f,sand}$ in Eq. (9), that the effective conductivity for the mortar system decreases with increasing sand content. Noting that the $(1-V_{f,sand})^{3/2}$ theoretical curve represents the idealized medium in which the ITZ effect on conductivity is zero, then the ITZ effect on electrical resistivity of a practical mortar would be positive (i.e., to reduce the conductivity of the paste–sand system) if the experimental data falls below the theoretical line (determined by Eq. (9)). The opposite would be true if the experimental data lies above the theoretical curve.

3. Results and discussion

The ACIS results for the mortars in this study will be presented. The representative AC impedance spectra in the real–imaginary complex plane for the 1- and 28-day mortars with silica sand and crushed limestone sand, respectively, are shown in Figs. 2 and 3.

The impedance behavior in the early hours of hydration (e.g., at 5 h) was quite similar to that reported previously [8,9]. That is, the semicircle did not immediately appear in the high-frequency region and the bulk resistance of the fresh mortars decreased with increasing superplasticizer dosages. The lower resistance corresponding to a greater dosage of superplasticizer had been explained by the increased ionic concentration of the pore solution, mainly due to the Na^+ contributed by the sodium-salt superplasticizer molecules [8]. At 1 day, the high-frequency semicircle appeared for all specimens except for that with 1.5% superplasticizer (Figs. 2 and 3). Obviously, the superplasticizer, at

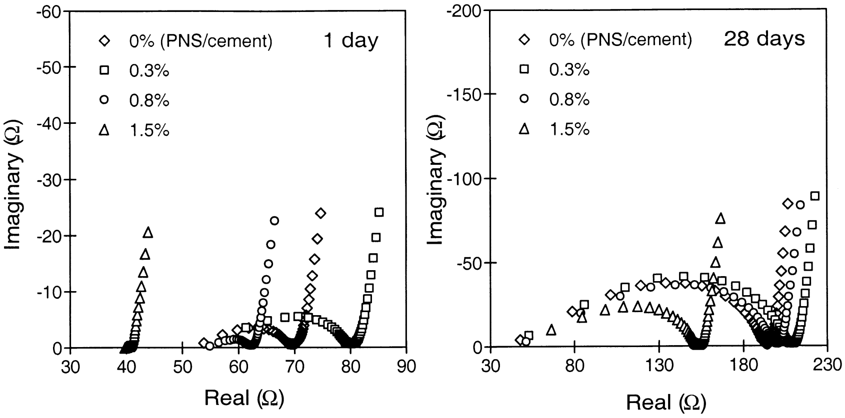


Fig. 3. AC Impedance spectra of crushed limestone mortars (S/C ratio = 1.0 and W/C ratio = 0.45) in the presence and absence of a PNS superplasticizer at 1 and 28 days (0% to 1.5% are superplasticizer content).

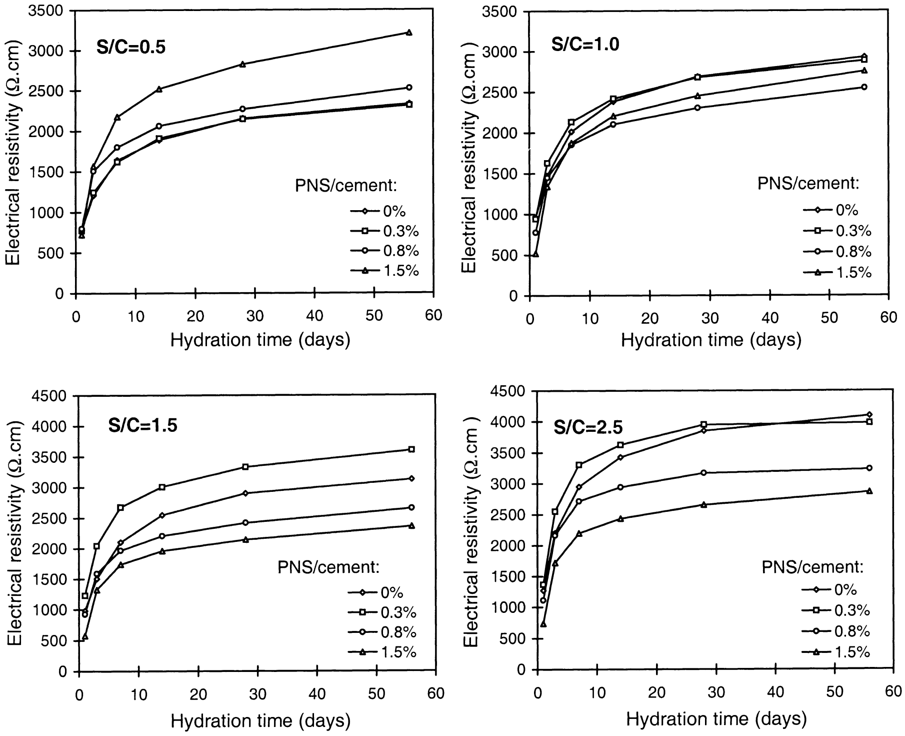


Fig. 4. Effect of varying dosages of a PNS superplasticizer on the overall electrical resistivity of silica–sand mortars. W/C ratio = 0.45.

a dosage of 1.5%, had a set-retarding effect for the mortars with a W/C ratio of 0.45. The extent of set retardation was greater than for mortars with a W/C ratio of 0.35 and a similar superplasticizer concentration used in Refs. [8,9].

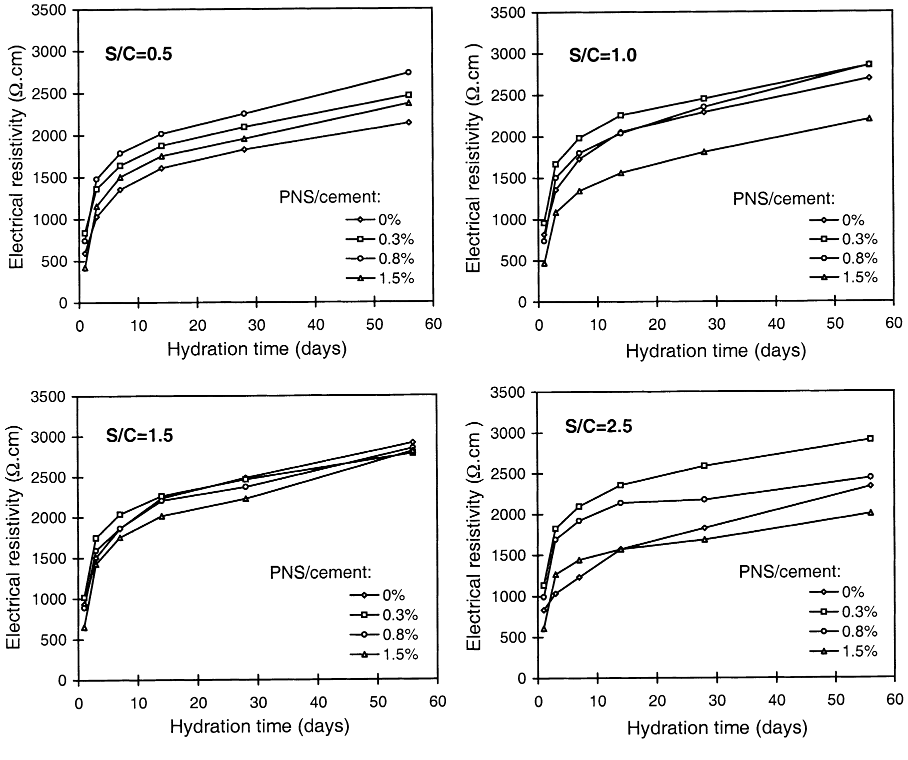


Fig. 5. Effect of varying dosages of a PNS superplasticizer on the overall electrical resistivity of crushed limestone–sand mortars. W/C ratio = 0.45.

The overall resistivity values of all the mortars with varying S/C and PNS dosages tested at various hydration times are exhibited in Figs. 4 and 5. The overall electrical resistivity, ρ, was calculated from the following Eq. (10):

$$\rho = R\frac{A}{d} \tag{10}$$

where R, A and d are defined in Eq. (2). A greater overall (bulk) resistivity value (Figs. 4 and 5) may be an indicator of a denser interfacial zone and bulk matrix, modified pore size distribution or reduced capillary connectivity [8,13,18]. The following is a summary of the results presented in Figs. 4 and 5 for the specimens hydrated for periods greater than 1 day.

(1) At S/C ratio = 0.5, the superplasticized mortars, with either silica sand or crushed limestone sand, had higher overall resistivity values compared to those of control mortars. The resistance generally increased with increasing superplasticizer content.

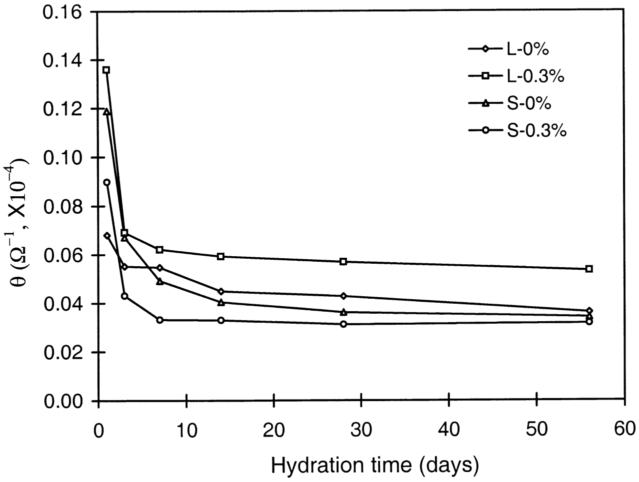
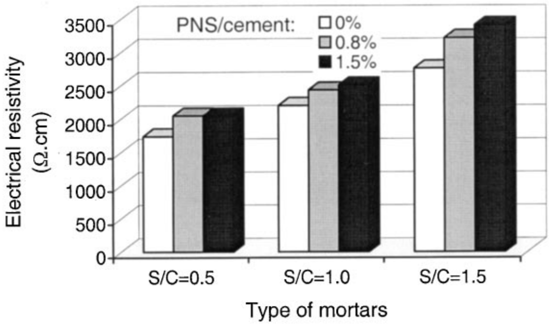
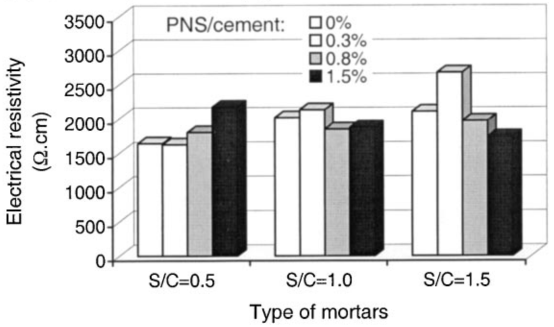


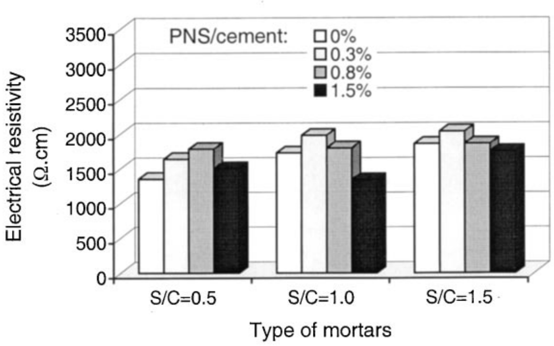
Fig. 7. Effect of PNS superplasticizer on the interfacial excess conductance, θ, of two types of mortars vs. time of hydration. L denotes limestone sand mortars and S silica sand mortars. 0% and 0.3% are the plasticizer contents. S/C ratio: 0.5–2.5, W/C ratio: 0.45.



(a) W/C=0.35; Silica sand [9]



(b) W/C=0.45; Silica sand



(c) W/C=0.45; Crushed limestone sand

Fig. 6. Effect of W/C ratio on the electrical resistivity of PNS superplasticized mortars at 7 days.

(2) At S/C ratio = 1.0, 1.5 and 2.5, the resistivity values were higher for silica sand mortars with 0.3% superplasticizer, and for limestone sand mortars with superplasticizer dosages of up to 0.8%, in comparison with those of control mortars. The resistivity for mortars with 1.5% superplasticizer was lowest among all the mortars.

(3) The silica sand mortars had greater resistivity values compared with crushed limestone mortars at all hydration times.

In previous works [8,9], we investigated the effect of varying superplasticizer dosages on the microstructural and interfacial characteristics of silica sand mortars prepared with W/C ratio = 0.35. At 1 day and afterwards, all superplasticized mortars exhibited higher electrical resistance values vs. control mortars [8,9]. The differences in resistivity values shown in Figs. 4 and 5 are, therefore, attributed to the higher W/C ratio (= 0.45) used. A comparison of the electrical resistivity values is made in Fig. 6 for mortars with different W/C ratio at 7 days. It is possible that at W/C ratio = 0.35, the trapped water released by the deflocculating action of the superplasticizer preferentially wets the deflocculated cement grains for hydration. This may occur at the expense of thickening the water layer on the sand grains in the ITZ. At W/C ratio = 0.45, the released trapped water may further dilute the paste system. An improvement of the transition zone, resulting from the superplasticizer, would depend on the balance between the positive action of deflocculation, high dispersion, more efficient hydration, etc., and the negative effect of increased water layer thickness, bleeding and segregation. An excessive dosage of superplasticizer (1.5%) resulted in the cement paste becoming too fluid. The fine aggregate was no longer maintained in suspension and bleeding and segregation occurred. The water layer thickness around the aggregate was likely increased. The higher the S/C ratio, the greater would be the number of sand–paste interfaces, and the "water layer" or interfacial effect would be more pronounced. The latter may explain why, at high superplasticizer dosages, the electrical resistivity of mortars with higher S/C ratios (> 1.0) decreased while that for mortars with low S/C ratios increased (Fig. 6b and c).

The electrical resistance of limestone mortars increased with the amount of superplasticizer for dosages of up to 0.8% (Fig. 5). An increase was observed for superplasticized silica sand mortars containing a dosage of 0.3% only (when S/C ratio ≥ 1, Fig. 6b). This may be due to the angular shape of the crushed limestone sand that had a greater surface area and hence, more free water was needed for wetting the aggregates. It was, however, unexpected that the limestone sand mortars had lower resistance values compared with silica sand mortars at all hydration times (Figs. 4 and 5). The crushed limestone sand, compared to silica sand, was expected to have a denser ITZ and thus, higher resistance values. It is generally believed that a chemical reaction may occur between the calcareous aggregate and the cement paste. The enhanced bond, due to mechanical interlocking between the aggregate and the paste, was also expected to provide a more intact transition zone. The greater tortuosity of the ITZ, due to the presence of irregularly-shaped aggregate, generally results in a thinner zone containing less large oriented crystals of CH. It is possible that some limestone dust, which adhered to the crushed limestone aggregate, hindered the formation of a potentially good paste–aggregate bond. An alternative possibility would be that the presence of superplasticizer molecules at the interface modified the nature of the chemical reaction between the limestone sand and the cement components.

The interfacial excess conductance values (θ) vs. time of hydration are plotted in Fig. 7 for mortars containing 0.0%

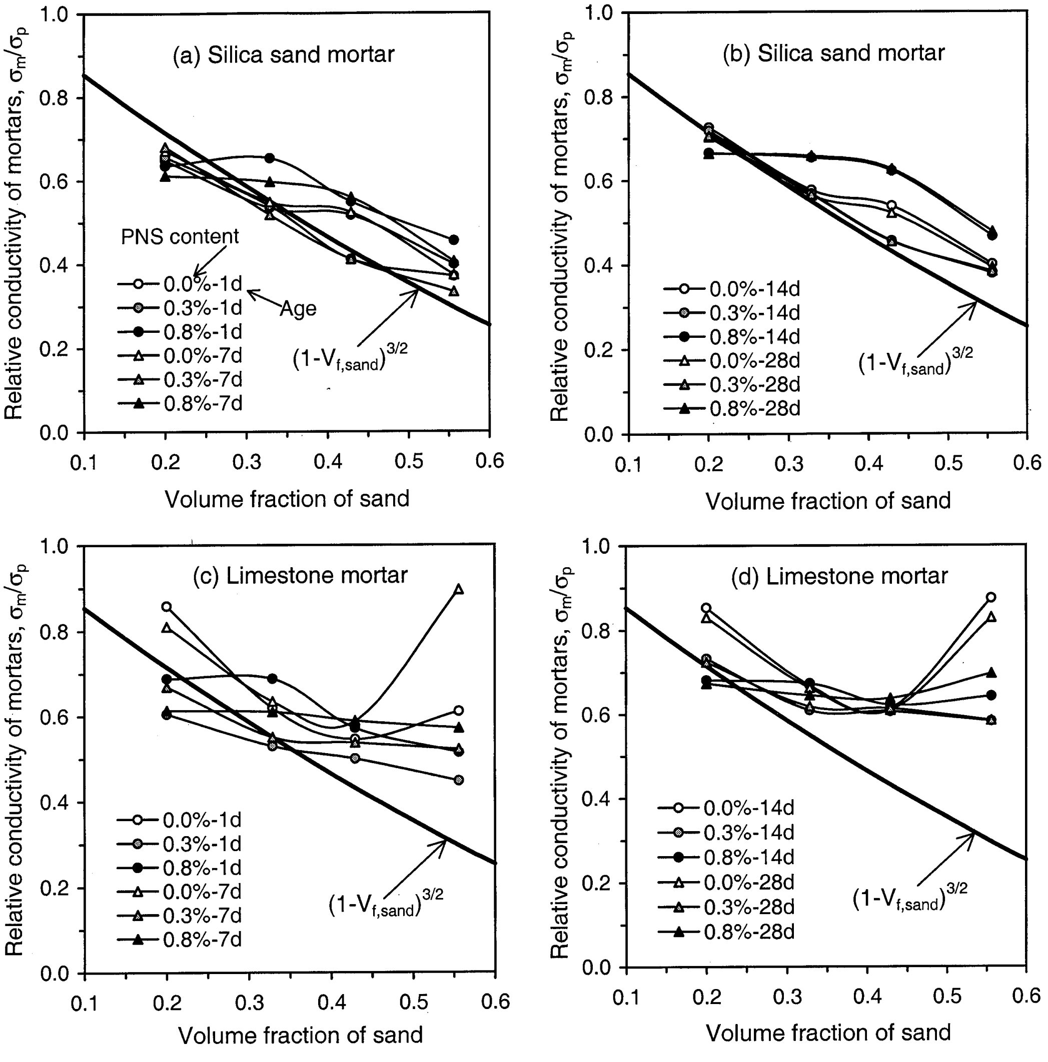


Fig. 8. A comparison of the relative electrical conductivities (mortar to paste) for mortars with and without PNS superplasticizer at various hydration times and volume fractions of sand. PNS sodium salt superplasticizer with dosages of 0%, 0.3% and 0.8%, W/C ratio = 0.45; S/C ratio = 0.5, 1.0, 1.5 and 2.5 by mass.

and 0.3% superplasticizer. The interfacial excess conductance model [Eq. (1)] could not be applied to the mortars with 0.8% and 1.5% superplasticizer used in this study since it was found that the relationship between the conductivity and the aggregate volume for the mortars with 0.8% and 1.5% superplasticizer was non-linear, due to the combined effect of high W/C and S/C ratios and high concentration of superplasticizer. Nevertheless, it is apparent from Fig. 7 that the silica sand mortars with 0.3% superplasticizer resulted in smaller interfacial excess conductance values compared to control mortars. This is in agreement with the impedance results, indicating that the superplasticizer addition (0.3%) had positively modified the interfacial zone microstructure.

For limestone mortars, the superplasticized mortars with 0.3% dosage exhibited greater interfacial excess conductance than control mortars (Fig. 7). This is not in agreement with the impedance results (Fig. 5), in which the mortars with a dosage of 0.3% had higher resistivity values than the control. It is noted that the θ parameter represents relative values of resistivity only [Eq. (1)]. The θ value of the superplasticized mortar, in comparison with that of the control mortar, would be greater if the modification or improvement by the superplasticizer in the bulk paste were more pronounced than that in the transition zone region in the same mortar. As mentioned earlier, the observed "anomaly" could be caused either by limestone dust on the aggregate surface hindering the development of a good paste–aggregate bond, or by the presence of superplasticizer molecules at the interface, possibly modifying the nature of the chemical reaction between the limestone sand and the cement components. Further work on these possible mechanisms is needed.

Fig. 8 shows the relative or normalized conductivity of the experimental mortars, σ_m/σ_p, at hydration times of 1, 7, 14 and 28 days, compared with Bruggeman's $(1-V_{f,sand})^{3/2}$ theoretical curve for ideal mortar. It is seen that the majority of the experimental data fall above the theoretical curve, indicating that, as a whole, the ITZ effect on electrical resistivity was negative. That is, the presence of ITZ reduced the overall resistivity of mortars. The effect is more pronounced with greater sand inclusions (e.g., S/C > 1.5, or equivalent sand volume fraction > 0.43 in Fig. 8).

Fig. 8 shows that mortars with 0.3% superplasticizer resulted in lower relative conductivity values in all cases compared to non-superplasticized experimental mortars. The data points for mortars with sand volume fraction of 0.2 (S/C ratio = 0.5) and superplasticizer dosages of 0.3% and 0.8% fall below the theoretical curve. This would either imply that these mortars had a denser ITZ or a more favorable ITZ microstructure compared to their corresponding bulk matrix, or that the Bruggeman's equation [Eq. (9)] is inaccurate for the mortar system. At other S/C ratios, mortars with 0.8% superplasticizer had greater relative conductivity, except for limestone mortars with a sand volume fraction of 0.56. This might be caused by the low W/C ratio (0.45) in relation to the high volume fraction (0.56) of the limestone sand used.

4. Conclusions

The effect of adding PNS superplasticizer to the electrical resistivity of mortars (by inference on ITZ quality) is influenced by W/C and S/C ratios, type of aggregate, and dosage levels of the superplasticizer. Improvement of transition zone characteristics by superplasticizer in low W/C ratio mortars does not necessarily occur in high W/C ratio mortars due to possible bleeding, segregation, increased water layer thickness around the aggregate and, in the case of high S/C ratio, the increased number of aggregate–paste interfaces. The PNS superplasticizer may increase the electrical resistivity of mortars with high W/C ratios of appropriate dosage levels. An overdose can have negative effects especially for mortars with high W/C and S/C ratios.

Compared to control mortars, crushed limestone sand mortars with PNS superplasticizer showed increase in impedance in most cases, while superplasticized silica sand mortars showed increase only for those with low S/C ratios or low dosage of superplasticizer. The limestone sand mortars were found to have smaller impedance values vs. silica sand mortars at all hydration times. This may be a result of dust that adhered on the crushed limestone aggregate, which hindered the development of a potentially good paste–aggregate bond. Another possibility could be that the existence of superplasticizer molecules at the interface and a concomitant modification of the nature of the chemical reaction between limestone sand and cement components. Further work on these possible mechanisms is needed.

The hardened silica sand mortars with 0.3% superplasticizer had smaller interfacial excess conductance values in agreement with impedance results. This implies the existence of denser interfacial transitions zones compared to those of control mortars. The hardened limestone sand mortars with 0.3% superplasticizer, however, had greater interfacial excess conductance values that were not in agreement with the impedance results. This observed "anomaly" might occur when superplasticizer beneficially modified the microstructure of the mortar system as a whole but the modification in bulk paste was more pronounced than that in the transition zone region in the same mortar.

The experimental values of σ_m/σ_p, the relative conductivity (i.e., the conductivity ratio of mortar and paste) of mortars, are compared with the theoretical curve predicted by the Bruggeman's asymmetrical effective medium theory. The majority of the experimental data falls above the theoretical line, indicating that, as a whole, the ITZ effect on electrical resistivity was negative (e.g., to reduce resistivity). The effect is more pronounced with greater sand inclusions. Lower relative conductivities resulted for mortars with low S/C ratios and appropriate dosages of the superplasticizer. These are fully consistent with impedance results. It would appear that a plot of the relative conductivity values of experimental mortars vs. the volume fraction of aggregate (compared with Bruggeman's theoretical curve) is appropriate for assessing the effect of superplasticizer on the ITZ characteristics.

Acknowledgments

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