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An assessment of the relative permeability of cement systems using AC impedance techniques

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Abstract

Aspects of the rapid chloride permeability test (AASHTO T277/ASTM C1202) were investigated using the AC impedance technique. Permeability and impedance measurements were performed at different ages on the various cement pastes prepared with or without silica fume and/or superplasticizer. The elastic modulus of the pastes was also determined. The addition of silica fume and/or superplasticizer had no significant effect on the elastic modulus of the pastes at the same water/cement ratio. The addition of silica fume significantly increased the impedance and decreased the total charge passed (total coulombs) irrespective of the actual chloride penetration. The naphthalene sulfonate-type of superplasticizer had no significant impact on the impedance, and the total charge passed. Linear relationships between the impedance, total coulombs, and initial current were observed. It is apparent that the impedance is an equivalent indication of the relative permeability and the total charge passed. Therefore, it appears possible to develop a new simple and rapid method to assess the relative permeability of the cement systems using the AC impedance technique.

Keywords: Permeability; Elastic moduli; AC impedance; Chloride; Cement paste

The corrosion of steel reinforcement in concrete structures is a major concern to the construction industry. This has fostered global research efforts in the development and investigation of the chloride permeability/penetration tests. The rapid chloride permeability test [1] (AASHTO T277 [2]/ASTM C1202 [3]) is one of the most widely used. Workers have found the test useful to determine the relative permeability of concrete in spite of questions concerning its theoretical relevance[4]. This test provides a quick and simple method to assess the chloride permeability or migration in concrete. However, it should be used with caution and the results should be interpreted with a clear understanding of the principles behind the test and the concrete permeability.

In this study, characteristics of the rapid chloride permeability test were investigated using AC impedance measurements. The effects of the test itself on neat cement and cement-silica fume pastes prepared with and without a superplasticizer were determined.

1. Methods

1.1. Materials and specimen preparation

Type 10 portland cement, silica fume (SF), and a naphthalene sulfonate-type of superplasticizer (HRWR) were used to prepare the pastes. A water to cementitious materials (w/c) ratio = 0.45 was used for all pastes. In the silica fume pastes, silica fume was added by replacing an equal mass of 10% Portland cement. The dosage of the HRWR was 0.8% by mass of the cementitious materials, which is a normal dosage. The dry powder-type superplasticizer in an appropriate amount was added to the water before mixing with the cement. The mixing was done in a standard bowl-type mixer in accordance with the ASTM C305 procedures.

Four paste systems with w/c = 0.45 were made in this study:

- cement paste with HRWR at normal dosage;
- cement paste without HRWR;
- cement paste containing 10% SF and HRWR at normal dosage;
- cement paste containing 10% SF without HRWR.

The fresh mixed slurry (paste) was cast into a tubular mold $\varnothing$ 102 $\times$ 200 mm or $\varnothing$ 32 $\times$ 390 mm. The molds were sealed to avoid the evaporation of moisture from the

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pastes and placed on the rolling table. The pastes were rotated for 1 day to prevent segregation. The pastes were demolded and then stored in the lime-saturated water at the room temperature until the predetermined ages (i.e., [3], 7, 14, 28, and [56] days, etc.; the ages in the brackets are the extra ages for the elasticity and impedance measurements of the small specimens).

The pastes were subjected to various test methods, such as the rapid chloride permeability test, AC impedance technique, and modulus of elasticity measurement, at the predetermined ages.

1.2. Test methods and procedures

The rapid chloride permeability test was conducted in accordance with the AASHTO T277/ASTM C1202 procedures. One step of the sample conditioning was omitted. Since the pastes were continuously stored in lime-water until the test, the sample conditioning was not necessary. A thermocouple was inserted into the specimen to monitor the temperature changes during the test.

The AC impedance spectra of the pastes were obtained with an AC impedance analyzer. In the AC impedance measurement, one plate-shaped metal electrode was placed at each end of the specimen disc. Both ends of the specimen disc were flat. A wet, thin paper towel was placed between the electrode plate and the specimen, and a small pressure was applied on the electrode plate in order to maintain a good contact between the electrode and specimen. The AC impedance measurement was performed on two groups of the specimens. The impedance was obtained from the same specimen at the different ages for one group of the specimens ($\varnothing$ 32 $\times$ 30 mm). In this way, the error from the different specimens at different ages can be eliminated. In the other group of specimens ($\varnothing$ 102 $\times$ 51 mm), the impedance was measured before and after the rapid chloride permeability test on the same specimen. In contrast to the specimens of the first group, the measurements on the second group of specimens were carried out on different specimens at the different ages since the rapid chloride permeability test can be considered intrinsically destructive.

The modulus of the elasticity (Young's modulus) of the pastes was determined by the pulse velocity measurements. Based on the method described by Winslow [5], the velocity of a dilation wave through the slender rod-type paste was measured and used to calculate the Young's modulus. The specimens were $\varnothing$ 32 $\times$ 390 mm, with a length-to-diameter ratio of about 12:1.

Each measurement was performed on at least two specimens, and the average was reported.

2. Results and discussion

2.1. Results of the rapid chloride permeability test

Figs. 1a and 1b show the current vs. time relations for the neat cement and silica fume pastes, respectively. The total charge passed (total coulombs) decreased with increasing age. For the neat cement pastes, the initial current is high and then the current increases significantly with increasing time. For the silica fume pastes, the initial current is low and the current is nearly unchanged over the period of the test. Even if the other factors such as w/c ratio and age remain the same, the total coulombs for the silica fume pastes is approximately one order of magnitude less than that for the neat cement pastes. This result suggests that the silica fume pastes have a much lower permeability than the neat cement pates. However, the result is only qualitative. That is, it would be incorrect to assume that the permeability of the silica fume pastes is only about one-tenth of that of the neat cement pastes. It also appears that the presence of the HRWR does not significantly affect the total coulombs for both the neat cement and silica fume pastes with the same w/c ratio.

The changes in temperature of the pastes during the test are indicated in Figs. 2a and 2b for the neat cement and silica fume pastes, respectively. The temperatures in the pastes rise during the test, and the rate of temperature rise decreases in the later period of the test. In the neat cement pastes, the range of temperature rise is much higher than that in the silica fume pastes due to the high initial current.

2.2. Results of the Young's modulus measurement

Fig. 3 shows the modulus of elasticity vs. age relations. At the earlier ages (e.g., before 14 days), the elasticity of the pastes increases with age. The rate of increase in elasticity decreases at the later ages. The modulus of elasticity values of all four types of the pastes are similar at a given age. The neat cement pastes containing HRWR have marginally lower modulus of elasticity values than the pastes without HRWR. The modulus of elasticity of the silica fume pastes with and without HRWR is intermediate between these two. It appears that the HRWR has no significant effect on the modulus of elasticity of the pastes, especially on that of the silica fume pastes. In other words, the modulus of elasticity is not sensitive to the presence of HRWR and/or silica fume as long as the w/c ratio remains the same.

2.3. Results of the AC impedance measurement

The typical AC impedance spectra (imaginary vs. real) of the cement pastes are shown in Fig. 4. The impedance on the real axis varies with the age and the presence of HRWR.

Figs. 5a and 5b are plots of the resistivity vs. age for the neat cement and silica fume pastes. Each relation was obtained from the same specimen at the various ages. For both neat cement and silica fume pastes, the impedance increases with age. The neat cement pastes show a slight increase in impedance during 28–56 days, whereas the impedance of the silica fume pastes still increases considerably after 28 days. The addition of HRWR results in a slight increase in impedance of both neat cement and silica fume pastes.

The impedance of the saturated pastes depends mainly on their pore structure (porosity, pore-size distribution, and

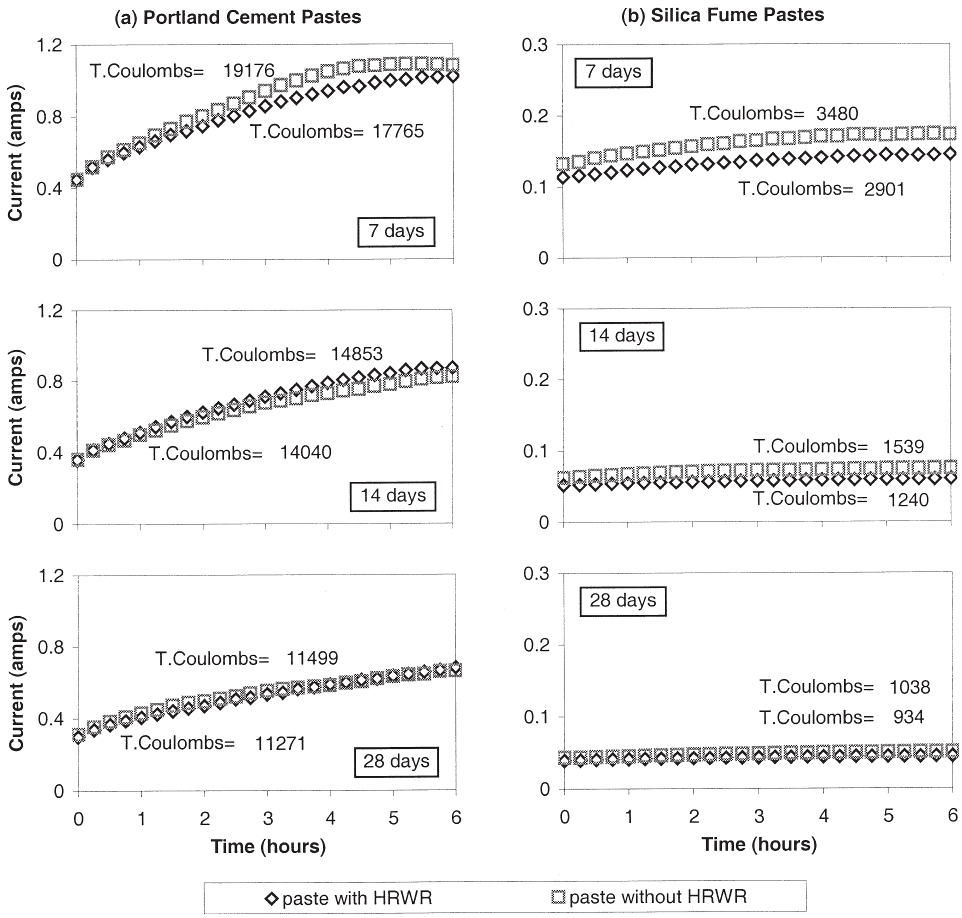

Fig. 1. The rapid chloride permeability test results: the current vs. time relations.

tortuosity) and pore solution chemistry (total ionic concentration). The pore structure becomes finer (lower porosity, smaller pore sizes, and less connection between the pores) with the hydration process. This fine pore structure can result in an increase in impedance. In a general sense, a lower ion concentration in the solution leads to a lower electrical conductivity or higher impedance. Of the common ions in the pore solution of the cement pastes, OH^- ions have much higher conductivity than the other ions [6]. Therefore, a lower pH value in the paste pore solution causes a higher impedance. According to the pore solution analysis [Table III in reference 7], the OH^- ion concentration and total ionic concentration of the pure cement pastes change little from 7 to 84 days. However, in the silica fume pastes, both OH^- ion concentration and total ion concentrations decrease significantly with increasing age. As a result, the increase in impedance of the neat cement pastes is mainly attributed to the finer pore structure with the hydration

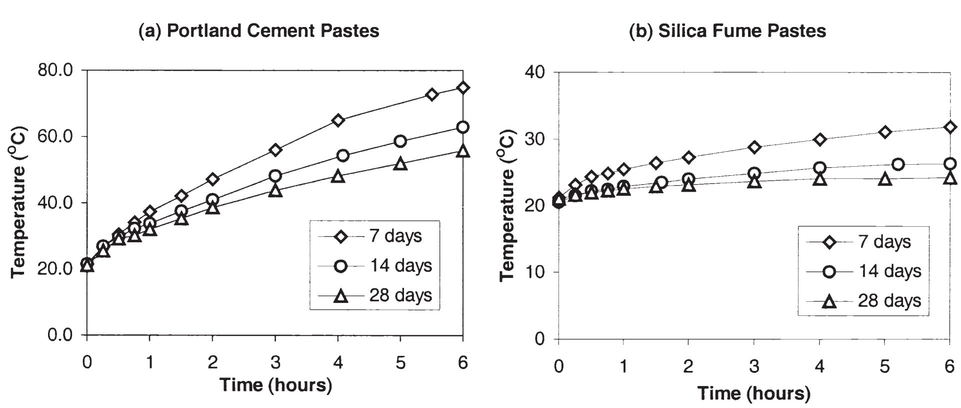

Fig. 2. The temperature in the pastes during the rapid chloride permeability test.

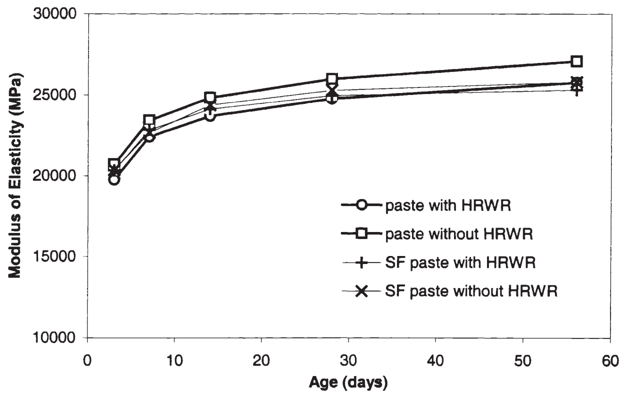

Fig. 3. The modulus of elasticity vs. age relations for portland cement pastes with and without silica fume and HRWR.

process, whereas the increase in impedance of the silica fume pastes results not only from the finer pore structure, but also (more importantly) from the significant reduction in pH value and total ionic concentration of the pore solution. The factors affecting the concrete conductivity and permeability are discussed in detail elsewhere [8].

The presence of HRWR decreases the impedance of the solution. In this study, the impedance of the lime-saturated solution (water) was 121 Ω-cm, while that of the lime-saturated solution containing 18% HRWR was 59 Ω-cm. However, Figs. 5a and 5b suggest that the addition of HRWR increases the impedance of both neat cement and silica fume pastes. Based on the earlier discussion, HRWR may alter the pore structure of the pastes so that the impedance increases, even though HRWR may decrease the impedance of the pore solution.

2.4. The relationship between the initial current and the total coulombs

The linear total coulombs vs. initial current relation, as shown in Figs. 6a and 6b, can be derived from the data in

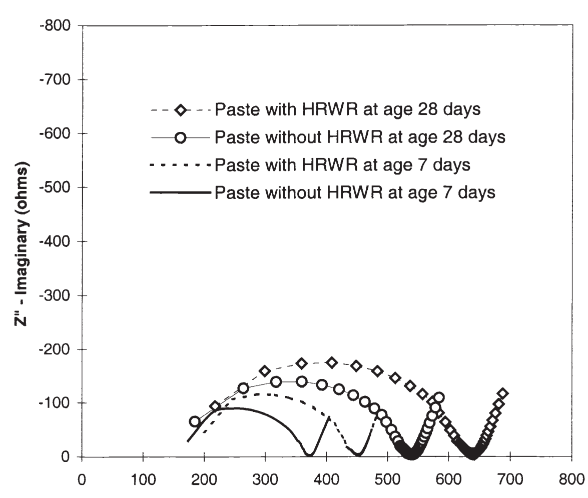

Fig. 4. The typical AC impedance spectra of the portland cement pastes.

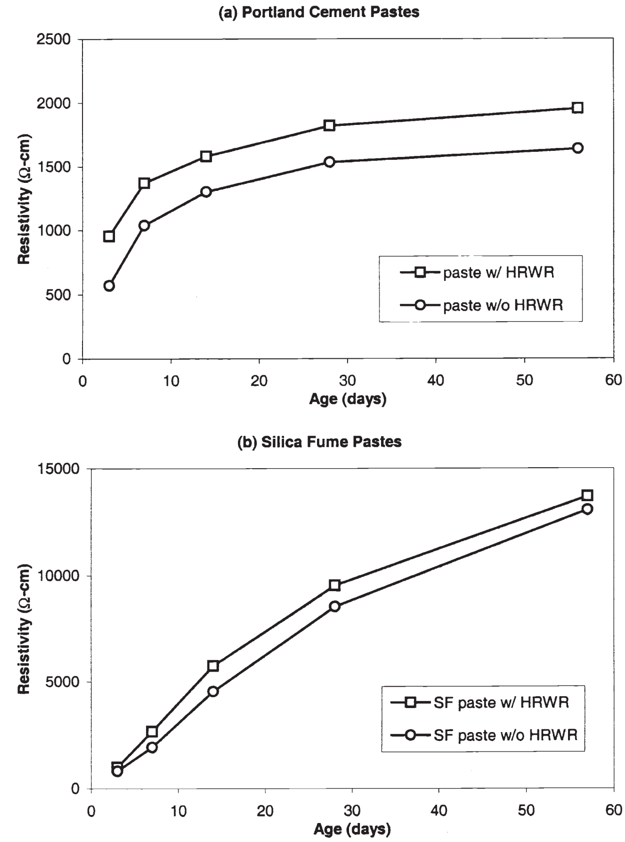

Fig. 5. The resistivity vs. age relations.

Figs. 1a and 6b. A lower initial current in the silica fume pastes leads to an even better linear relation with a high linear correlation coefficient (the R^2 value). The linear relations for the neat cement and silica fume pastes are similar to the other researchers' results for concrete [9,10].

2.5. The relationship between resistivity and the reciprocal of the total coulombs

The resistivity of the large disc-type pastes was determined before and after the rapid chloride permeability test (AASHTO T277/ASTM C1202) was conducted. The trend of the results was similar to those based on the small specimens shown in Fig. 5. The relationship between resistivity and the reciprocal of the total coulombs is linear for both neat cement and silica fume pastes before and after a 6-h period under 30 V applied potential (Figs. 7a and 7b).

The resistivity vs. the reciprocal of the total coulombs relations before and after the 6-h period (30 V applied potential) are either parallel (for the neat cement pastes) or overlap (for the silica fume pastes). The difference in resistivity is attributed to the changes in microstructure and pore solution chemistry of the pastes after a high electrical potential was maintained for 6 h. The low initial current results in the low difference in resistivity before and after a high electrical applied potential. A low current results in a low temper-

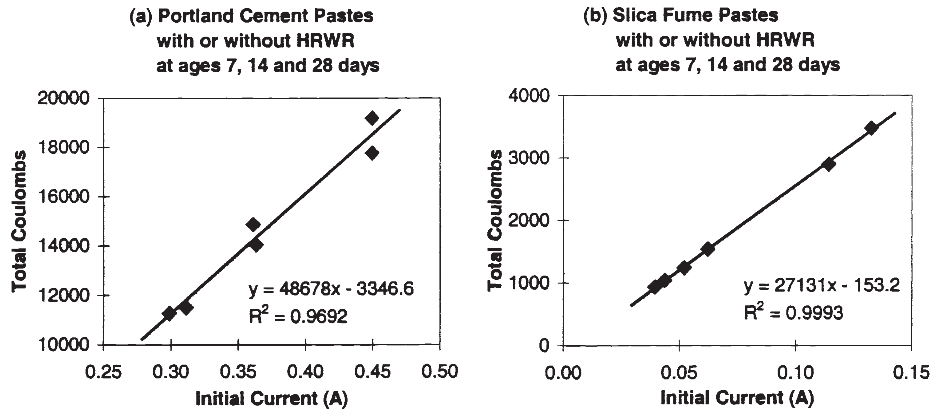

Fig. 6. The total coulombs vs. initial current relations for portland cement with and without silica fume.

ature rise, and hence has a less significant impact on the microstructure and pore solution (ion mobility and solubility). The linear relationship between the conductivity and total charge passed (total coulombs) was also obtained by Feldman et al. [9] for the concrete, similar to the results for the pastes.

2.6. The relationship between resistivity and the reciprocal of the initial current

In principle, the resistivity is inversely proportional to the electrical current. Thus, the resistivity of the saturated pastes before a high electrical potential is applied should be proportional to the reciprocal of the initial current. This relation was confirmed in this study, as demonstrated in Figs. 8a and 8b.

In summary, the addition of HRWR or silica fume appears to have little or limited effect on the modulus of elasticity of the pastes as long as the w/c ratio remains the same. The naphthalene sulfonate-type of HRWR slightly increases the impedance of the pastes, and this increase in impedance is even less for the silica fume pastes. In contrast, the addition of silica fume markedly increases the impedance of the pastes, and hence results in the very low total coulomb value (total charge passed). The results suggest a very low chloride permeability for the silica fume pastes, according to the criteria of the rapid chloride permeability test (AASHTO T277/ASTM C1202). However, the actual penetration of the chloride in the concrete may be only slightly reduced by adding silica fume [11]. Therefore, the total charge passed is only a qualitative indication of the "relative" permeability. This significant reduction in impedance by the addition of silica fume is attributed mainly to the change in the chemistry of pore solution (i.e., the considerable reduction in pH value and total ion concentration) and to the change in microstructure of the pastes (i.e., the fine pore structure).

The linear relationships have been established between the initial current and total coulombs, between the resistivity and reciprocal of the total coulombs, and between the resistivity and reciprocal of the initial current. These linear relationships imply that a similar or equivalent indication of the "relative" permeability to that obtained from the rapid chloride permeability test can be obtained by simply measuring the impedance of the saturated paste or concrete. The merits of the existing test have been subjected to considerable debate. Therefore, the significance of these linear rela-

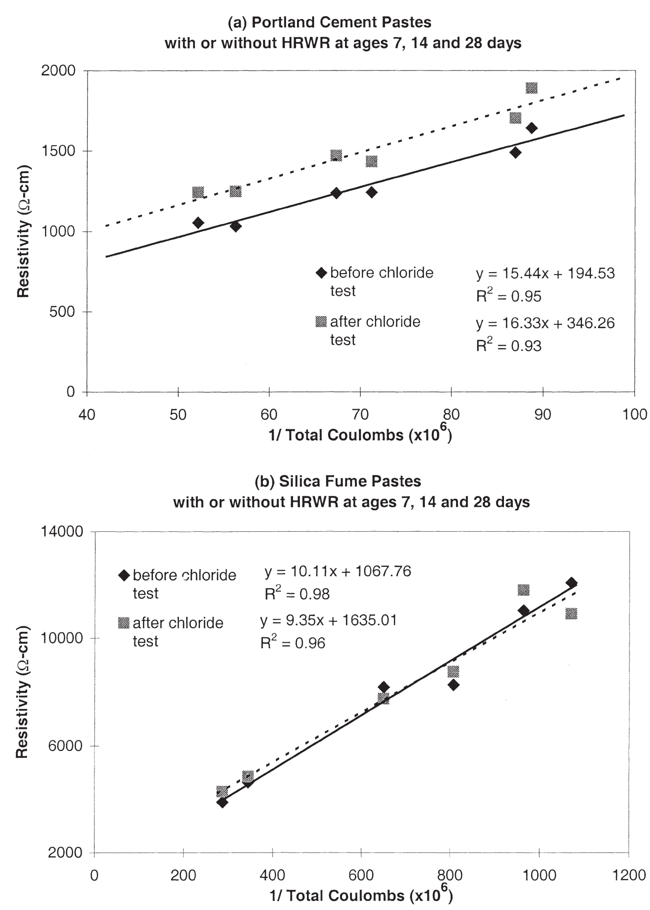

Fig. 7. The resistivity vs. reciprocal of total coulombs relations for portland cement pastes with and without silica fume.

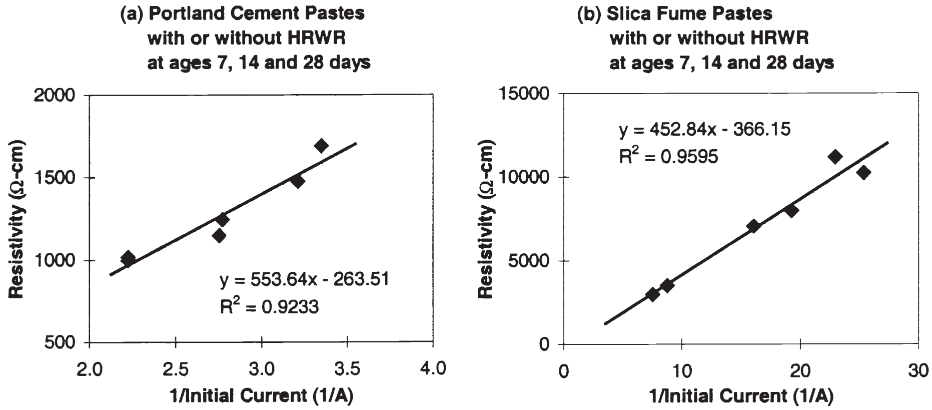

Fig. 8. The resistivity vs. reciprocal of the initial current relations for portland cement pastes with and without silica fume.

tionships is that they provide a promising opportunity for the development of a new, simple, and rapid permeability method as an alternative method of AASHTO T277/ASTM C1202.

3. Conclusions

The modulus of elasticity values of the pastes (prepared at w/c ratio = 0.45) were not sensitive to the presence of silica fume and/or HRWR. In contrast, the total charge passed (total coulombs) was significantly reduced or the impedance of the pastes dramatically increased by the addition of silica fume, even if the actual permeability was only marginally reduced. The naphthalene sulfonate-type of HRWR slightly increased the impedance or decreased the total charge passed (total coulombs). Its impact on these electrical properties was not significant.

The linear relationships exist between the initial current and total coulombs, the resistivity and the reciprocal of the total coulombs, and the resistivity and the reciprocal of the initial current. It is suggested that the resistivity (impedance) is an equivalent indication of the relative permeability to the total charge passed in AASHTO T277/ASTM C1202. As a result, it is possible to develop a new, simple, and rapid method for the assessment of the relative permeability of the cement systems using the AC impedance technique.

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