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Selection of superplasticizer in concrete mix design by measuring the early electrical resistivities of pastes

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Abstract

Electrical resistivity measurement was used to study the early setting and hardening process of pastes, with different dosages, for 2 types of superplasticizer. The inflection point (P_i) was found on the differential curve of electrical resistivity for each sample. A time ratio, K_t, is defined as the inflection time ratio of the pastes with superplasticizer to the paste without superplasticizer and a resistivity ratio, K_r, is defined as the ratio of resistivity of the pastes with superplasticizer to the resistivity of paste without superplasticizer at 24 h. The results show that K_t is linearly positive to setting time and K_r is linearly positive to compressive strength at 24 h.

The criterion for the selection of superplasticizer is proposed using these definitions. The most suitable superplasticizer is one which gives the mixture a higher K_t with a longer setting time and a higher K_r with a rapid strength gain in the hardening period for the saturation dosage at a fixed water cement ratio.

Keywords: Electrical resistivity; Superplasticizer; Saturation point; Setting and hardening

1. Introduction

Superplasticizers (SP) are widely used in concrete and have become common components of concrete, and the concrete properties are significantly influenced by such incorporation. For practical purposes, one of the key points in designing a concrete mix is to select the most suitable type and optimum dosage of superplasticizer. There are many methods to evaluate superplasticizers from a rheological point of view, such as the flow-table method of ASTM C230-90 [1], or alternatively, a mini-slump cone test developed by Kantro [2], and the Marsh cone test reported by Aïtcin et al. [3]. However, the effects of the superplasticizer on controlling setting time and maintaining the rate of compressive strength development is not known, and conventional setting time and strength testing needs to be undertaken.

It was reported that electrical response characteristics measurement has appropriate sensitivity in monitoring the hydration of cementitious materials [4–6], and some work has been published on various aspects of superplasticizers. Gu et al. [6] presented the microstructure of pastes containing superplasticizers using AC impedance and other methods to determine the mechanism of the superplasticizers effect. Torrents et al. [7] qualitatively studied the retarding effect of superplasticizer on cement setting, and Li and Wei [8] presented the effect of a retarder on cement pastes from the analysis of the microstructure and the hydration system solution. The reported research concentrated on theoretical viewpoints; however, applications using the resistivity or conductivity of fresh paste have not been significantly studied. McCarter and Afshar [9] proposed a time ratio and quantified the effect of calcium chloride and sugar on cement setting by the peaks on the dielectric constant curves. A similar method is adopted and developed in the present work in order to choose a more suitable superplasticizer.

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The aim of this work is to provide a fast way to evaluate and select superplasticizer, by using a combination of the Marsh cone and resistivity measurement. The Marsh cone was used to determine the saturation dosage of the superplasticizer, which is considered as the maximum dosage to be used. Based on this dosage, it is possible to narrow the choice of SP content by trial on the paste or concrete design. Generally, setting behaviour must be slow enough to enable concrete to be early handled from transportation to polish process in construction, however, on the other hand, after the concrete has been placed rapid hardening is often desirable. To select a suitable SP, the work of identifying the setting and hardening information of the paste on a resistivity–time curve ($\rho - t$) is carried out, and penetration resistance and compression tests are then conducted as parallel investigations. The methodology follows the procedures shown in Fig. 1.

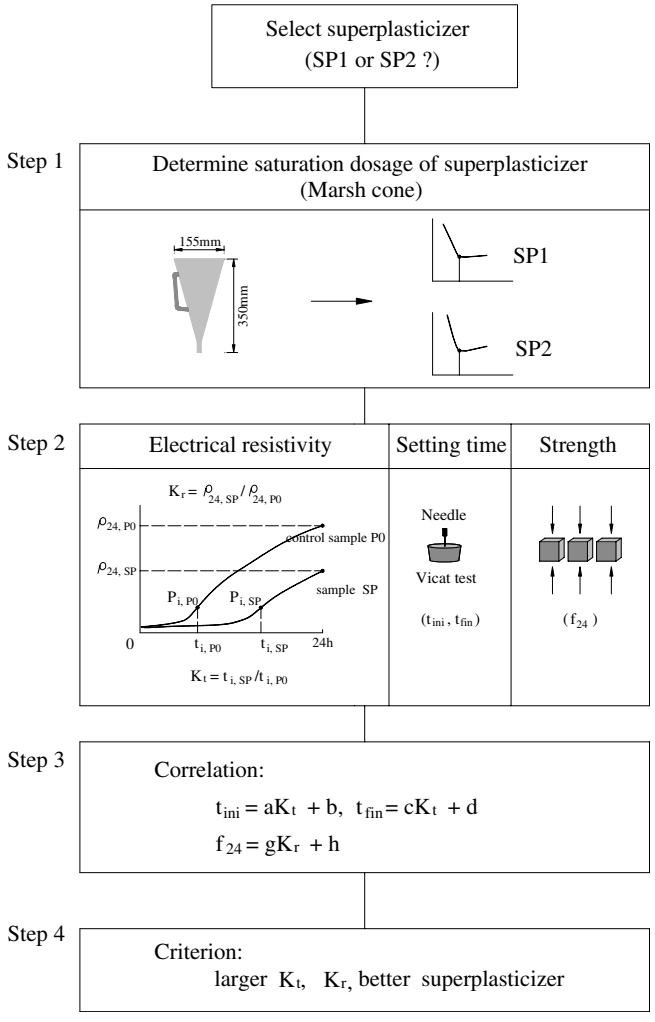

Fig. 1. Schematic presentation for selecting a suitable superplasticizer.

2. Raw materials

Ordinary Portland cement (OPC), meeting the requirement of ASTM type I, was used in the study. The chemical composition of the cement is given in Table 1.

Two types of superplasticizers were used in different cement pastes, namely a naphthalene-based superplasticizer (SP1) as a solid powder, of specific gravity of 1.21, and a polycarboxylate superplasticizer (SP2) with a solid content of 23% and a specific gravity of 1.02.

3. Sample preparation and testing methods

3.1. Fluidity

Cement pastes were prepared for fluidity testing using a Marsh cone, of body height 350 mm, orifice height 60 mm, upper orifice diameter 55 mm and lower orifice diameter 4.56 mm, as shown in Fig. 1. The cement pastes all have water/cement ratio of 0.3, respectively with incorporation of superplasticizer SP1 of 0.2%, 0.4%, 0.6%, 0.8%, 1.0% and 1.2%, and SP2 of 0.15%, 0.2%, 0.25%, 0.3%, 0.35% and 0.4%, by solid content with respect to percentage of cement by weight.

A reference volume of 800 ml of paste was poured into the cone and the time taken for 200 ml of the paste to flow through the orifice was recorded.

Marsh cone flow-time decreases with an increase in superplasticizer up to a value beyond which additional superplasticizer is no longer beneficial; this value is the saturation point of the superplasticizer. The saturation dosage of SP measured by the Marsh cone test suggests the maximum content to be used in cement paste or concrete.

3.2. Electrical resistivity

The electrical resistivity of the pastes was carried out by a non-contacting electrical resistivity measurement technique [10,11]. Seven paste mixes, each with a water/cement ratio (w/c) of 0.3, were prepared for resistivity, setting and strength measurement, using two types of superplasticizers in variable dosages. These dosages were determined, based on results of the Marsh cone tests, with the saturation dosage, a lower dosage and an excessive one for each superplasticizer.

3.3. Setting time

The setting time of paste was determined by means of a Vicat needle measurement. The needle diameter was 1.13 mm, and the interface at the test ring bottom and the glass plate was glued to avoid leakage of the paste.

Table 1
The chemical composition of cement (%)

Sample	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	LOI
Cement	69.66	20.01	3.27	1.39	1.12	3.78	0.02	0.03	0.72

The initial setting time was determined when the Vicat needle penetrates 25 mm into the sample and the final setting time is the time when the needle makes an impression on the surface of the paste without penetration.

3.4. Compressive strength

Cubes of size $100 \times 100 \times 100$ mm were prepared for compressive strength testing at the designated ages.

All the pastes were mixed for 2 min at low speed and 2 more minutes at high speed using a pastry mixer. The tests were conducted at a temperature of 20 ± 2°C and relative humidity of 95 ± 5%.

4. Results and discussion

4.1. Determination of the saturation dosage of superplasticizer by Marsh cone test

The flow-time curves from the Marsh cone tests at 5 min and 60 min with SP1 and SP2 are shown in Fig. 2a and b, respectively.

From Fig. 2a, it can be seen that the flow-time decreases with the increase of SP1 dosage, until a dosage of 0.8% is reached at which the flow-time is 140 s. Beyond this point, the flow time tends not to decrease further, indicating that the saturation point is 0.8%. This leads to the choice of 0.4%, 0.8% and 1.2% (lower, saturation and excessive amounts) as dosages to be used in paste mixes for other tests shown in Table 2.

The fluidity loss of the pastes at 60 min is described by a decreasing ratio in flow-time. The fluidity loss appears to have a decreasing trend with increase of the dosages at 60 min. The fluidity loss of the paste with its saturation dosage is 3.57%.

From Fig. 2b, as expected, the flow-time decreases with increase of SP2 dosage, and SP2 reaches its saturation point at a dosage of 0.25%, and a paste flow-time of 96 s. The flowability of the pastes is sensitive to SP2 content so that values of 0.15%, 0.25% and 0.35% are chosen, as shown in Table 2. A low paste viscosity can be deduced from the flow time, and the fluidity loss of the paste with its saturation dosage is approximately 0% at 60 min.

As a result of comparison of SP1 and SP2, SP2 reaches its saturation point at a smaller dosage and higher fluidity than SP1, and much less flowability loss is observed, suggesting that SP2 has better compatibility with the cement than SP1.

For final selection of a superplasticizer, it is necessary to make further tests based on the setting-control and strength gain that can be detected by the electrical resistivity measurement.

Based on the Marsh cone results, the saturation dosage, a lower dosage and an excessive dosage were used for these tests. The control paste (sample P0), the pastes containing superplasticizer SP1 (sample SP1-0.4, SP1-0.8 and SP1-1.2) and the pastes with superplasticizer SP2 (sample SP2-0.15, SP2-0.25 and SP2-0.35) are tabulated in Table 2.

4.2. Electrical resistivity characteristics and peak points on the differential curves

Fig. 3a shows the bulk electrical resistivity development with time ($\rho(t) - t$) for the seven samples. Fig. 3b displays

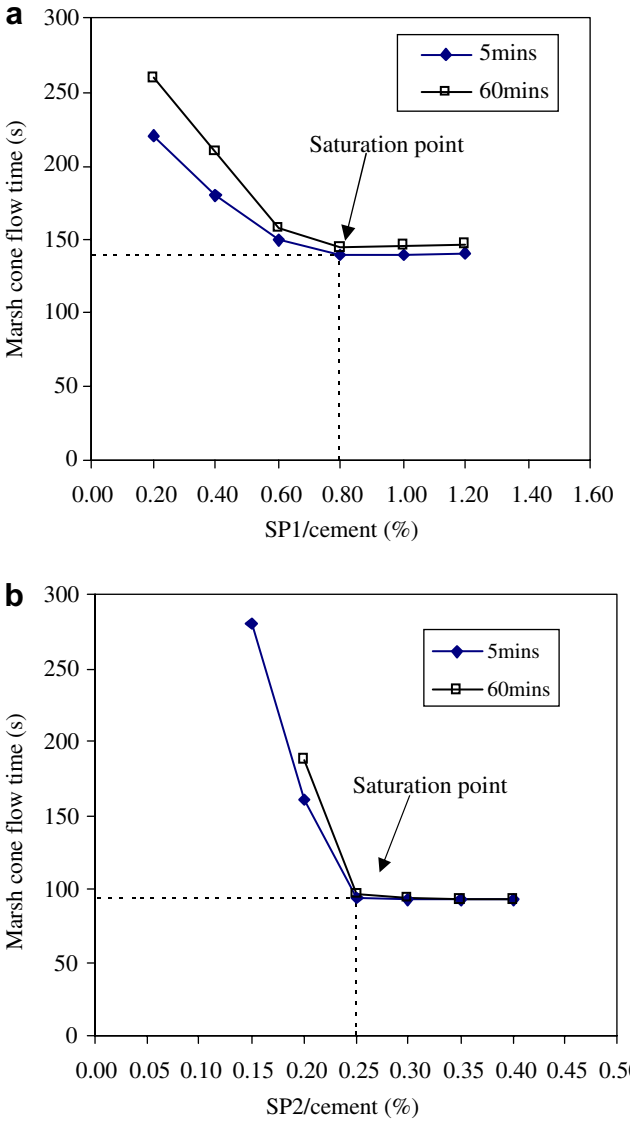

Fig. 2. The Marsh cone flow time of the pastes with the superplasticizers: (a) the flow time of the pastes with SP1 at 5 min and 60 min and (b) the flow time of the pastes with SP2 at 5 min and 60 min.

Table 2
Paste mix proportions for resistivity, setting time and strength tests

Mix no.	w/c ratio	SP1 (%)	SP2 (%)
P0	0.3		
SP1-0.4	0.3	0.4	
SP1-0.8	0.3	0.8	
SP1-1.2	0.3	1.2	
SP2-0.15	0.3		0.15
SP2-0.25	0.3		0.25
SP2-0.35	0.3		0.35

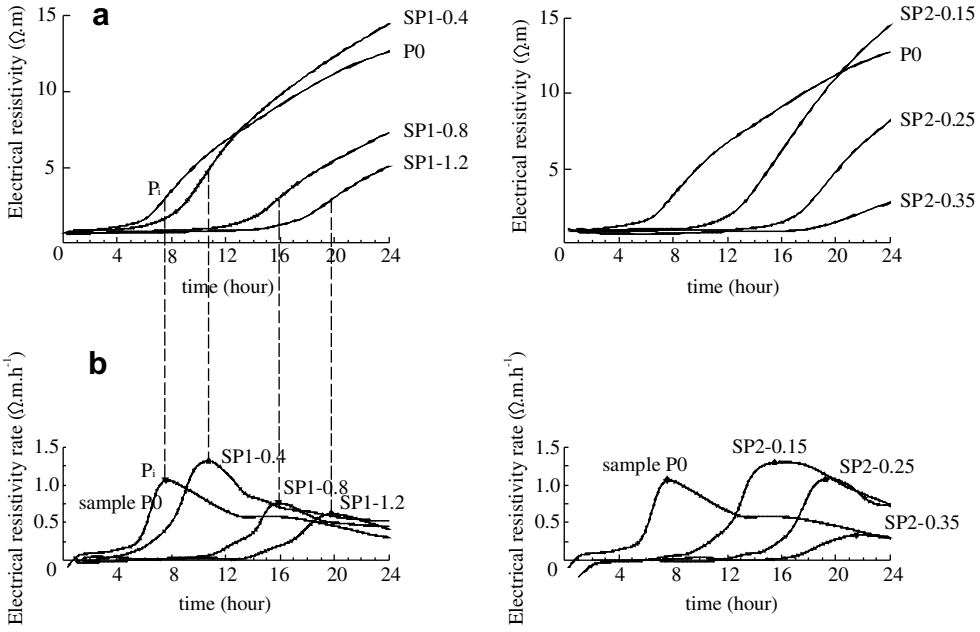

Fig. 3. Electrical resistivity/time response of the seven samples during 24 h: (a) resistivity development (b) the rate of change in resistivity development.

differential curves $\left(\frac{d\rho(t)}{dt} - t\right)$ for the samples, which give indication of the rate of resistivity development.

The curve shape of the curves in Fig. 3a is sigmoid or S-shaped. All curves follow a pattern that begins with a slow start, followed by a rapid increase, and then a slow rise. There is a peak point (P_i) for each sample on the differential curve $\frac{d\rho(t)}{dt} - t$, marked as the solid dots shown in Fig. 3b. P_i stands for the inflection point and maximum slope of the curve in Fig. 3a and corresponds to the maximum value point of the $\frac{d\rho(t)}{dt} - t$ curve in Fig. 3b.

The resistivity values at 24 h (ρ_{24}) and the times (t_i) at which the inflection points occur for all the samples are listed in Table 3. It is readily seen that the time t_i is delayed with the addition of superplasticizer SP1 or SP2 and this delay increases with the SP/C dosage. It appears that the ρ_{24} values of sample SP1-0.4 and SP2-0.15 are higher than that of the control sample P0, and the other samples have lower ρ_{24}. The experimentally observed changes in the electrical response can be further analyzed.

4.3. Inflection time ratio K_t and resistivity ratio K_r

To further evaluate the effect of a superplasticizer on resistivity ρ_{24} and time t_i, two parameters, inflection time ratio K_t and resistivity ratio K_r, are proposed. The parameters are defined as Eqs. (1) and (2).

$$K_t = \frac{t_{i,SP}}{t_{i,P0}} \tag{1}$$

$$K_r = \frac{\rho_{24,SP}}{\rho_{24,P0}} \tag{2}$$

where $t_{i,P0}$ is the inflection time of the control paste, $t_{i,SP}$ is the inflection time of paste incorporated with superplasticizer, $\rho_{24,P0}$ is the resistivity of the control paste at 24 h, $\rho_{24,SP}$ is the resistivity of paste incorporated with superplasticizer at 24 h.

K_r and K_t are calculated and shown in Table 3. It can be seen that K_t increases with the content of SP1 or SP2, and K_r is also influenced by the incorporation of the superplasticizers. The two definitions given attempt to give an quantitative indication of the retardation effect of the superplasticizers on setting time, which implies the time availability for maintaining the workability of the pastes and the effect of superplasticizer on resistivity and strength, further analysis will be conducted later.

Table 3
Values of ρ_{24}, t_i and K_r, K_t of electrical resistivity

Sample	ρ_{24}(Ω m)	t_i (hour)	K_r	K_t
P0	12.33	7.45	1.00	1.00
SP1-0.4	14.38	10.79	1.17	1.45
SP1-0.8	7.20	16.00	0.58	2.15
SP1-1.2	5.15	19.76	0.42	2.65
SP2-0.15	14.88	15.78	1.21	2.12
SP2-0.25	8.36	19.50	0.68	2.62
SP2-0.35	2.69	21.74	0.22	2.92

4.4. Setting time and the relationship between setting time and K_t

The increase in initial and final setting times (t_{ini}, t_{fin}) of the paste mixes incorporating superplasticizers SP1 and SP2, when compared to the control paste, are presented in Fig. 4a and b. As seen in Fig. 4a, the superplasticizer SP1 prolonged the initial setting time from 12% to189%, and the final setting was increased from 34% to 188%. From Fig. 4b, superplasticizer SP2 prolonged the initial setting time from 89% to 199%, and the final setting was increased from 101% to 256%. It can be seen that the

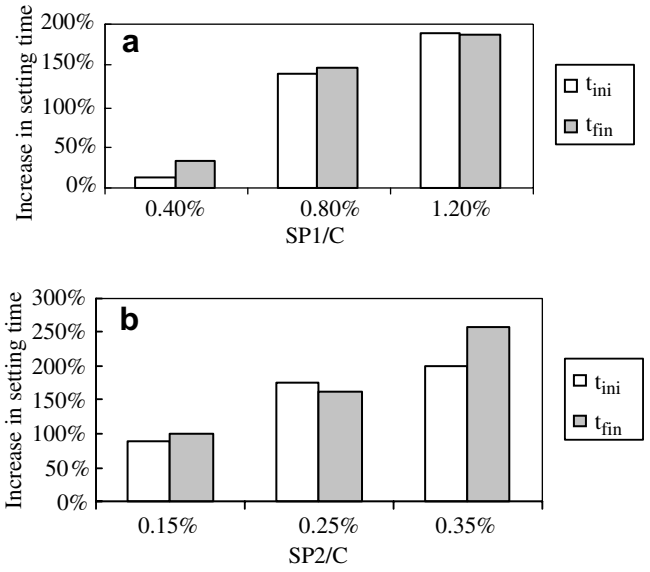

Fig. 4. Influence of the superplasticizers on setting time: (a) increase in setting time of the pastes with SP1 and (b) increase in setting time of the pastes with SP2.

superplasticizer SP2 is more effective in delaying the setting time than superplasticizer SP1, which is consistent with the results observed in K_t in Table 3.

Fig. 5 shows the relation between setting time and K_t, as described in Eqs. (3) and (4). It can be seen that there is a linear trend between the initial setting time and K_t, and the final setting time and K_t. Hence, K_t can be an indication of the setting time; the larger the K_t, the more the setting retardation, i.e. longer time availability for maintaining the workability of the mixture.

$$t_{ini} = aK_t + b = 4.0851\ K_t - 1.1698 \quad (3)$$

$$t_{fin} = cK_t + d = 5.8807\ K_t - 1.7874 \quad (4)$$

4.5. The strength f_{24} and the relationship between f_{24} and K_r

The compressive strengths for all the samples are shown in Table 4. It can be seen that the strength f_{24} at 1 day (24 h) increases when a small dosage of SP1 or SP2 is used,

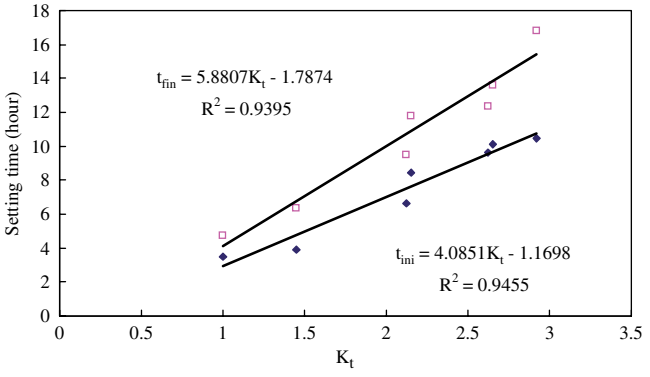

Fig. 5. Correlation of setting time (t_{ini}, t_{fin}) and K_t.

Table 4
Compressive strength of the paste mixes

Sample	Compressive strength (MPa)		
	1d	2d	28d
P0	41.31	48.53	64.97
SP1-0.4	42.47	50.52	69.17
SP1-0.8	25.16	42.47	63.05
SP1-1.2	23.65	35.23	49.05
SP2-0.15	49.89	62.22	65.82
SP2-0.25	40.79	56.46	80.45
SP2-0.35	20.15	36.84	61.89

and then decreases when there is an increase of the dosage of the superplasticizers. The strength results at 1 day appear to have the same change trend with the superplasticizer, as observation of the resistivity ratio K_r in Table 3 shown. It can be seen that there is a linear relationship between the strength ratio and K_r as shown in Fig. 6 and Eq. (5).

$$f_{24} = gK_r + h = 27.981\ K_r + 13.669 \quad (5)$$

The strength gain essentially contributes to the increase in the fraction of the internal hydration products. The hydration products block the path of ion movements, and this leads to an increase in the bulk electrical resistivity. Therefore, electrical resistivity development is comparable with strength gain for the paste mixes. It is implied in Fig. 6 that the correlation of the compressive strength ratio and K_r appears to be independent of dosage for the SP1 mixes and the SP2 mixes.

It can be concluded that the higher K_r corresponds to a higher compressive strength ratio, then K_r can be an indication of strength development.

Hence, the electrical resistivity measurement dynamically represents the hydration process during the first day after casting and it can provide the setting and hardening characteristics. It is feasible that a suitable superplasticizer type and optimum dosage can be selected based on characteristic points and the resistivity development trend of the electrical resistivity curve, according to the engineering requirements in the operation schedule and compressive strength development.

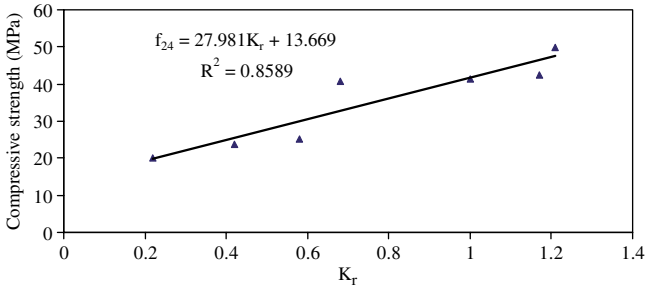

Fig. 6. Correlation of compressive strength f_{24} and K_r.

4.6. Criterion for selecting superplasticizer

The criterion for selecting superplasticizer is listed below:

(1) Determine the saturation dosage of superplasticizers SP1 and SP2 by the Marsh cone testing. The saturation dosage of superplasticizers SP1 and SP2 in this paper are 0.8% and 0.25%, respectively.
(2) Obtain the electrical resistivity curves of paste without superplastizer, with saturation dosage of superplastizer SP1 and with a saturation dosage of superplastizer SP2. In this paper, the three samples are P0, SP1-0.8 and SP2-0.25.
(3) Compare K_t and K_r for the pastes with SP1 and SP2. The one with a larger K_t and K_r is preferentially selected.

As described above, a higher K_t indicates a longer setting time and having a longer workable period. Higher K_r indicates a faster resistivity development and strength gain after setting. When comparing two or more superplasticizers, the one with a higher K_t and K_r will be selected.

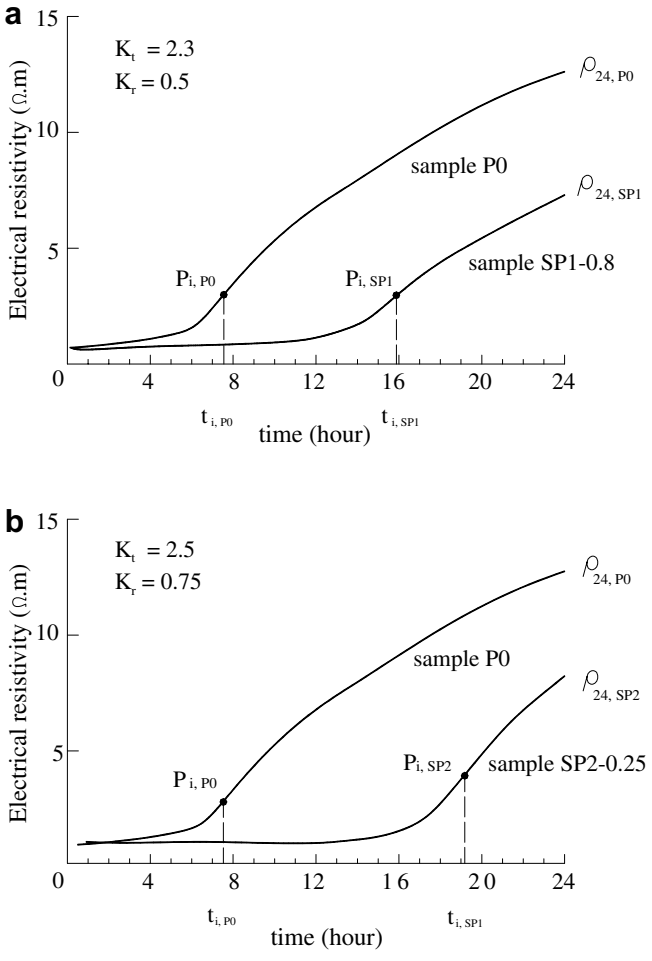

Fig. 7. The comparison of SP1-0.8 and SP2-0.25.

The comparison of SP1-0.8 and SP2-0.25 is shown in Fig. 7a and b. The larger K_t (=2.5) of sample SP2-0.25 compared to that (=2.3) of sample SP1-0.8 indicates that SP2 is more effective in maintaining the workability of the paste. The higher K_r (=0.75) of sample SP2-0.25 represents a higher strength gain, contributing to more hydrates being formed.

When a better superplasticizer is determined, its optimum dosage for meeting the engineering requirements in workable period and strength can be determined according to the method for obtaining Eqs. (3), (4) and (5). The equations for determining optimum dosage can be obtained by just changing dosages of the selected superplasticizer to do the correlation, following the same procedures as shown in Figs. 5 and 6; afterwards, K_t and K_r can be calculated according to the setting time and strength from engineering requirements; finally, the optimum dosage can be selected from electrical resistivity measurement results.

The significance of the study is that the combination of the Marsh cone test and the resistivity measurement can provide a simple and alternative method to select a suitable superplasticizer and determine its optimum dosage.

5. Conclusions

The main conclusions can be drawn as follows:

1. K_t is the inflection time ratio of the pastes on the electrical resistivity development curve with superplasticizer to the paste without superplasticizer. The physical meaning of K_t indicates that a larger K_t has a longer retardation of setting and a longer workable period.
2. K_r is the ratio of resistivity of the paste with superplasticizer to the resistivity of paste without superplasticizer, at 24 h. The physical meaning of K_r implies that a larger K_r has a larger compressive strength gain.
3. The criterion for selecting a superplasticizer is as follows. First, determine the saturation dosage of superplasticizers (SP1 and SP2) by Marsh cone testing; secondly, obtain K_t and K_r from the resistivity and the differential curves of the control sample, superplasticizer SP1 and superplasticizer SP2. A larger K_t and K_r sample with superplasticizer is preferentially selected in the design of a paste or concrete mixture. This study proposes a methodology for selecting a suitable superplasticizer, and the optimum dosage, from a general consideration of engineering requirements, involving the concrete operable period, from mixing, transportation, casting to polishing, for scheduling construction; and strength gain for determining the time of formwork removal.

Acknowledgement

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