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Influence of alkali on restrained shrinkage behavior of cement-based materials

Zhen He[a], Zongjin Li[b,*]

[a]State Key Laboratory of Water Resource and Hydropower Engineering Sciences, Wuhan University, China
[b]Department of Civil Engineering, The Hong Kong University of Science and Technology, Hong Kong, China

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Abstract

Experiments have been conducted to study effects of high alkalinity on restrained shrinkage behavior and cracking sensitivity of cement-based materials at early ages. The restrained shrinkage test has been conducted with an ellipse ring setup and the initial cracking time was monitored with a continuous conductive strip. Alkali content and alkali type as well as the shrinkage–hydration relationship have been studied. The experimental results have shown that the cracking sensitivity of a cement-based material is increased with an increase in alkali content. The influence of the excess alkali on the cracking sensitivity is more obvious for cement paste with a low water-to-cement ratio (w/c) than that with a high w/c. The hydration processes and microstructure development of cement paste have been investigated using heat of hydration measurement and electrical resistivity measurement. The superimposed resistivity curve and heat evolution curve provide more comprehensive understanding on factors influencing shrinkage development.

Keywords: Alkali; Early-age cracking; Shrinkage; Hydration; Cement

1. Introduction

The properties of a concrete can be influenced to a great extent by the minor composition of Portland cement, such as alkali. The alkali content in Portland cement may range from 0.3% to 1.5% by weight of cement as Na_2O equivalent (Na_2O+0.64K_2O) depending on the composition of raw materials and manufacturing technology. The form, amount and type of alkali significantly influence early hydration reactions and microstructure development of cement-based material [1,2]. Many authorities suggest limiting the total available alkali content of concrete, often to less than 3 kg/m^3, which should account for the contribution from all concrete components [3]. However, modern cement-based materials frequently contain higher amounts of alkali. Past experience has demonstrated that the effectiveness of different supplementary cementing materials depends on the total concrete alkali content [4,5]. Many researchers have studied the influence of alkali (or excess alkali) on properties of concrete, with a large concentration on alkali–silica reaction (ASR). However, very little attention has been paid to early-age cracking of cement-based materials resulting from high alkalinity.

Early-age cracking of cement-based materials is influenced by many factors, including material composition, mixture proportions, shrinkage rate, stress or creep relaxation, degree of structural restraint and production procedures [6–10]. Recent studies have been conducted on concrete to better understand relevant material properties and testing techniques [6]. Free shrinkage alone may not offer sufficient information on the behavior of concrete structures because virtually all-concrete elements are restrained to a certain extent [7]. Restrained shrinkage is often considered to be the main cause of cracking in concrete [8–10]. Tensile stress is generated in concrete due to the restrained deformation by boundary conditions. Therefore, there is a competition inside the materials between the development of tensile stress and the development of tensile strength that evolves

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* Corresponding author.
E-mail address: zongjin@ust.hk (Z. Li).

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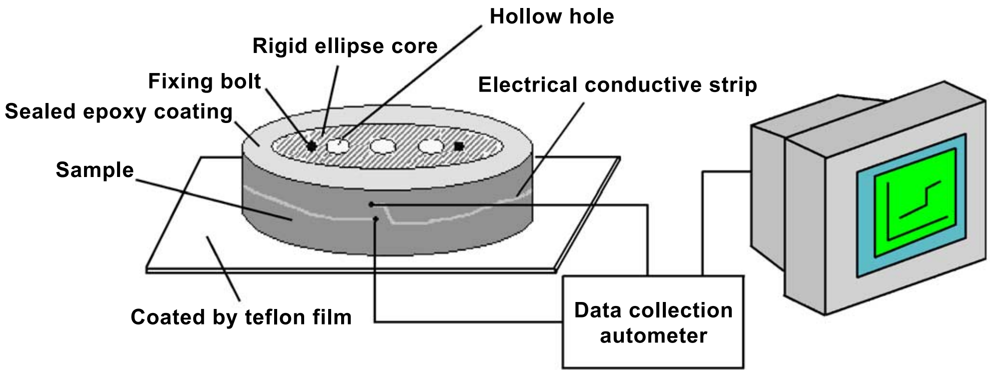

Note: The dimensions of ellipse sample as following

Outer ellipse long axis (mm)	Outer ellipse short axis (mm)	Inner ellipse long axis (mm)	Inner ellipse short axis(mm)	Height (mm)
600	240	560	200	80

Fig. 1. Restrained shrinkage test setup.

with time [11]. Crack will form when the stress exceeds the tensile strength at a certain age. It is well known that alkali can accelerate the hydration of Portland cement. Meanwhile, the internal drying caused by accelerated hydration process together with thermal contraction due to alkali may contribute to the shrinkage of cement-based materials. The possible effect of alkali on shrinkage behavior of cement-based materials at early ages has attracted a great attention of many researchers [12,13].

To better understand the influence of alkali on early-age cracking of cement-based materials, a series of test has been conducted on specimen containing alkali. Information presented in this paper is the result of restrained shrinkage test using a newly developed ellipse ring system [14], which utilizes its shape to induce a high stress concentration factor. With the new system, the initial cracking time can be automatically recorded because a continuous conductive strip is adopted in the system. The tests have been carried out with different water-to-cement ratios (w/c), and different types and content of alkali. To investigate the influencing mechanism of alkali on the early-age cracking properties of cement-based materials, hydration heat rate, resistivity and flexural strength of corresponding cement system have been measured. It is found that the excess alkali does influence the early-age cracking behavior of cement-based materials, although the relationship may not be straightforward.

2. Test method

Restrained drying shrinkage tests are conducted using a special apparatus with an automatic monitoring system for cracking development (see Fig. 1). In this apparatus, a rigid ellipse is used to restrain the shrinkage of an ellipse-ring-shaped specimen surrounding it. It is well known that an elliptical shape can generate a high stress concentration than

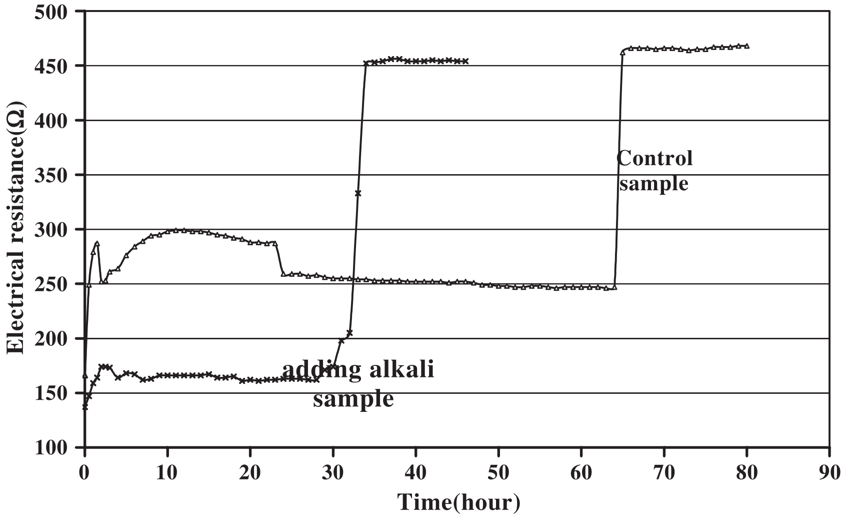

Fig. 2. Initial cracking time detected by automatic recording system.

Table 1
Chemical compositions of cement (% by weight)

	Oxide components	
Result of chemical analysis	CaO	63.12
	SiO_2	20.83
	Al_2O_3	6.28
	Fe_2O_3	2.47
	MgO	1.16
	SO_3	2.04
	Na_2O	0.25
	K_2O	0.61
	TiO_2	0.21
	f-CaO	0.44
	LOI	1.03
Na_2O e.q.(Na_2O+0.64K_2O)		0.64
Potential cement composition	C_3S	47.12
	C_2S	24.17
	C_3A	12.46
	C_4AF	7.52

a circular shape does. A flat board with the surface coated with a layer of Teflon is used as a base to carry the specimen and the rigid ellipse. The effect of Teflon is to reduce the friction between the specimen and the baseboard. Along the circumferential surface of the ellipse ring specimen, a strip made of an electroconductive material (carbon) with extremely low strength is attached. At the opening of the contour strip, two electrodes are used to connect the contour into a closed loop through a universal meter. It also acts as an analogue to a digital converter and transfers the data to a computer. When the test starts, a voltage is applied to the loop and the meter is used to monitor the resistance of the loop. Once shrinkage crack forms, the conductive curve will be broken and the resistance will suddenly increase, as shown in Fig. 2. Compared to the traditional method, in which the occurrence of crack is confirmed by eye observation, the newly developed method can provide accurate initial time for a shrinkage crack with a width of 0.2 mm or less.

The mortar samples were prepared with ordinary Portland cement (OPC), two dosages of alkali, two types of alkali and two w/c. Mortars were made of one part of cement and two parts of sand by mass. The fineness modulus of sand was 1.86. Alkalinity was increased by adding sodium hydroxide or potassium hydroxide in mixing water as Na_2O%, e.q. by mass of cement. Results of chemical analysis of OPC and its mineral compositions are shown in Table 1. There was 0.64% Na_2O e.q. presented in plain cement. Mix proportions of specimens for restrained shrinkage test, hydration heat test and resistivity of cement paste are listed in Tables 2–4, respectively.

Table 2
Mix proportions of specimens for restrained shrinkage (ring) test

Sample no.	Cement	Sand	NaOH (Na_2O e.q.), %	KOH (Na_2O e.q.), %	w/b
Control-1	1	2	0	0	0.40
N1	1	2	0.645 (0.5)	0	0.40
N2	1	2	1.290 (1.0)	0	0.40
K1	1	2	0	0.903 (0.5)	0.40
K2	1	2	0	1.806 (1.0)	0.40
C2	1	2	0	0	0.55
N4	1	2	0.645 (0.5)	0	0.55
N5	1	2	1.290 (1.0)	0	0.55

Table 3
Different cement pastes for the hydration test

Sample no.	By weight (g)			w/c
	Cement	Water	NaOH	
Control-1	30	12	0	0.40
Control-1+0.645%NaOH	30	12	0.193	0.40
Control-1+1.290%NaOH	30	12	0.387	0.40
Control-3	30	16.5	0	0.55
Control-3+0.645%NaOH	30	16.5	0.193	0.55
Control-3+0.645%NaOH	30	16.5	0.387	0.55

The restrained shrinkage specimens were cured in a controlled environment chamber at 28±1 °C and over 95% of relative humidity until the age of 18 h. Then, the outer molds of ring specimens were stripped off. After demolding, the top surface of the mortar ring was sealed using epoxy resin without hardener, so that drying would be allowed only from the lateral face. Then, the specimens were tested under a condition of 28±1 °C of temperature and 50% of relative humidity.

Mix proportion of samples for the flexural strength test was the same as that for the ring test. The size of the samples for bendy test was 40×40×160 mm. Molds of the samples were removed at the same time and moved to the same curing condition with the ring specimen. Their flexural strength was measured at the age of the initial cracking of the corresponding ring sample.

Hydration heat evolution of cement paste was measured by a JAF Calorimeter. Six specimens were tested in two groups. One group was prepared with a w/c of 0.40 and the other with 0.55. In each group, a plain cement paste was used along with a paste containing different dosage of alkali (see Table 3). Each specimen was cast in a sealed installation container to prevent heat escaping. Hydration heat of each paste was measured for 72 h.

Resistivity of the cement pastes has been measured by a noncontacting resistivity meter. The schematic of

Table 4
Different cement pastes for the resistivity test

Samples	By weight (g)			w/c
	Cement	Water	NaOH	
Control-1	800	320	0	0.40
Control-1+0.645%NaOH	800	320	5.16	0.40
Control-1+1.290%NaOH	800	320	10.32	0.40
Control-3	800	440	0	0.55
Control-3+0.645%NaOH	800	440	5.16	0.55
Control-3+0.645%NaOH	800	440	10.32	0.55

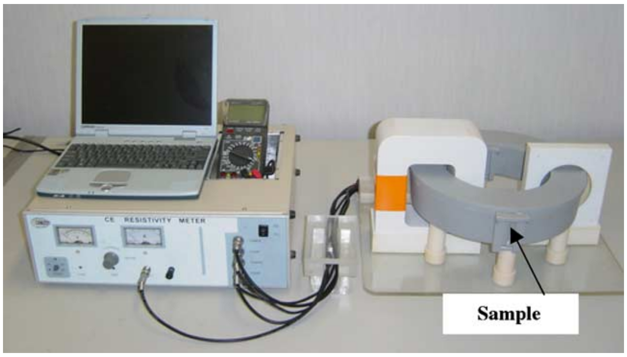

Fig. 3. Setup of the electrical resistivity measurement system.

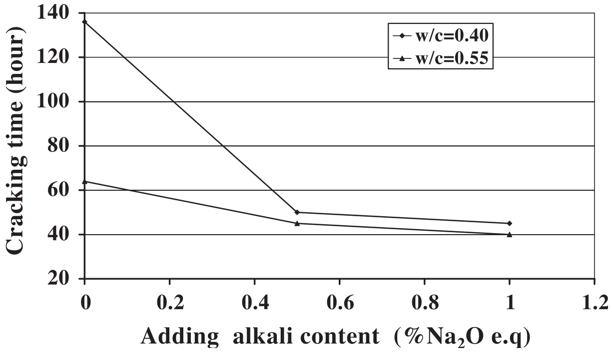

Fig. 4. Effect of NaOH content and water–cement ratio on initial cracking time of mortars.

resistance measurement is shown in Fig. 3. The method adopts a transformer principle and eliminates electrodes. A transformer usually consists of two coils of wire wound on the same core. The primary coil is the input coil of the transformer and the secondary coil is the output one. Mutual induction causes voltage to be induced in the secondary coil. In the new system, the cement-based specimen is a ring with a trapezoid section. The core with wires acts as the primary and the specimen ring acts as a secondary coil of the transformer. There are no electrodes, and thus, the problems involved with electrodes, such as polarization, gas releasing and contacting, are all eliminated. To verify the reliability of the new device, a calibration is done with 0.1 N KCl electrical conductivity at 24.5 °C using this device. The standard value of 0.1 N KCl electrical solution is 0.01276 $\Omega^{-1} \cdot \mathrm{cm}^{-1}$ at 24.5 °C. The measured value using the newly developed device is 0.01271 $\Omega^{-1} \cdot \mathrm{cm}^{-1}$ at 24.5 °C. The difference is less than 0.4%. It indicates that the noncontacting electrical measurement device provides an accuracy method. The measured resistivity curve can be used to interpret the hydration process as well as microstructure development of a cement paste with or without excess alkali. More details regarding noncontacting resistivity measurement can be found in Ref. [15].

3. Results and discussions

3.1. Initial cracking time

The initial cracking time for specimens with different alkali content and w/c is shown in Fig. 4. The two plain specimens (without adding alkali but different w/c) showed that the initial cracking time reduced from 136 h for the specimen with w/c of 0.40 to 64 h for the specimen with w/c of 0.55. It was reasonable because a higher w/c provided more free water and thus led to a higher drying shrinkage. If considering the factor of alkali content alone, it could be seen that a higher alkali content resulted to an earlier initial cracking. For instance, for the specimen made of w/c of 0.40, the addition of 0.5% Na_2O e.q. led to an initial cracking time of 50 h and addition of 1.0% Na_2O e.q. led to an initial cracking time of 45 h. Hence, alkali content in cement-based materials should be limited more rigorously due to early-age shrinkage behavior.

Influence of different alkali types on initial cracking time is shown in Fig. 5. It could be seen that the effect of K^+ on the initial cracking time was slightly higher than that of Na^+.

Cracking time reflects the sensitivity to cracking of cement-based materials. It should be pointed out that influence of alkali on early-age cracking is a complex issue. Alkali may influence the early shrinkage through the fast self-shrinkage caused by accelerated hydration plus thermal contraction. However, these effects were sometimes considered as second-order effect.

3.2. Flexural strength at age of initial cracking

The bending tests were conducted to obtain the flexural strength. The samples for the flexural strength test were cast separately and cured under either wet or dry conditions. The specimens cured under dry condition have gone through the same curing, demolding and storing conditions like the ring specimens for restrained shrinkage test. The bending tests were conducted at the age when the cracking initiated and the results are shown in Fig. 6. As expected, the specimens that were cured under drying conditions showed a lower flexural strength than the specimens that were cured under

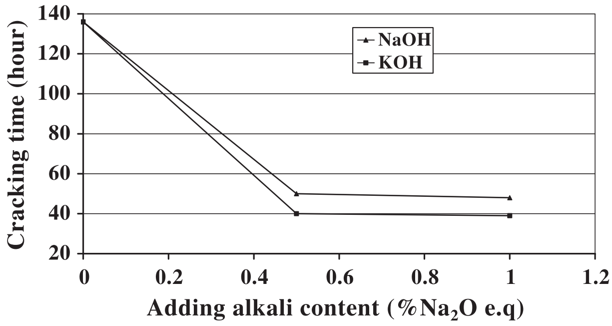

Fig. 5. Effect of alkali content and alkali type on initial cracking time of mortars.

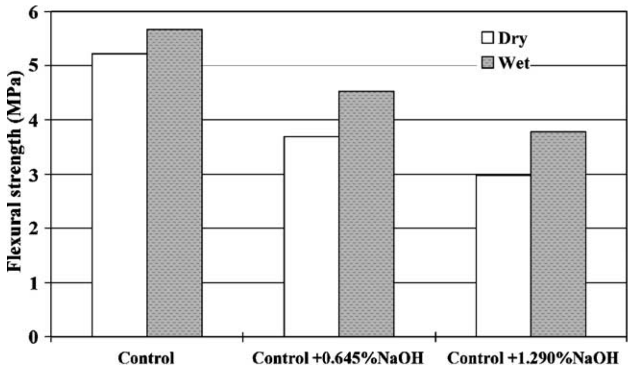

Fig. 6. Flexural strength of mortars at the age of initial cracking time.

wet condition. The control specimen had the highest flexural strength, followed by the specimen with 0.5% alkali which was followed by the specimen with 1.0% alkali. The specimen with higher alkali content cracked earlier because the restrained shrinkage stress developed faster than that of flexure strength. Once the development of tensile stress was over the development of tensile strength, crack would occur.

3.3. Hydration heat

The heat evolution measurement reflects the kinetics of chemical reaction of cement compound. The maximum value on a heat evolution curve characterizes the highest reaction rate of C_3A or C_3S. Although thermal effect on shrinkage was negligible because of the small cross-section in this study, the influence of different hydration processes and microstructure formation rates due to different alkali contents should be taken into account. Samples with two w/c and two dosages of alkali were prepared for the hydration evolution heat test. The test results for two groups of specimens with w/c of 0.40 and 0.55 are shown in Figs. 7 and 8, respectively. Two general observations can be found from the figures. First, the peaks in the rate of heat evolution curve for specimens with alkali addition occur ahead of the heat evolution peaks in the specimen without addition of alkali. Second, the maximum values of the rate of heat evolution for specimens with addition of alkali are higher than that of the specimen without addition of alkali. It is implied that adding alkali can accelerate the hydration of cement.

The accelerated hydration process results in the rapid hydration and loss of water, especially in low relative humidity environment (less 50% RH). The interaction of high drying restrained shrinkage (short cracking time) and thermal deformation led to an increased risk of cracking.

3.4. Electrical resistivity

The experiment results of electrical resistivity are shown in Fig. 9 (a and b). The results of heat evolution are superimposed in the figure to help to understand the hydration process and hardening microstructure formation of different cement pastes at early age. From the characteristic of the curves, it can be found that cement component affected hydration and shrinkage behavior significantly.

The resistivity measurement represents the global change of cement microstructure and ion concentration. It can be used to interpret the connectivity of hydration products and volume of porosity. It is a more accurate index of microstructure development [15]. It can be seen that the resistivity curves show the same trend with the heat curves of a cement paste. The curves go down first and climb up when the lowest point was reached. This period corresponds to the dissolution period in a hydration process. The lowest point might be regarded as the maximum conducting point. After resistivity reaches its minimum, the curves change their slope and start to rise because of sedimentation–crystal period. The turnover point I indicates a beginning of fast development of connection of hydration products, which

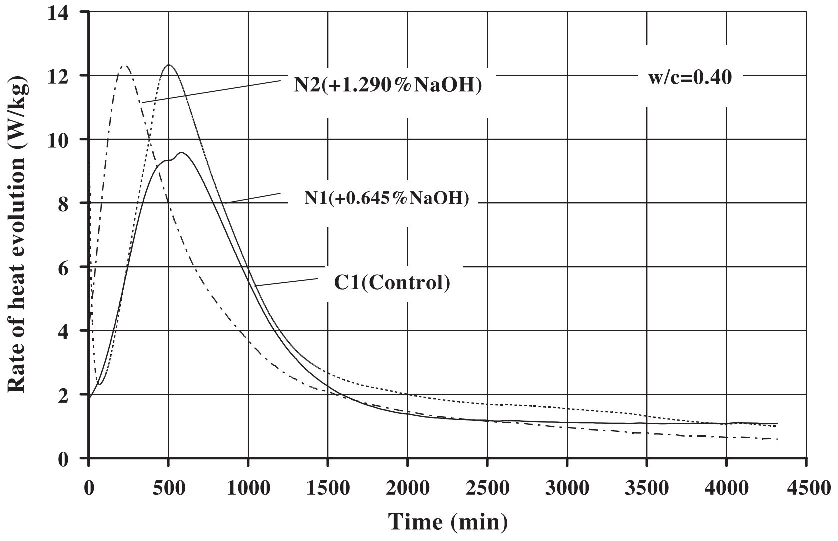

Fig. 7. Rate of hydration heat evolution of cement pastes (w/c=0.40).

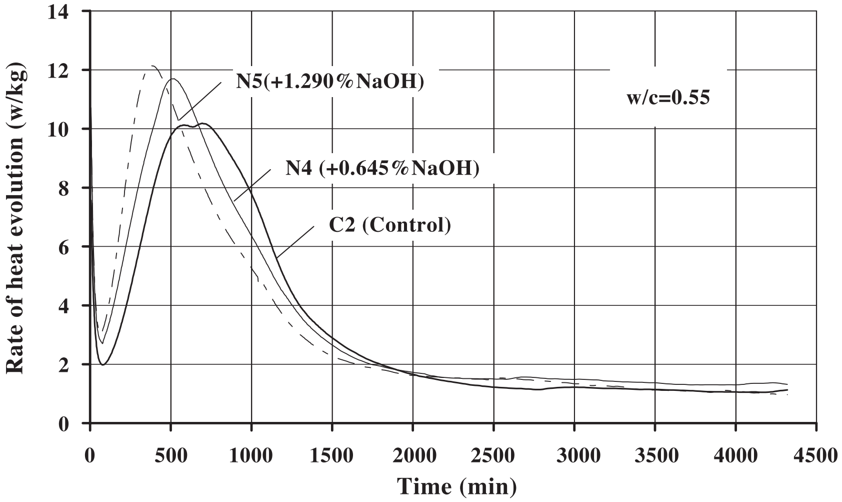

Fig. 8. Rate of hydration heat evolution of cement paste (w/c=0.55).

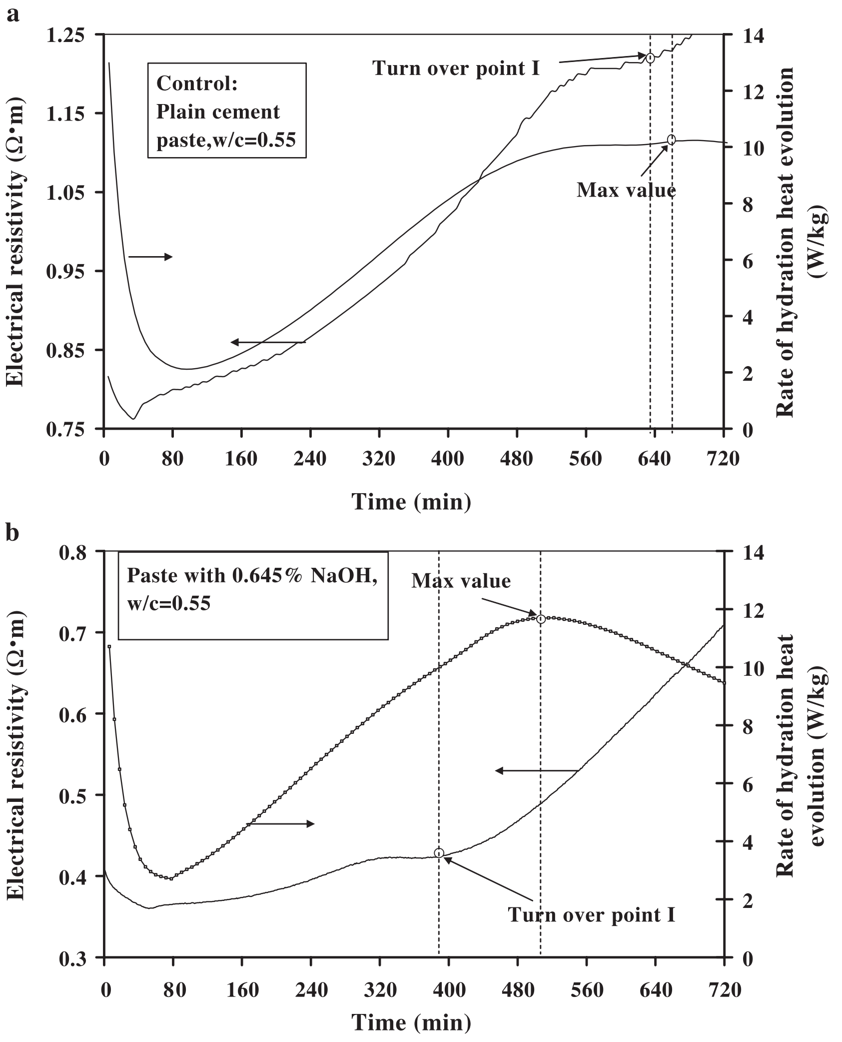

Fig. 9. (a) Relationship between resistivity and hydration heat of plain paste when w/c=0.55. (b) Relationship between resistivity and hydration heat of paste with 0.645% NaOH when w/c=0.55.

corresponds to the final setting and start of hardening. At this rate, the diffusion of ions and solid reaction holds majority role.

Fig. 9a and b shows the resistivity curves for a plain cement specimen (control) and a specimen with additional 0.645% NaOH under same w/c condition. It can be seen from the figure that the resistivity curve of the specimen with high alkalinity has the lower minimum point than that of the control specimen. However, its plateau period is shorter than that of the control specimen. NaOH is an accelerating admixture that can increase the ion concentration at the dissolution period and influence the hydration of cement later.

For the specimen with w/c of 0.55, the turnover point on the resistivity curve (point I in Fig. 9) of cement pastes with high alkalinity on the resistivity curve occurs at about 6 h, but the turnover point of plain cement paste occurs at about 10 h. By comparing the turnover point on the resistivity curve to the maximum value on the heat evolution curve, it can be found that the turnover point on the resistivity curve is far ahead of the maximum value of heat evolution for specimens with additional alkali (see Fig. 9b). On the other hand, the time difference between the turnover point of the resistivity curve and the maximum value of the heat evolution curve is very small for the plain cement specimen (see Fig. 9a). The higher internal shrinkage due to loss of absorbed water happens sometime after hardening while thermal contraction is gently higher when heat revolution reaches its maximum. Hence, for the specimen with additional alkali, the internal shrinkage and thermal contraction superimposed at their higher values, which subsequently can lead to a fast development of shrinkage stress when there is restraint. However, because the hardening in plain mortar occurs later, the superposition of the internal shrinkage and thermal contraction does not happen at their peak region for plain cement specimen. Thus, the crack sensitivity of the plain mortar is less than that of the mortar with excess alkali.

4. Conclusions

Based on the results in this paper, the following conclusions can be drawn.

- Under the current study, when alkali content is increased, the crack sensitivity of cement-based materials increases. The increase of alkali has a stronger effect in prompting occurrence of cracking at early ages for the mortar specimen with a low w/c than that with a high w/c.
- The hydration heat and resistivity measurement proved that the additional alkali could lead to a quicker and earlier chemical reaction. The superimposed resistivity curve and heat evolution curve provided a better understanding on the relationship between hydration process and early-age shrinkage behavior.
- The difference between inflection point on the resistivity curve and maximum value on heat evolution could be used as an index for the microstructure development and crack sensitivity at early ages for cement-based materials.

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