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The early hydration of alkali-activated slag: developments in monitoring techniques

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Abstract

Developments in the application of electrical methods in the study of the early hydration reaction kinetics of alkali-activated slag are presented. Work focuses on monitoring the change in both conductance and capacitance over the initial 24–48 h hydration with electrical measurements taken over the frequency range 1–100 kHz. In the current study, sodium hydroxide and sodium silicate are used as activators. The work highlights the frequency dependence of capacitance and, to a lesser extent conductance; in addition, over the duration of the test, both these electrical parameters undergo significant changes which can be interpreted in terms of mechanisms of hydration. It is shown that electrical methods could be exploited as a convenient technique in characterising the reactivity of these materials with alkaline activators. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Alkali-activated pozzolanic materials represent a viable alternative to Portland cement based cementitious systems and a means of utilising by-products produced by industrial manufacturing processes. The cementitious qualities of the by-product, hence their use as an alternative to Portland cement based binders, depend upon a number of factors, not least,

1. the mineralogical composition of the raw materials which resulted in the production of the by-product;
2. the process by which the by-product is converted into a pozzolan (e.g. calcination temperature, fineness of grinding); and,
3. the type of alkali used to activate the pozzolan.

Characterisation of the pozzolan in terms of its early hydration behaviour with a particular activator represents one area which must be considered before such materials can be fully developed and exploited.

The early hydration and reaction kinetics of alkali-activated binders have normally been studied using isothermal conduction calorimetry [1–5]. Whilst there has been extensive research on the application of electrical methods in the study of Portland cement binders (see for example [6–18]) their application to alkali-activated pozzolans is limited. Studies have been confined to fixed-frequency conductance measurements on materials activated with calcium hydroxide [19–22]. However, the electrical response of a material contained between a pair of electrodes at a particular frequency, f, of applied electrical field can be written as

$$Y = G + j2\pi fC,$$

where G and C represent, respectively, the conductance and capacitance of the complex admittance, Y, and $j = \sqrt{-1}$. Ionic conduction effects through the interstitial water phase will be quantified in G whereas polarisation processes [23] are quantified by the capacitance, C.

The prime motivation of the current work was to develop electrical techniques as a means of studying early hydration characteristics of alkali-activated pozzolans. Of particular interest were:

(a) the change in the capacitance of the mixture during early hydration; and,

(b) the influence of frequency of applied field on both the capacitance and conductance.

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2. Materials and methods

2.1. Measurements and test cell

Samples were contained within perspex cells of internal dimensions 50 × 50 × 50 mm and considered large enough to obtain representative electrical measurements. Electrical contact was established by means of 50 × 50 × 3 mm (thick) stainless steel electrodes which were attached to opposite faces of the cell. Both conductance and capacitance measurements were taken using an impedance analyser (Hewlett Packard 4263B) operating at three spot frequencies covering two decades viz. 1, 10 and 100 kHz. Lead inductive effects were automatically nulled from the incoming data. Both the internal sample temperature and ambient laboratory temperature were monitored using a multimeter (Hewlett Packard 3457 A). A PC was used for automatic data logging of all measurements (viz. capacitance and conductance at all test frequencies; internal sample and ambient temperatures). Test measurements were taken every 10 min over a test period extending up to 48 h. All tests were carried out in a temperature controlled laboratory 20 ± 1°C. Due to sample preparation and set-up procedures, test measurements started 15 min after initial mixing.

2.2. Materials and sample preparation

Ground granulated blast-furnace slag was used in the current work with composition: 41.6% CaO, 34.3% SiO_2, 12.6% Al_2O_3, 8.3% MgO, 0.6% Fe_2O_3, 0.2% Na_2O, 0.5% K_2O. The specific surface area was 694 m^2/kg and specific gravity 2.90. Reagent grade sodium hydroxide (NaOH) and waterglass having a SiO_2/Na_2O ratio (i.e. modulus) of 2.0 were used as activators. The compositions are presented in Table 1, with the concentration in grams/litre. Ground slag was mixed with the alkaline solutions with a liquid : solid ratio of 0.4 (by mass). The mixes were compacted into test cells with the surface of the sample levelled with the top of the cell. The top surface of the sample was covered with a perspex sheet.

Table 1
Concentration of alkaline activators

Test designation	Formula	Na_2O g/l	SiO_2 g/l
0.01M NaOH	NaOH	0.31	–
0.1M NaOH	NaOH	3.1	–
1.0M NaOH	NaOH	31	–
1.5M waterglass (modulus = 2)	$Na_2O \cdot SiO_2$	93	180

3. Results and discussion

Graphs are presented in the form of conductance (*G*, in Siemens) versus time and capacitance (*C*, in Farads) versus time at the test frequencies. Although data were logged every 10 min over the test period, for clarity, data markers have been omitted from the plots. Typical results are presented to highlight the testing methodology.

3.1. Conductance versus time

Fig. 1(a)–(c) display the change in conductance for slag activated with NaOH and Fig. 1(d) with waterglass. Each figure also presents the conductance at each test frequency.

Considering the lowest concentration of NaOH (Fig. 1(a)), it is evident that the conductance response can be divided into several distinct regions. A region extending from initial mixing up to approximately 3 h (designated Stage I on Fig. 1(a)). Over this period there is a rapid increase in conductance signifying an increase in ionic concentration in the aqueous phase. This would imply a dissolution process whereby ions move into solution. There follows a region of gradual reduction in conductance (3–19 h) which would indicate a period of reduced chemical activity within the mixture (Stage II). Parallels can obviously be drawn with the dormant or induction period during the early hydration of ordinary Portland cement. Over the period 19–23 h, the conductance undergoes a rapid reduction and would imply a period of intense chemical activity (Stage III). Over this stage the mixture would be increasing in rigidity i.e. setting. From 23–30 h, the rate of change of conductivity reduces indicating a reduction in intensity of chemical activity (Stage IV). From 30 h onwards, there is a general slowing down in chemical activity with gradual infilling and accretion of hydration products (Stage V).

Increasing the NaOH concentration has the effect of reducing the dormant period (Stage II) and at the highest concentration (Fig. 1(c)) Stages I and II and the initial portion of Stage III are not evident. It is postulated that both these stages are occurring during sample set-up procedures and have thus gone undetected. It could be inferred from the conductance response that as the concentration of NaOH activator increases, the intensity of chemical activity increases.

The response from the mixture activated with waterglass (Fig. 1(d)) indicates similar regions to the NaOH activated slag although during Stage I, a decrease in conductance was detected over the initial 30 min before increasing. The end of Stage I and beginning of Stage II is estimated to occur at 2 h; Stage III begins at 5 h; Stage IV at 7 h and Stage V at 15 h.

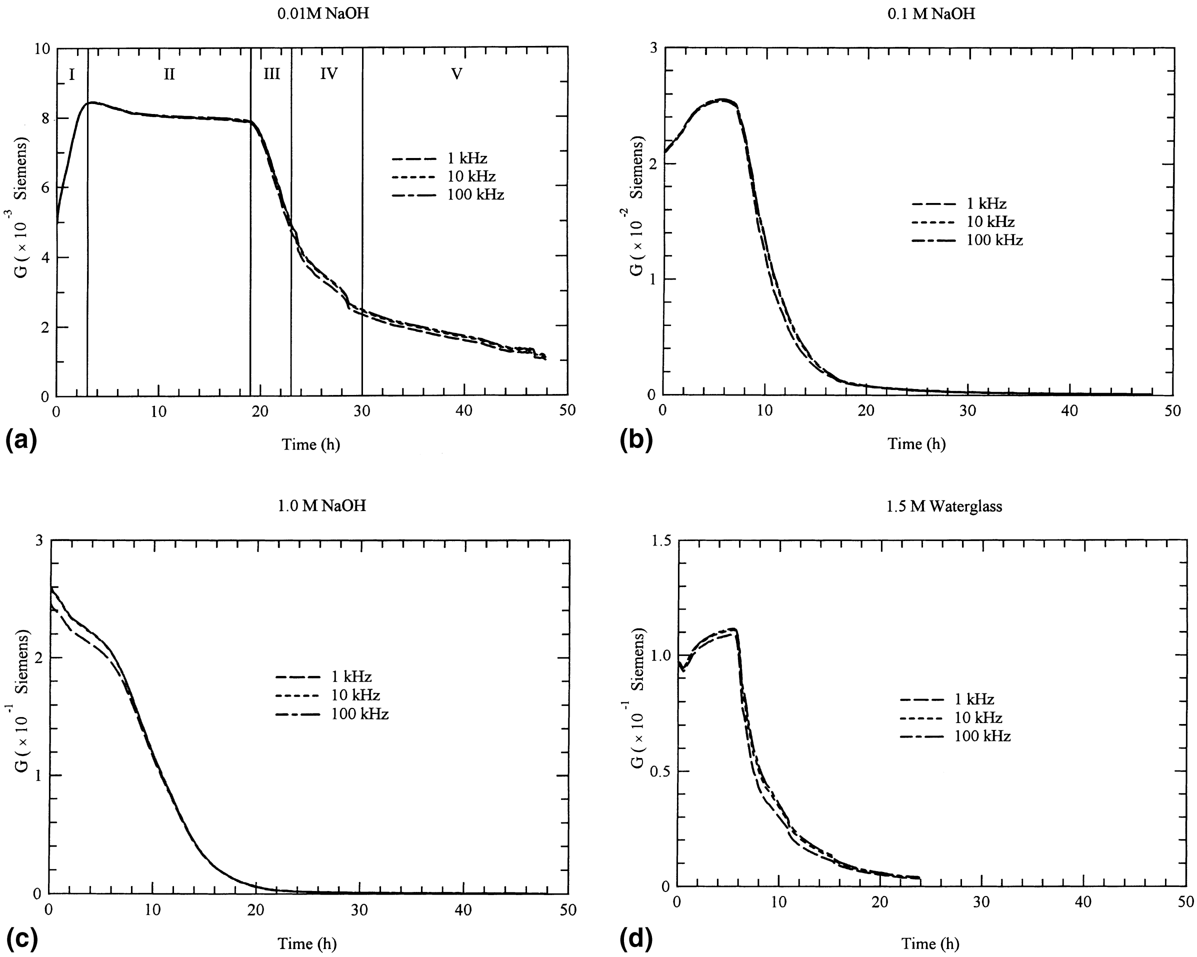

Fig. 1. Conductance versus time response at the test frequencies for slag activated with: (a) 0.01 M NaOH; (b) 0.1 M NaOH; (c) 1.0 M NaOH; (d) 1.5 M waterglass.

Over the frequency range considered, increasing the frequency of applied electrical field has little effect on the conductance response.

3.2. Capacitance versus time

Fig. 2(a)–(c) display the change in capacitance for slag activated with NaOH and Fig. 2(d) for slag activated with waterglass at each test frequency. Unlike conductance over the frequency range 1–100 kHz, the capacitance of the mixture can decrease by up to three orders of magnitude.

Consider Fig. 2(a) in the first instance. For comparative purposes, the times of Stages I–V identified from conductance measurements (Fig. 1(a)) have been transferred onto Fig. 2(a) at all test frequencies. The capacitance responses tend to mirror the conductance response over Stages I and II; however, during Stage III (i.e. the acceleratory period) significant differences occur. The sample capacitance rises rapidly over this stage with values increasing by a factor of approximately three relative to Stage II values. This feature is present at all test frequencies although its prominence is dependent upon:

(a) the frequency of applied electrical field; and,
(b) the concentration of the alkaline activator (NaOH in this case).

It is noteworthy that this increase occurs at exactly the same time as the conductance decreases. The peak in capacitance at 1 and 10 kHz also coincides with the end of Stage III identified from conductance measurements and discussed above. After peaking, the capacitance decreases rapidly (deceleratory period) as the rigidity of the mixture increases (Stage IV) which then leads into Stage V where capacitance values show a more gradual decrease.

Increasing the concentration to 0.1 M results in a more prominent capacitance peak at all frequencies. The peak in capacitance is not evident in Fig. 2(c) with 1.0 M NaOH activation. As with the conductance values, this has occurred during the set-up procedures and has thus gone undetected and only Stages IV and V are detected.

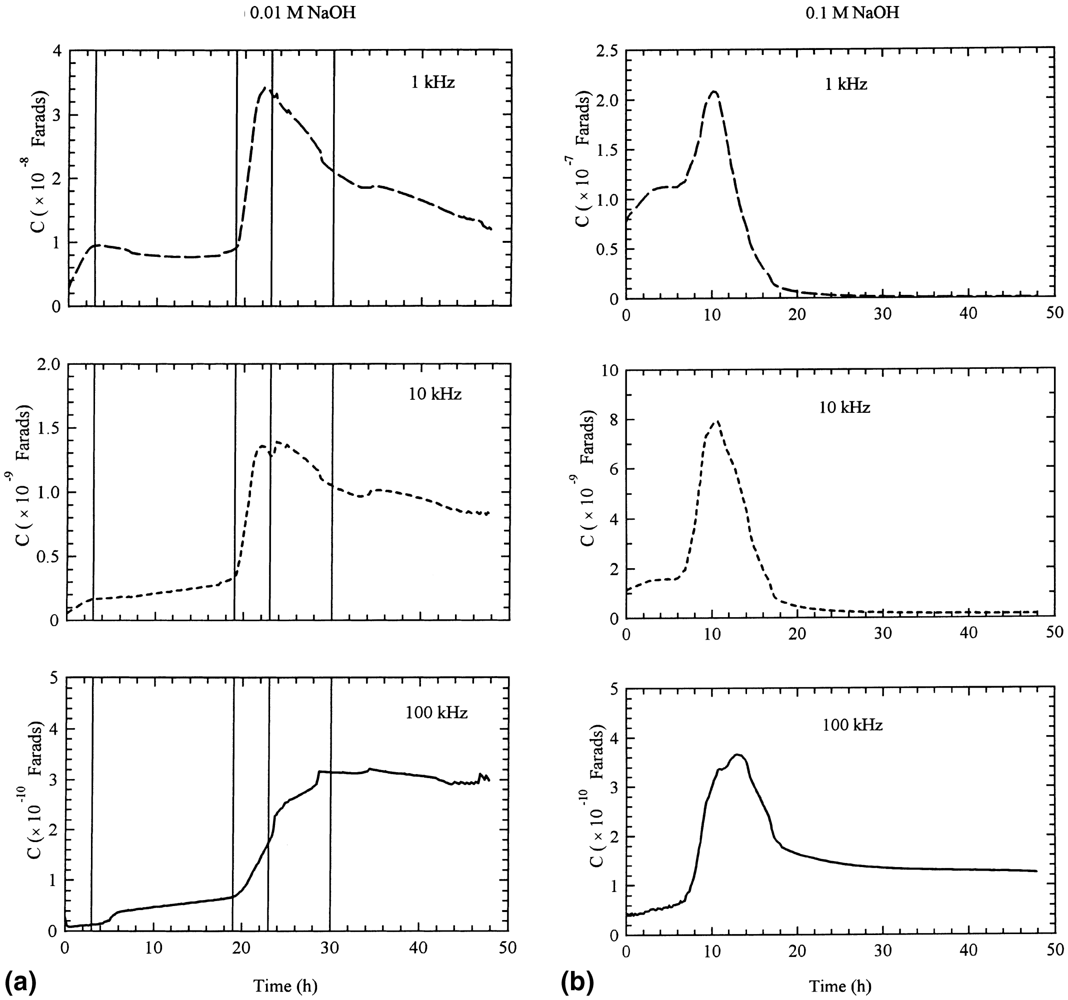

Fig. 2. Capacitance versus time response at the test frequencies for slag activated with: (a) 0.01 M NaOH; (b) 0.1 M NaOH; (c) 1.0 M NaOH; (d) 1.5 M waterglass.

Another interesting feature of Fig. 2(a) and (b) concerns the values of capacitance (at 100 kHz) occurring during Stage V. For these two concentrations of NaOH, capacitance values over Stage V are higher than values attained over Stages I and II. This would be related to the concentration of NaOH as an effective activator and has resulted in a porous mocrostructure. Work is continuing in this respect.

Waterglass activation (Fig. 2(d)) displays a similar peak in capacitance during Stage III, although over Stage I, where the conductance is seen to decrease (Fig. 1(d)) the capacitance response at 100 kHz increases rapidly over the initial 30 min. This would imply some initial chemical activity on the surface of the grains.

In order to explain the transitory peak in the capacitance over Stage III, consider the schematic diagram shown in Fig. 3 where the crystal outgrowths from the surface of the slag grain into the aqueous phase result in stiffening of the mixture. An analogy can be drawn between this crystal growth and a series of thin, highly resistive sheets with an ionic solution contained between them. Under the action of an applied alternating field, ions of opposite charge build up on either side of these sheets whose capacitance will be directly proportional to the exposed area of the sheet, A, and inversely proportional to its thickness, t, (see Fig. 3). Ions trapped in the aqueous phase between the sheets are 'unavailable' for ionic conduction processes but will produce a capacitive effect. The capacitance response would infer a rapid increase in surface area during this stage as the mixture increases in rigidity. The peak is short-lived as infilling of the pore space with hydration products result in reducing capacitance viz. t increases and A decreases.

3.3. Internal temperature versus time

Fig. 4(a)–(c) displays the change in internal temperature of the slag mixture with increasing concentration of NaOH and Fig. 4(d) for waterglass, with the samples

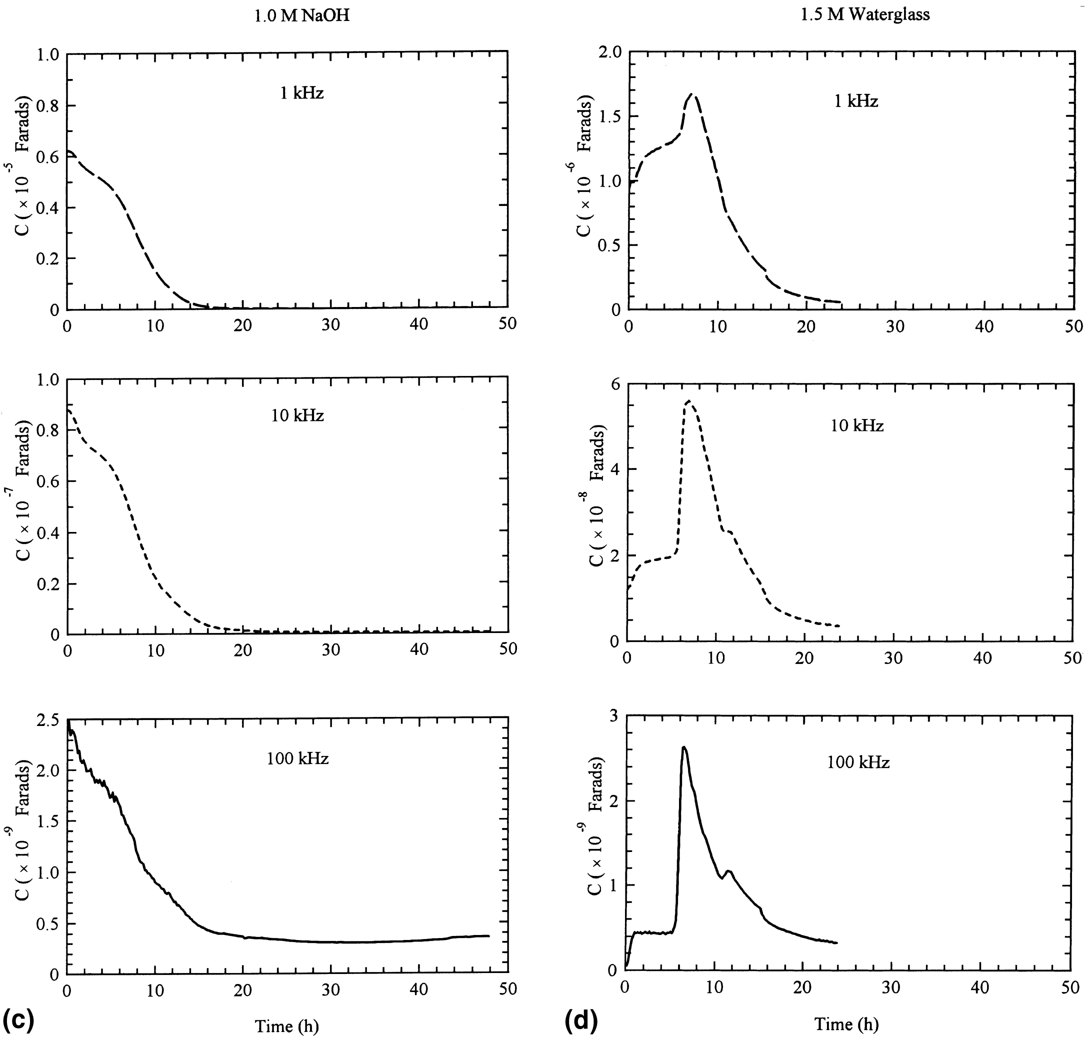

Fig. 2. (*continued*)

hydrating under natural laboratory conditions (i.e. non-isothermal). From Fig. 4(a) and (b) the internal temperature variations within the sample simply follow the natural fluctuations in laboratory temperature (i.e. 20 ± 1°C) and little can be deduced from these measurements. For the highest concentration of NaOH (Fig. 4(c)), the period 6–16 h after mixing indicates a rise above ambient and is attributed to exothermic processes within the sample. From Fig. 4(c), the internal sample temperature rises to 21.9°C at 10 h, i.e. 1°C above ambient; after 15 h, the temperature follows that of ambient. This would corroborate the interpretation of capacitance and conductance responses that setting is occurring at this time.

From Fig. 4(d), the waterglass mixture indicates an immediate rise in temperature over Stage I, identified from electrical measurements as an initial decrease in conductance/increase in capacitance (see Fig. 1(d) and 2(d)). The internal temperature then decreases back to ambient and it is interesting to note that there is no detectable temperature rise above ambient where conductance values (Fig. 1(d)) are seen to drop rapidly and the capacitance peaks (Fig. 2(d)).

4. Concluding remarks

The overall aim of the work was to highlight the information which can be obtained from electrical testing of alkali-activated systems during early hydration, where the electrical response is quantified by the conductance and capacitance. In the current work, the testing methodology was used on a slag activated with NaOH and waterglass setting and hardening under non-isothermal conditions and new data have also been presented in this respect.

From the capacitance and conductance response, a number of distinct regions can be identified over the test

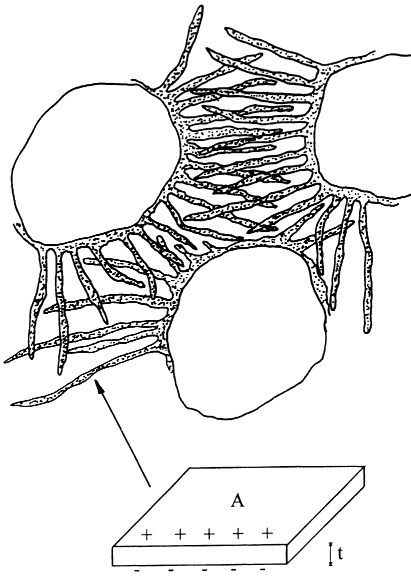

Fig. 3. Schematic diagram to show possible explanation of increase in capacitance during Stage III.

period. These regions can be considered as indicative of the stages of hydration; rate chemical activity and change in rigidity of the mixture. The capacitance response was shown to be frequency dependent whereas, conductance varied little over the frequency range under consideration. An important and unique feature of the capacitance response concerned the occurrence of a transitory peak at the time of setting. A physical interpretation of this feature was proposed.

The method has considerable scope for use as an additional (and complementary) tool to study the hydration of such materials; assessing new materials and assessing activator/pozzolan combinations.

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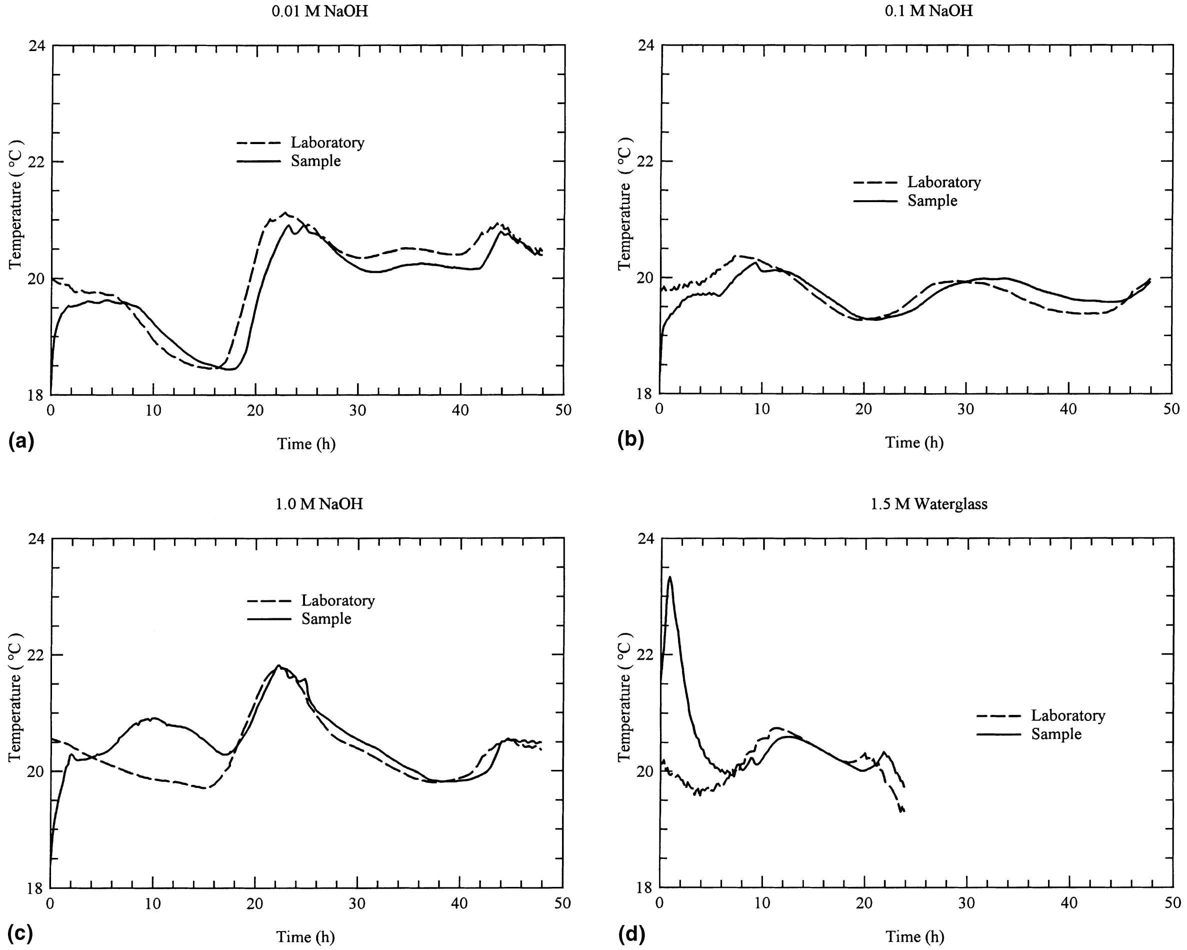

Fig. 4. Internal sample temperature and laboratory temperature during test for: (a) 0.01 M NaOH; (b) 0.1 M NaOH; (c) 1.0 M NaOH; (d) 1.5 M waterglass.

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