Thermal and chemical activation of fly-ash: Electrical response during early hydration

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Pozzolanic materials represent a replacement for ordinary Portland cement (OPC) and a means of utilizing by-products produced by certain industrial manufacturing processes. One of the most widely available pozzolanic materials is pulverized fuel ash or fly-ash, which is a by-product from the generation of electricity from coal-fired power stations (usually anthracitic/bituminous coals). The fly-ash reacts in the alkaline conditions created by the Portland cement to form calcium silicate hydrates which, in the longer term, enhance both the strength and durability of the concrete. The use of materials such as fly-ash, as a partial replacement for OPC in concrete, is now assuming an important role in the drive for more sustainable construction materials and practices. Moreover, there is scope for direct activation of fly-ash with a suitable activator, or combination of activators, to produce non-OPC cementitious systems which may be of lower strength but could find numerous applications in, for example, masonry mortars, grouts or non-clay bricks. Such applications would considerably increase the utilisation of fly-ash and reduce the accumulating stockpiles of this material.

Electrical property measurements have widely been used to study the early hydration of the Portland cement and in the study of admixtures on hydration [1–7]. In this wor , the electrical response of chemically and thermally activated fly-ash is presented to highlight how this testing methodology could be extended to study phase transition (i.e., liquid to solid) and reaction kinetics of this group of materials from initial gauging through setting and hardening and as a technique in the assessment of a particular activator or combination of activators.

In the experimental program, samples were contained within sealed plexiglas cells of internal dimensions of 50 mm × 50 mm × 50 mm. Electrical contact was established by means of 50 mm × 50 mm × 3 mm (thick) stainless steel electrodes which were attached to opposite sides of the cell. Conductance measurements were taken using a Hewlett Packard 4263B LCR meter operating at a frequency of 100 kHz; lead inductive effects were nulled from the incoming data. Conductance measurements were taken every 10 min over the test period which, in some tests, extended up to 6 days. Tests were carried out in a temperature controlled cabinet at ambient temperatures of 20 °C; 37 °C and 54 °C (± 1 °C).

A low lime ash (ASTM Type F) was used throughout with oxide analysis: 50.5% SiO_2; 24.7% Al_2O_3; 7.4% Fe_2O_3; 2.6% CaO; 1.5% MgO; 3.0% K_2O; 0.8% Na_2O; 0.8% SO_3, and 5.3% loss on ignition. The fineness of the ash, when measured in terms of percentage mass retained on the 45 μm sieve, was 9.5%. The following standard mix formulation was used: samples were prepared by dry blending the fly-ash with reagent-grade calcium hydroxide in the ratio 4:1 (by mass) and then mixing with:

(1) distilled water—the resulting mixture denoted F/C;
(2) distilled water in which sodium sulphate (Na_2SO_4) was dissolved at a dosage of 14.2 g /100 g water (1 mol/l)–the resulting mixture denoted F/C/NS; and
(3) distilled water in which sodium hydroxide (NaOH) was dissolved at a dosage of 4 g /100 g water (1 mol/l)–the resulting mixture denoted F/C/NH .

The liquid/solid ratio was held constant at 0.4; the cell constant was 16.84/m, which enabled the measured conductance to be converted to conductivity, in Siemens per meter (S/m).

Fig 1a displays the change in conductivity for the mixtures when mixed with 1, 2 and 3 mentioned above, at an ambient temperature of 20°C. For comparative purposes, the response from an ordinary Portland cement (ASTM Type I) paste, mixed with distilled water at a water°cement ratio of 0.4, is also presented in Fig. 1 (denoted OPC). Fig. 1a presents the ratio σ_t/σ_o, where σ_t is the conductivity at time *t* after the start of the tests and σ_0 is the value of conductivity at the start of the test; σ_0 is presented in the figure legend. (For clarity not all data markers are presented on these curves.) As the Portland cement paste sets and increases in rigidity, the conduction pathways through the interstitial aqueous phase become more tortuous which will result in a decrease in conductivity. This is clearly evident in Fig.1a over the period 2–10 hr and corroborates previous studies [see, for example, 1–7].

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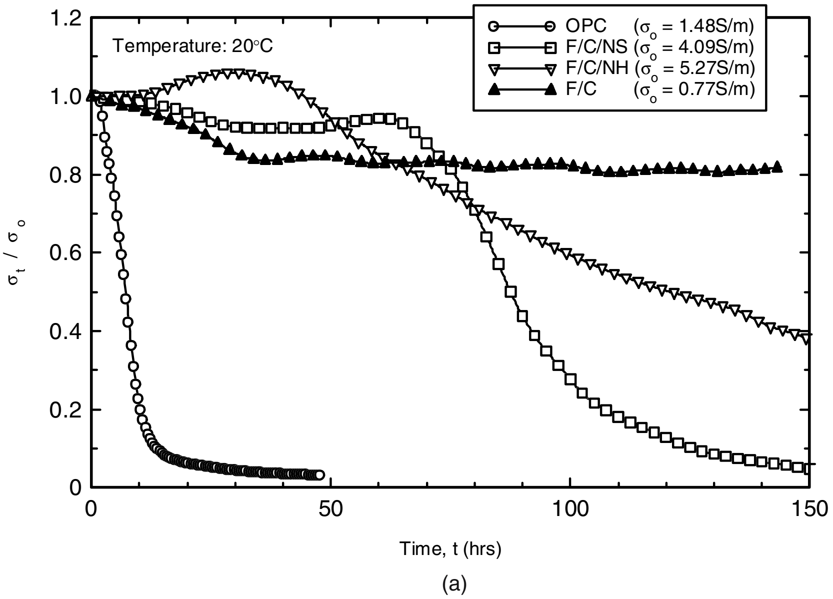
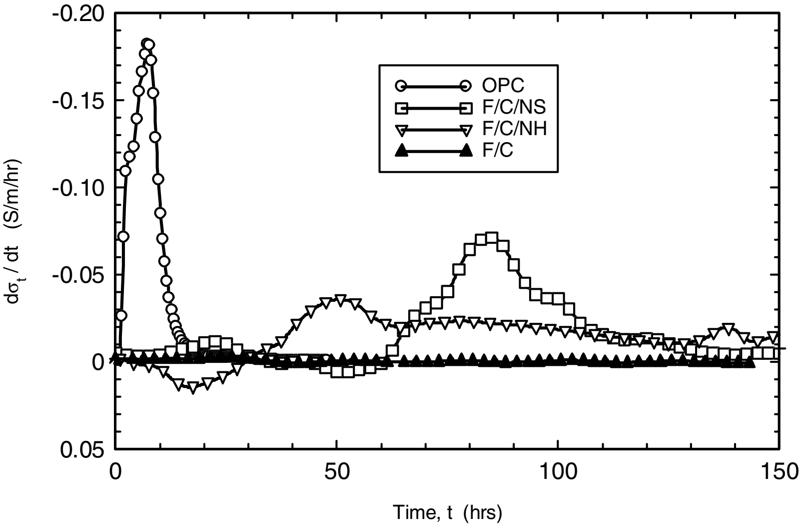


(a)



(b)

Figure 1 (a) Variation in conductivity for fly-ash mixtures and ordinary Portland cement (OPC) at room temperature; and (b) derivative of the conductivity versus time curves presented in (a).

Consider, now, the F/C/NS mixture in Fig. 1a The response displays an initial dormant region of relatively constant conductivity followed by a region of more rapid decrease over the period 65–100 hr. This signifies an increase in rigidity of the mixture; the intensity of the decrease is, however, considerably less than that of the OPC mixture. The F/C/NH mixture displays a decrease in conductivity at approximately 48/ hr, although the slope —$d(\sigma_t/\sigma_0)dt$ is considerably less than that of the F/C/NS mixture. Regarding the latter, this would indicate a sluggish reaction at this temperature, despite the fact that a highly alkaline environment is conducive to the pozzolanic reaction. The conductivity response from the F/C mixture would indicate little chemical activity within the mixture, hence increase in rigidity, over the 6 day test period.

Since the decrease in conductivity is indicative of the increase in rigidity of the mixture, hence microstructural development, the derivative of conductivity versus time curve must quantify the intensity of chemical activity within the mixtures. Fig. 1b presents the derivative of the conductivity curves in Fig. 1a which, as anticipated, maximizes over the period when the paste is setting.

Figs 2 and 3 present the response from the flyash mixtures placed at ambient air temperatures of 37°C and 54°C (note change in scale for time axis). It is evident that all three systems now display a region characterised by a more marked decrease in conductivity in comparison to their counterparts held at 20°C. The response implies that the intensity of chemical activity has been enhanced at the elevated temperatures. Particularly noticeable is the

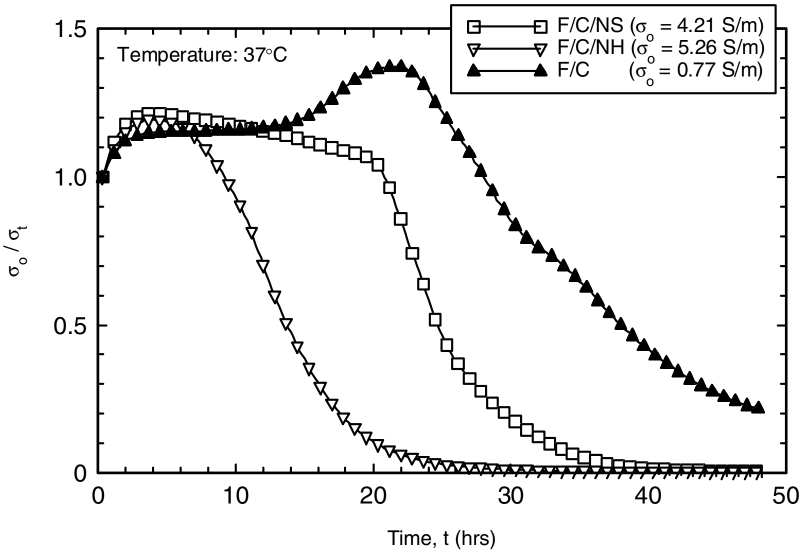


Figure 2 Conductivity versus time response for fly-ash mixtures at 37°C.

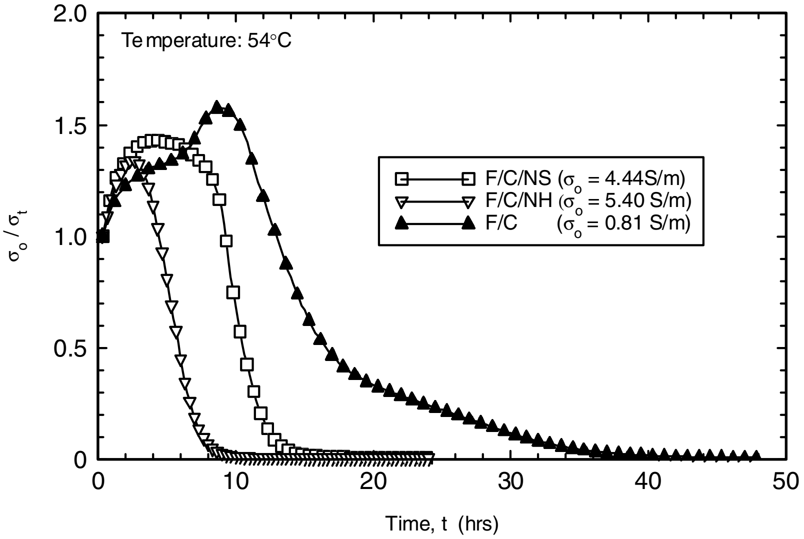


Figure 3 Conductivity versus time response for fly-ash mixtures at 54°C.

response for the F/C mixture which now displays a definite decrease in conductivity and is indicative of an increase in rigidity of the paste over the test period. It is also evident that the fly-ash mixed with sodium hydroxide, which has a slow reaction at room temperature, now displays more intense chemical reaction at elevated temperatures. Increasing the ambient temperature results in a decrease in the setting time of the mixtures and an increase in the intensity of chemical reaction over the period of setting.

In summary, new data on the electrical properties of chemically and thermally activated fly-ash systems have been presented. The work has shown that electrical property measurements have considerable scope for development as a technique to study of the setting, hardening and early hydration kinetics of this group of cementitious materials. As a consequence, it will, ultimately, allow a rapid assessment of the efficacy of a particular chemical activator or combination of activators at room temperature and elevated temperatures.

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