JOURNAL OF MATERIALS SCIENCE 31 (1996) 5299–5303

# The electrical conductance and hydration kinetics of artificial pozzolana–cement pastes

TH. M. SALEM
*Chemistry Department, University College for Girls, Ain Shams University, Cairo, Egypt*

Artificial pozzolana were made by firing of two types of clays at two temperatures (600 and 700 °C). Different artificial pozzolana–Portland cement pastes were made using a water/cement ratio of 0.40 by weight of the cement blend. Each cement paste was examined for hydration kinetics at 20 °C as well as electrical conductance at 20 and 35 °C. The results of hydration kinetics indicated a sort of phase transformation of hydration products at the intermediate stages of hydration. Electrical conductance studies demonstrated two maxima at 20 °C; only one maximum at 35 °C was detected at the early stages of hydration. All results could be related to the sequence of the initial hydration reaction and the mode of disruption of the electrically insulating coating layers around the grains of the cement constituents.

## 1. Introduction

Several studies were performed on the various characteristics of pozzolanic cements. Rozhkova [1] found that the hydration of Portland cement–gypsum–pozzolana systems in suspension was quite slow. Mehta [2] measured the porosity of blended cements in sulphate solutions and related the differences in pore-size distribution of the paste to the resistance to aggressive solutions, rather than chemical composition. The behaviour is controlled by the degree of the pozzolanic reactions before the sulphate exposure. Bensted [3] briefly discussed chemical considerations of sulphate attack and considered the effect of slag, pozzolana, and high alumina cements. Studies on the sulphate resistance of Portland–pozzolana cements containing up to 50% burnt common clay or China clay, have been conducted [4]. In addition, the properties of Portland pozzolanic cement containing up to 30% Homra (calcinic Nile silt), 1% or 2% lime, and 1% gypsum, were investigated by Taha and El-Didamony [5]. Samanta [6] investigated the hydration characteristics of Portland–pozzolanic cements prepared by partial substitution of calcined clay and China clay in Portland cement. Sulphated Portland–pozzolana cement compositions were made by incorporating gypsum, and these showed a higher degree of hydration at a given moist curing time than the non-sulphated cements.

The electrical conductance of cement pastes was studied by Calleja [7], where two conductivity maxima were observed. The setting behaviour of cement pastes was explained on the basis of electrical conductivity by Szuk [8]. The relations between electrical conductivity and the physical properties of cement pastes was also reported in the literature [9]. The electrical conductivity of the pastes made from cement and clinker materials were also investigated during setting and hardening [10].

Recent studies [11–14] dealing with the electrical properties of cement pastes during the first 24 h hydration indicated that the rate of strength development was greatest when the electrical properties were also undergoing significant changes. The effects of various curing media, e.g. chloride solution, sea-water and sulphate solution, on the electrical conductance of hardened cement pastes (Portland, slag and blended cement) were studied by Abd-El-Wahed and Hekal [15]. The locations and intensities of the conductivity maxima were affected by the nature and amount of the aggressive ions in the curing media.

The objective of the present work was to study the dependence of the variations in the electrical conductance associated with the hydration reaction of some artificial pozzolana cement pastes on the rate of the hydration–hardening process.

## 2. Experimental procedure

The materials used in this study were ordinary Portland cement, mixed type of shale/clay deposit, and montmorillonite clay. The chemical oxide composition of these materials is given in Table I.

Each type of clay was first dried at 110 °C for 48 h, then crushed and passed completely through a 1 mm British Standards (B.S.) sieve. The crushed clays were burnt at 600 and 700 °C for a soaking period of 4 h and then quenched in air. The artificial pozzolanas (burnt clays), thus produced, are then ground in a ball mill and passed completely through a 75 μm B.S. sieve.

Eight Portland cement–artificial pozzolana solid mixtures were prepared as follows.

Mix Ia 50% clay burnt at 600 °C + 50% Portland cement.

TABLE I Oxide composition of Portland cement, mixed type and montmorillonite clays

| Oxide | Portland cement | Mixed type clay | Montmorillonite clay |
|---|---|---|---|
| $SiO_2$ (%) | 21.75 | 47.49 | 48.63 |
| $Al_2O_3$ (%) | 6.86 | 19.96 | 28.24 |
| $Fe_2O_3$ (%) | 1.78 | 9.26 | 7.35 |
| $TiO_2$ (%) | – | 1.04 | 0.24 |
| CaO (%) | 63.80 | 1.91 | 2.78 |
| MgO (%) | 2.74 | 2.12 | 1.98 |
| $Na_2O$ (%) | – | 3.06 | 1.03 |
| $K_2O$ (%) | – | 1.21 | 0.26 |
| $SO_3$ (%) | 1.46 | 1.07 | 0.36 |
| Ign. loss (%) | 1.80 | 12.70 | 9.17 |

Mix Ib 50% mixed clay burnt at 700 °C + 50% Portland cement.
Mix IIa 50% montmorillonite clay burnt at 600 °C + 50% Portland cement.
Mix IIb 50% montmorillonite clay burnt at 700 °C + 50% Portland cement.
Mix IIIa 30% mixed clay burnt at 600 °C + 70% Portland cement.
Mix IIIb 30% mixed clay burnt at 700 °C + 70% Portland cement.
Mix IVa 30% montmorillonite clay burnt at 600 °C + 70% Portland cement.
Mix IVb 30% montmorillonite clay burnt at 700 °C + 70% Portland cement.

For conductivity measurements, the Portland cement–artificial pozzolana pastes were made by mixing each solid mixture with distilled water at 20 °C using an initial water/solid ratio of 0.40; mixing was done for 3 min continuously. Each fresh paste was then transferred into a cylindrical plastic sample holder (16 mm internal diameter) with stainless steel electrodes at both sides with 12 mm distance between them. The electrical conductance of each paste was measured at various time intervals, ranging from 3.5 min up to 3 days at 20 and 35 °C.

For hydration kinetics, the Portland cement–artificial pozzolana pastes were made using a water/solid of 0.40 by weight. The specimens were moulded into 1 in (2.5 cm) cubes and cured in a moist atmosphere at 100% relative humidity for various hydration periods of 1, 3, 7, 14, 28, 90 and 180 days. After each time interval, the hydration of the hardened cement paste was stopped [16], and then the samples were dried and kept in a desiccator. The combined water content, $W_n$(%), was determined as the ignition loss of the dried specimen.

## 3. Results and discussion
### 3.1. Hydration kinetics
Hydration kinetics of the various artificial pozzolana–Portland cement pastes were studied mainly by determining of the chemically combined (non-evaporable) water contents, $W_n$ (%), at various ages of hydration. The results of non-evaporable water contents $W_n$ (%) are shown in Fig. 1 as a function of age of hydration for hardened pastes made from Portland cement and mixed-type clay burnt at 600 and 700 °C, respectively. For all of the hardened Portland cement–burnt mixed clay pastes, a continuous increase appeared in the combined water content with increasing age of hydration up to the final stages of the hydration process (180 days). During the early stage of hydration, the hydraulic reactivity of the artificial pozzolanas made from burnt mixed clay depends primarily on the burning temperature. It was found that the hydraulic reactivity of mixed-type clay burnt at 600 °C is higher than that at 700 °C. Therefore, higher values of combined water contents were obtained upon hydration of all Portland cement–artificial pozzolana mixtures made from mixed-type clay at 600 °C.

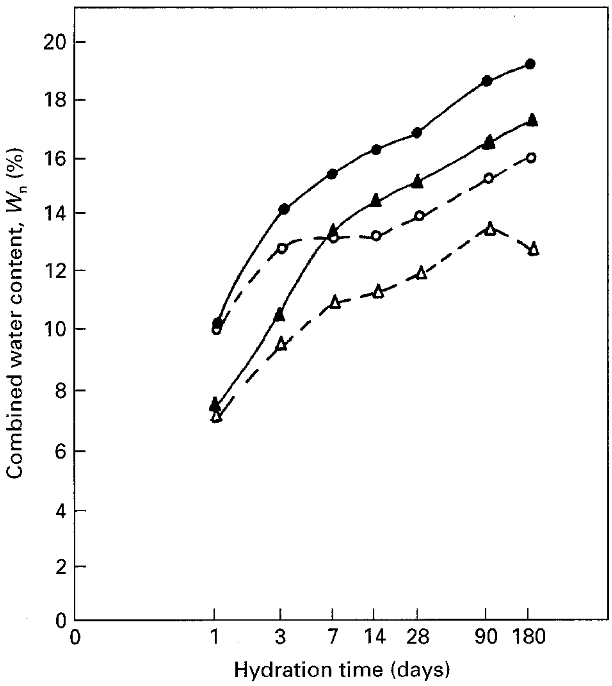


*Figure 1* The chemical combined water content, $W_n$, as a function of age of hydration for hardened pastes made from Portland cement and mixed-type clay burnt at 600 and 700 °C, respectively. (○) Ia, (△) IIa, (●) IIIa, (▲) IVa.

Obviously, a rapid hydraulic interaction between Portland cement and artificial pozzolanas takes place after 1 day hydration at room temperature leading to noticeable amounts of combined water contents for all pastes investigated. Later, the $W_n$ contents increase gradually with age of hydration up to the final stages of hydration.

In general, the pozzolanic activity of the artificial pozzolanas was found to decrease with increasing of burning temperature of the mixed-type clay. However, the chemical composition, as well as the physical state of the hydration products, obtained during hydration of these Portland cement–artificial pozzolana pastes, were found to vary with age of hydration and with the burning temperature of the clay. Moreover, the hydraulic reactivity of the artificial pozzolana increases with increasing proportion of Portland cement in the solid mixture, regardless of the burning temperature of the clay.

Fig. 2 shows the results of chemically combined (non-evaporable) water contents, $W_n$ (%), as a

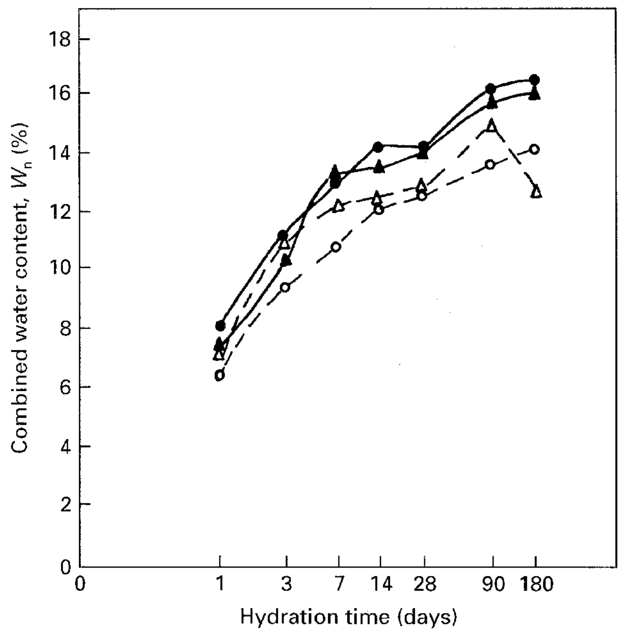


*Figure 2* The chemical combined water content, $W_n$, as a function of age of hydration for hardened pastes made from Portland cement and montmorillonite clay burnt at 600 and 700 °C, respectively. (○) Ib, (△) IIb, (●) IIIb, (▲) IVb.

function of age of hydration for the various Portland cement–burnt montmorillonite pastes containing montmorillonite burnt at 600 and 700 °C, respectively. During the early stages of hydration, the combined water content increases with increasing proportion of Portland cement. Therefore, the main hydration products formed during the early hydration of these Portland cement–burnt montmorillonite mixture are those of Portland cement and not of the artificial pozzolana.

The $W_n$ contents exhibited a continuous increase with increasing age of hydration. In some cases, however, the $W_n$ values showed a decrease with increasing hydration at the final stages of hydration. This is mainly attributed to the transformation of the initially formed hydrates, having a high water content, into other hydrates having a lower water content.

## 3.2. Electrical conductivity

The conductivity–hydration time curves obtained for the pastes made from equal proportions of Portland cement and the artificial pozzolanas, prepared by firing of mixed-type and montmorillonite type clays at 600 and 700 °C, are shown in Figs 3 and 4 at the hydration temperatures of 20 and 35 °C, respectively.

The conductance–time curves shown in Fig. 3 indicate two conductivity maxima associated with two main hydration stages. The initial hydrolysis of the Portland cement constituents might be responsible for the first conductivity maximum after the first few minutes of hydration of the pozzolana–cement pastes at 20 °C; the charge carriers are mainly $Ca^{2+}$, $OH^-$, $SO_4^{2-}$ and alkali ions. Then, the slight decrease in conductivity values is mainly attributed to the formation of electrically insulating layers around the grains of the pozzolana cement. Later, the second conductivity maximum is primarily due mainly to the disruption

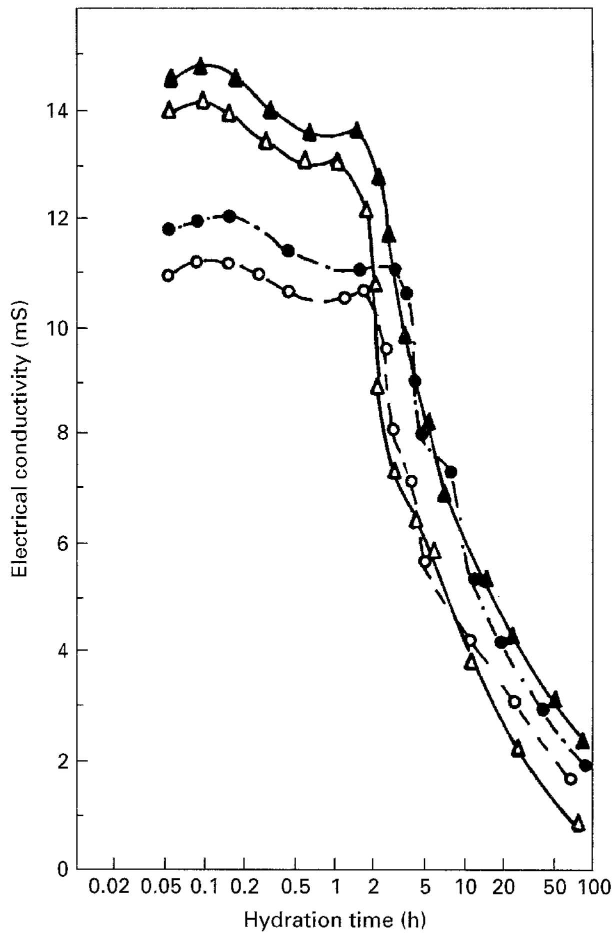


*Figure 3* Electrical conductivity–time curves obtained for pozzolana–cement mixes. (○) Ia, (△) IIa, (●) Ib, and (▲) IIb made from Portland cement (50%) and burnt clay (50%) at 20 °C.

of the initially formed insulating coatings around the cement grains and/or the transformation of ettringite ($C_3A \cdot 3\ CaSO_4 \cdot 32\ H_2O$) to the monosulphate hydrate ($C_3A \cdot CaSO_4 \cdot 18H_2O$) [17]. At the later ages of hydration, a sharp decrease in the conductivity values was observed due to the rapid consumption of the number of ions as a result of the formation of cement hydration products. Evidently the results of Fig. 3 indicated also that the artificial pozzolana made from burnt montmorillonite is more hydraulically active than the pozzolana made from burnt mixed-type clay; therefore, the two conductivity maxima of the hydrated burnt montmorillonite–cement blends (Mixes IIa and IIb) are shifted to shorter hydration times compared with those of the burnt mixed clay–cement blends (Mixes Ia and Ib). At higher burning temperatures of the clay (700 °C), the hydraulic reactivity of the artificial pozzolana produced increases leading to higher conductivity values, especially at the early stages of hydration; therefore, the conductivity values of the pozzolana cement mixes Ib and IIb are higher than those of mixes Ia and IIa.

The conductance–time curves obtained for the same artificial pozzolana–cement mixes at 35 °C are shown in Fig. 4. The results of Fig. 4 indicate only one conductivity maximum at the first 6–8 min hydration reflecting a reasonable increase in the rate of hydration at 35 °C as compared with the rate at 20 °C. Moreover, an inflection in the conductance–time

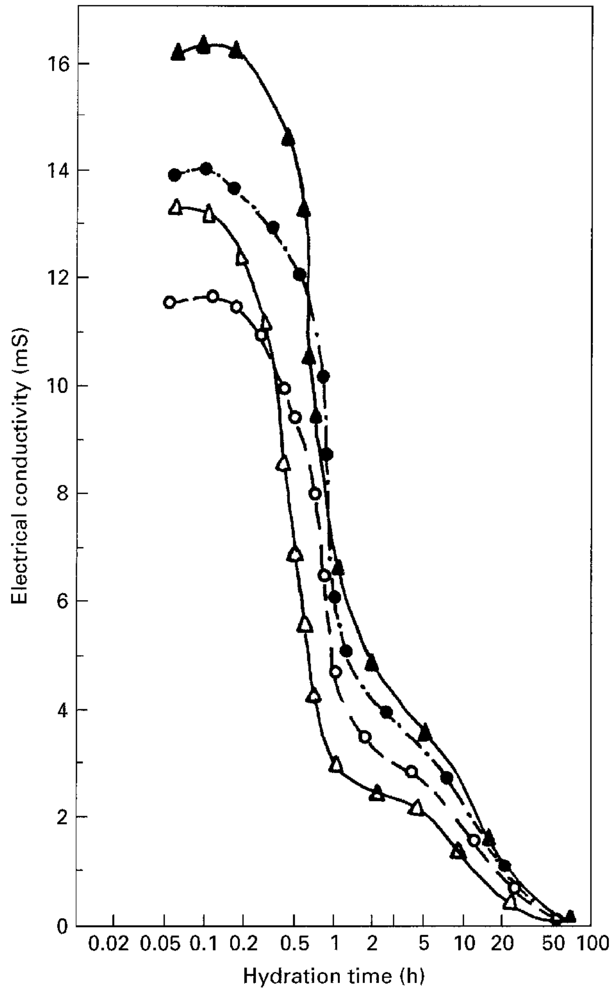


*Figure 4* Electrical conductivity–time curves obtained for pozzolana–cement mixes. (○) Ia, (△) IIa, (●) Ib, and (▲) IIb made from Portland cement (50%) and burnt clay (50%) at 35 °C.

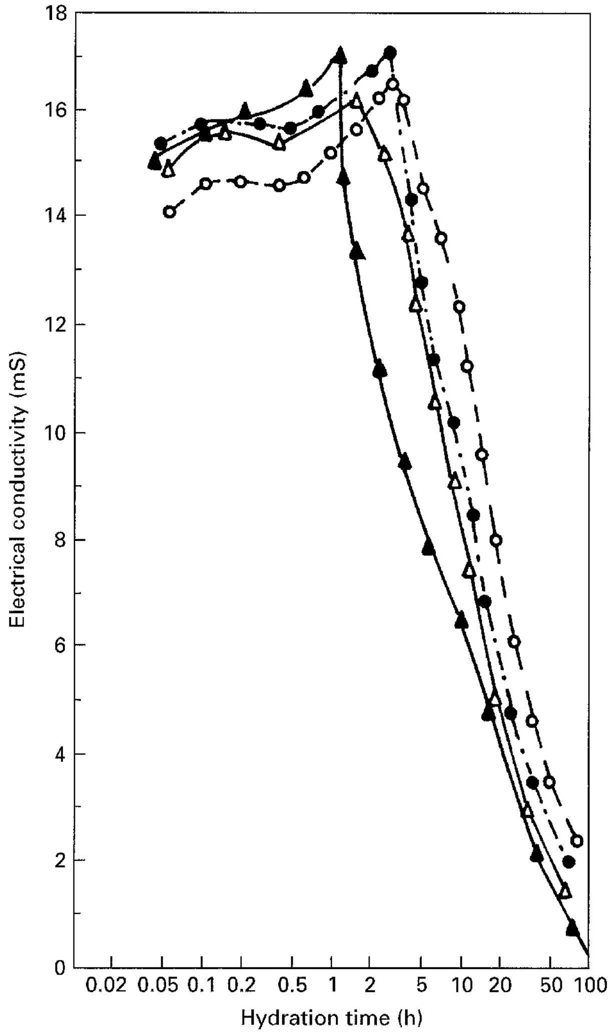


*Figure 5* Electrical conductivity–time curves obtained for pozzolana–cement mixes. (○) IIIa, (△) IVa, (●) IIIb, and (▲) IVb made from Portland cement (70%) and burnt clay (30%) at 20 °C.

curves was observed at the later stages of hydration located approximately at the time of hydration corresponding to the second conductivity maximum at 20 °C which is mainly due to a compensation effect between the increase in the number of ions as a result of the ettringite–monosulphate transformation and the decrease in the number of ions as a result of the formation of hydration products. Obviously, the first conductivity peak appeared in the conductogram earlier and became sharper, reflecting an increased rate of hydration at 35 °C.

Figs 5 and 6 represent the conductance–time curves, obtained for pozzolana–cement mixes IIIa, IIIb, IVa and IVb made from Portland cement (70%) and burnt clay (30%), at 20 and 35 °C, respectively.

The results of Fig. 5 demonstrate the existence of two conductivity maxima in the conductograms obtained at 20 °C. These maxima are located at higher conductance values indicating a relatively higher rate of hydration by increasing the proportion of Portland cement in the pozzolana–cement mixtures III and IV. Obviously, burnt montmorillonite–cement mixes IVa and IVb are more hydraulically reactive than burnt mixed clay–cement blends mixes IIIa and IIIb. This result is clearly distinguished from the higher intensities of the conductivity maxima of the paste made from mixes IVa and IVb (containing burnt montmorillonite) as compared with those of mixes IIIa and IIIb (containing burnt mixed clay); a sharper decrease appeared in the conductivity values at shorter hydration times for the cement blends containing burnt montmorillonite, indicating the rapid formation and later accumulation of larger amounts of hydration products during the hydration of Mixes IVa and IVb as compared with those formed for the pozzolana cement pastes containing burnt mixed clay (mixes IIIa and IIIb). Again, the hydration reactivities of the pozzolana cements increase with increasing burning temperature. Therefore, the pastes made from mixes IIIb and IVb (burning temperature 700 °C) possess higher conductivity maxima in the early stages of hydration, compared with those of mixes IIIa and IVa (burning temperature 600 °C); a sharper decrease appeared in the conductance after the second maximum for the pozzolana cements containing burnt clay at 700 °C relative to those containing burnt clays at 600 °C.

Hydration of pozzolana–cement blends IIIa, IIIb, IVa and IVb at 35 °C results in a noticeable increase in the rate of hydration, a result which is associated with the following: (i) the appearance of only one maximum in the conductance–time curves for each of these mixes, (ii) a sharper decrease in the conductivity values

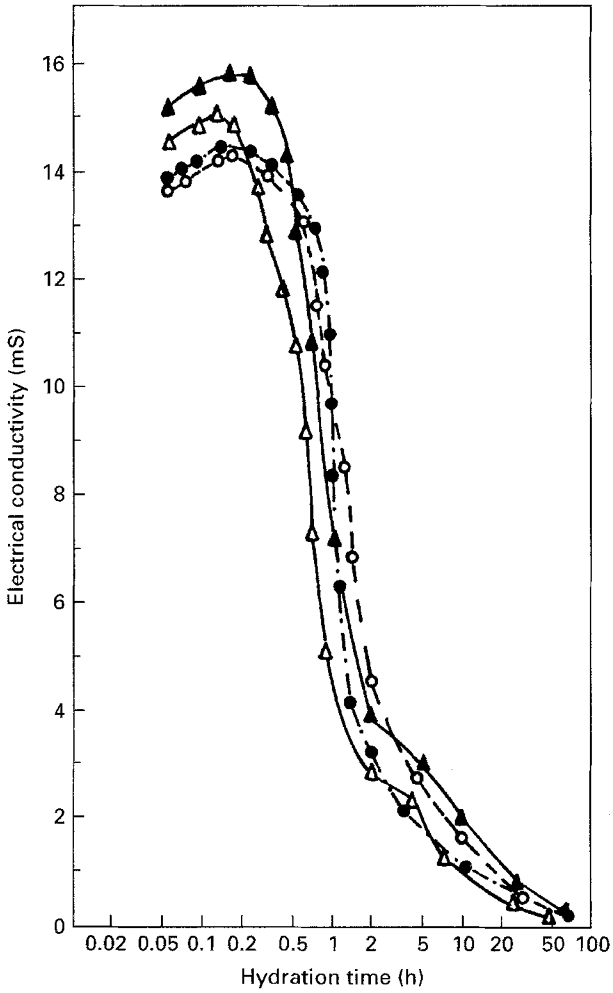


*Figure 6* Electrical conductivity–time curves obtained for pozzolana–cement mixes. (○) IIIa, (△) IVa, (●) IIIb, and (▲) IVb made from Portland cement (70%) and burnt clay (30%) at 35 °C.

after the maximum of each curve, and (iii) an inflection at the intermediate stages of hydration followed by a decrease in the conductance with time of hydration. Again, the increase in burning temperature of the clay samples from 600 °C to 700 °C is accompanied by an increase in the conductance values, indicating an increase in the hydraulic reactivity of the artificial pozzolana produced.

## 4. Conclusions

1. The combined water contents reveal that the pozzolanic activity of the artificial pozzolanas made from mixed-type clay decreases with increasing burning temperature, whereas it increases with increasing proportion of Portland cement in the solid mixture. During the early stages of hydration for the various Portland cement–burnt montmorillonite (at 600 and 700 °C) pastes, the combined water increases with increasing proportion of Portland cement.

2. The electrical conductance at 20 °C for the pastes made from equal proportions of Portland cement and burnt artificial pozzolana indicates two conductivity maxima associated with two main hydration stages. The results reveal also that the artificial pozzolanas made from burnt montmorillonite are more hydraulically active than the burnt mixed-type clay.

3. The electrical conductance at 35 °C for the same previous specimens shows one conductivity maximum reflecting a reasonable increase in the rate of hydration at 35 °C.

4. With increasing proportion of Portland cement in the pozzolana cement mixtures III and IV, the two conductivity maxima at 20 °C are located at higher conductance values, indicating higher rate of hydration. Again, only one conductivity maximum is observed at 35 °C for the same specimens.

## References

1. K. N. ROZHKOVA, *Stroit. Mater.* **7** (1981) 22.
2. P. K. MEHTA, *Cem. Concr. Res.* **11** (1981) 507.
3. J. BENSTED, *World Cem. Technol.* **12**(5) (1981) 178.
4. C. SAMANTA and M. K. CHATTERJEE, *Indian Ceram.* **22** (1980) 257.
5. A. S. TAHA and H-EL-DIDAMONY, *Ton ind-ztg.* **106**(1) (1982) 64.
6. C. SAMANTA, *Trans. Indian Ceram. Soc.* Hydration of Portland-pozzolanic cements, **41**(1) (1982) 7.
7. J. CALLEJA, *ACI J.* **49** (1952) 329.
8. G. SZUK, *Acta Techn. Acad. Sci. Hung.* **29** (1960) 429.
9. M. A. TAYLOR and K. ARULANANDAN, *Cem. Concr. Res.* **4** (1974) 881.
10. F. D. TAMAS, *ibid.* **12** (1982) 115.
11. W. J. McCARTER and A. B. AFSHAR, *J. Mater. Sci. Lett.* **3** (1985) 1083.
12. *Idem, Proc. Inst. Civ. Eng. (Lond.)* **79** (1985) 585.
13. *Idem, J. Mater. Sci. Lett.* **4** (1985) 405.
14. *Idem, Cem. Concr. Aggr.* **7** (1985) 57.
15. M. G. ABD-EL-WAHED and E. E. HEKAL, *J. Mater. Sci.* **8** (1989) 875.
16. H. EL-DIDAMONY, M. Y. HAGGAG and S. A. ABO-EL-ENEIN; *Cem. Concr. Res.* **8** (1978) 351.
17. S. A. ABO-EL-ENEIN, TH. M. SALEM, S. HANAFI, S. M. ABD-EL-WAHAB and S. L. MARUSIN, in "Proceedings of the 7th International Conference on Cement Microscopy", Texas, USA, March (1985) 277–87.

*Received 17 December 1993*
*and accepted 1 December 1995*