Fig. 5---Effect of the duration of the air drying on the water absorption of the surface of the concrete slabs



Fig. 6-Effect of vertical versus horizontal casting on the total amount of scaling residue



Mixture Number, W/(C+FA), Percentage of Fly Ash





Mixture Number, W/(C+FA), Percentage of Fly Ash

Fig. 8-Effect of the curing compounds on the total amount of scaling residue



Mixture Number, W/(C+FA), Percentage of Fly Ash

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Fig. 9— Effects of the curing compounds on the water absorption of the surface of the concrete slabs



# <u>SP 178-21</u>

# The Microstructure and Chloride Ion Diffusion Characteristics of Cements Containing Metakaolin and Fly Ash

by J.G. Cabrera and S.O. Nwaubani

<u>Synopsis</u>: Structural failures in concrete buildings are not common. Most of them are a result of poor concrete performance. The durability of concrete is related mainly to the performance properties of the hydrated cement paste and to the environmental conditions.

Absorption, permeability and diffusion are the main transport mechanisms by which deleterious substances like chlorides, sulphates and acids penetrate into concrete and cause damage. The strength of concrete is a good indicator of its structural adequacy but not of its durability, therefore designing concrete for durability requires the evaluation of its performance related properties.

This study evaluates the effect of pozzolanic additions to normal portland cement by measuring chloride diffusion constant and pore structure characteristics.

Keywords: cement; fly ash; pore size distribution; pozzolans.

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#### INTRODUCTION

Concrete made with normal portland cement (NPC) is the most versatile and widely used material in the world. It is comparatively cheap and can be made using very simple technology. In terms of cost of the components of concrete, the most expensive and less environmentally friendly component is the cement. To produce normal portland cement it is necessary to expend a large amount of energy, which in many developing regions of the world is onerous and costly. Natural and artificial pozzolans have been used since Roman times with varying degrees of success. Today, artificial pozzolans like fly ash (FA) and microsilica are used as additions to cement for the production of concretes which have good performance properties. There are large deposits of natural pozzolans which have not been used at all. A good example of these comprise the soils of the tropical and subtropical regions of the world, i.e. the red tropical soils which are the results of intensive chemical weathering and which contain appreciable proportions of amorphous and poorly crystalline silica and alumina minerals (1). These soils have been shown to be pozzolanic and potentially useful as additions to normal portland cement for the manufacture of durable concrete (2, 3).

This paper presents the results of a study dealing with the evaluation of the effect of pozzolanic additions to NPC by measuring chloride diffusion constant and pore structure characteristics. The pozzolans used were FA and two kaolinite clays. The kaolinite clays were used in their natural state and also

after thermal activation at 800°C for 2 hours, i.e. metakaolins. For reference purposes, the results are compared with NPC pastes.

#### MATERIALS

The two <u>kaolinites</u> (RTS) used in the study were obtained from Sri Lanka (4). These were prepared for use by air-drying, crushing and wet-sieving to pass the 75 $\mu$ m sieve and subsequent drying at 60°C. Both kaolinites were used either in their natural state or after subjecting them to thermal activation at 800°C for 2 hours and thus converted to metakaolins. Fig. 1 shows the effect of thermal activation on the mineralogy of the rts. The kaolinite mineral is dehydroxilated, its structure collapses and converts into an amorphous material. The <u>fly ash</u> used was obtained from Drax Power Station in the UK. The <u>cement</u> was normal portland cement complying with the requirements of BS 12 (5). A naphthalene formaldehyde condensate <u>superplasticiser</u> was used to control the consistency of the NPC+RTS mixtures. The physical properties and chemical oxide composition of all the materials are presented in Table 1.

#### SAMPLE PREPARATION AND CURING REGIMES

The code of cements used is given in Table 2 and the composition of the cement pastes is given in Table 3. The water/cement (W/C) of mixtures, 1 to 6, was maintained constant and equal to 0.4. To control the workability of the pastes it was necessary to use a superplasticiser for the pastes containing rts.

These pozzolans have high surface area and therefore require higher values of W/C to achieve the same workability of the normal portland cement paste. The workability of the pastes was measured following the procedure given in BS 4551 Method 1 for mortar workability using a flow-table (6). An average flow-table spread of  $192 \pm 3$ mm was adopted as the appropriate consistency.

Pastes labelled as mixture Nos. 7 to 10 were made without superplasticiser. To achieve the same consistency as mixtures 1 to 6, the W/C was increased (see Table 3). There was no significant difference between the workability of the normal portland cement control mixture and that containing FA at the 15% level of replacement used.

Three specimens were prepared for each mixture. After mixing, the pastes were placed in cylindrical moulds of 50mm diameter and 75mm height. They were vibrated for 5 minutes, sealed and placed in a 20 rpm rotating cylinder for 24 hours. This treatment avoided segregation of the paste. The specimens were then de-moulded and cured in two different environments:

- (a) 20°C and 100% relative humidity (RH); and
- (b) 45°C and 100% RH

Mixtures exposed to environment (a) were cured for 60 days and mixtures exposed to environment (b) for 21 days. These curing periods gave specimens (100 mm) of approximately the same compressive strength at the time of testing as those shown in Fig. 2.

The programme allowed for assessment of the effect of temperature of curing when the strength was maintained constant and the separate effects of pastes of equal workability obtained by either the use of a superplasticiser or the change of the W/C.

## Chloride-Diffusion Test

At the end of the curing period, four slices about 3-4mm thick, were cut from the central portion of each cylinder cured as previously indicated. The surfaces of each slice were polished to a smooth finish using emery paper and then mounted in the diffusion cells as shown in Fig. 3.

The experimental procedure adopted and the diffusion cells used are similar to the cells designed by Page et al (7). The diffusion cells were placed in a water bath, which was maintained at a constant temperature of 30°C throughout the experiment. As shown in Fig. 3, the light table tennis balls used as leads allowed the cells to float in the water bath.

Chloride ions moved through the paste due to the ion concentration difference. The concentration of ions in the right hand compartment of the cell was determined from aliquots collected over a period of two to three weeks. Chloride determinations were made using a double-beam ultraviolet spectrometer following standard spectrophotometric techniques.

## Determination of the Effective Diffusion Coefficients

The chloride concentration versus time relation for each specimen was plotted and a linear statistical equation fitted to the experimental points. The results were statistically acceptable with correlation coefficient  $r^2$  varying from 0.998 to 0.880. An example of the results of four specimens for mixture 2 cured at 45°C and 100% RH is given in Fig. 4.

Due to the possibility of chemical absorption and surface interaction between the diffusing ions and the pore walls of the paste, the chloride ions detected do not necessarily represent the actual total chloride diffusing into the test specimen. Therefore, in this test an "effective" rather than the true diffusion

coefficient is obtained. The assumption inherent in the application of this method, is that a linear gradient becomes established through the test specimen after an initial transient period necessary for the solid and liquid to come to equilibrium. The diffusion coefficient can then be obtained from the slope of the linear portion of the concentration/time curve according to Ficks' Law for quasi-steady state viz:

$$D = \frac{LV}{AC_1} x \frac{dC_2}{dt}$$
[1]

where:

D	=	Effective diffusion coefficient (cm <sup>2</sup> /sec)
t	=	time (seconds)
L	=	specimen thickness (mm)
A	=	cross sectional area of specimen (cm <sup>2</sup> )
V	=	volume of fluid in the receiving compartment (cm <sup>3</sup> )
$C_1, C_2$	=	concentrations of the chloride ions in the two compartments of
		the diffusion cell (moles/1)
dC <sub>2</sub> /dt	=	slope of the concentration versus time curve

The effective diffusion coefficients obtained using the above relationship are presented in Table 4 and in Fig.s 5 and 6. The values shown represent the average of the four slices from each mixture. The standard deviation of the four values per paste varied from 0.25 to 2.5 x  $10^{-9}$  cm<sup>2</sup>/sec.

#### Determination of Porosity and Pore Size Distribution

The paste specimens prepared and cured as previously indicated were also used for the analysis of pore structure by measuring the total porosity and pore size distribution of the mixtures dried at 105°C for 24 hours.

The pore size distribution was measured using mercury intrusion porosimetry with an apparatus capable of generating mercury intrusion pressures up to 414 MPa. The technique (MIP) is based on the relationship which exists between pressure and intrusion pore diameter which is obtained when the mercury-cement contact angle and the surface tension of mercury are known. For the test carried out in this study the contact angle was 130°C and the mercury surface tension 484 dynes/cm.

Table 4 shows the results of total porosity and total volume of capillary pores (pores with diameter greater than  $0.01\mu m$ ) obtained from the mip tests and also the chloride diffusion coefficients. Parameters to characterise pore size distribution of solids include selected ranges of pore sizes, average pore diameter, median pore diameter and total pore volume.

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Assessing the influence of pore structure on the ion diffusion characteristics of cements is important for the design of concretes of adequate performance, therefore, in this study a statistical analysis relating different pore characterising parameters to chloride diffusion was carried out. Statistical equations were obtained by relating various pore structure characterising parameters with the diffusion coefficient. The independent variable included in turn: various ranges of pore sizes, median pore diameter, capillary pore volume (pores >0.01  $\mu$ m) and total porosity.

From all the equations obtained the best correlation was found between the diffusion coefficient and the volume of capillary pores (volume of pores >0.01  $\mu$ m). The equation is of the following form:

$$\text{Log D} = 0.04 P_{c} - 10.8$$
 [2]

where:

D = Chloride diffusion coefficient (cm<sup>2</sup>/s) P<sub>c</sub> = Capillary pore volume (%)

The statistical indicators of the validity of the equations are:

Square of the correlation coefficient $r^2$	= 0.872
St. error of the dependent variable	= 0.142
St. error of the coefficient	= 0.0036

Another independent variable which could be used in practice is the total porosity of the cement paste. The equation and statistical parameters are:

$$D = 1.1 \times 10^{-8} P - 2.6 \times 10^{-7}$$
[3]

where:

P = Total porosity (%)

and:

Square of the correlation coefficient $r^2$	= 0.778
St. error of the dependent variable	$= 2 \times 10^{-8}$
St. error of the coefficient	$= 1.4 \times 10^{-9}$

As it can be seen, this equation is also valid statistically, but less accurate for prediction purposes.

#### DISCUSSION OF RESULTS

From the results presented in Tables 4 and equations 2 and 3 it is evident that the composition of the cement blends in terms of pozzolan, W/C and the presence of superplasticiser affect both performance-related properties i.e. chloride diffusion coefficient and pore structures. Environmental conditions represented in this study by "curing temperature" strongly affect the properties of the cement blends.

The data presented and the quantitative relations between pore structure and diffusion properties will be discussed in detail.

#### Influence of the Type of Pozzolan

The FA and the superplasticised RTS pastes exhibit lower effective diffusion coefficients than the NPC paste. This is due to the reaction between the pozzolan and the calcium containing phases in the hydrated cement paste. These reaction products which consist of calcium silicate hydrates (CSH), calcium aluminate hydrates (CAH) and calcium alumino ferrites (CAFH) reduce the total volume of pore spaces and produce a finer pore structure which makes the diffusion of ions difficult.

Pozzolanic blends like FA and RTS have a high chloride binding capacity which arises mainly from the ionic interaction which exists between the hydrates constituting the charged surfaces of the hydrated pozzolan-cement blend pore walls and the ions diffusing through them (8). The rate at which chloride ions can penetrate into concrete depends to a large extent on the nature and amount of cations associated with the hydrates i.e. on their electronegativity. This concept is supported by other researchers (8, 9, 10), whose results show that pozzolanic blends impart lower electronegative charge on the surface of the pore walls of cement pastes.

#### Effects of Thermal Activation

The XRD traces in Fig. 1, show that thermal activation decomposes the original cystalline form of the Kaolinite mineral in the raw RTS to a highly disordered and more reactive material, meta-kaolinite.

Used in this form, RTS-NPC blends are very effective in inhibiting the mobility of the chloride ions. For example, the effective diffusion coefficient of ARTS1 mixture is about 7 times less than that of the NPC control mixture and about 3 times lower than the NPC+FA blend. The effective diffusivities of the non-activated RTS blends are also several folds higher than those containing the activated RTS. This is due to the lower reactivity rate of the crystalline components which dominate the natural RTS composition.