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Behaviour of ASTM Type V cement hydrated in the presence of sulfonated melamine formaldehyde

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ASTM Types I and V Portland cements were hydrated up to 28 days in the presence of 0.3% and 0.6% sulfonated melamine formaldehyde (SMF), at a water/cement ratio of 0.35. Hydration was studied by conduction calorimetric and thermogravimetric analyses. The amount of $Ca(OH)_2$ produced, compressive strength and porosity were determined after 1, 3, 7 and 28 days of curing. The compressive strengths of all samples increased with the age of curing. In the period studied the values decreased in the order: Type I cement (reference) = Type I cement + SMF > Type V cement (reference) ≥ Type V cement + SMF. The superplasticizer addition retarded the development of heat in the cements, but more severely in Type V cements. Porosities were generally higher for samples with lower compressive strengths. In the presence of 0.6% SMF, the early low strengths in Type V cement mixtures could be attributed to lower degrees of hydration. At later ages, the microstructure rather than the degree of hydration determined the strength development. However, incorporation of 0.3% SMF in Type V cement did not affect its strength development.

1. INTRODUCTION

Superplasticizers are capable of reducing the water requirement of concrete mixtures while maintaining the same slump. They can be used also to increase the slump of concrete while maintaining the same water/cement ratio (*w/c*). When they are used to decrease the water requirements of a mixture, there is an increase in the compressive strengths of the hardened concrete, independent of the type of cement used [1]. Superplasticized concrete made with Type I cement will have either the same or a slightly higher 28 day compressive strength than a reference concrete at the same *w/c*. It is generally believed that superplasticized concrete made with Type V cement, at any particular *w/c* will exhibit similar behaviour.

Recent research has indicated that concrete made with Type V cement at *w/c* 0.40–0.50, and containing 0.6% of either sulfonated naphthalene formaldehyde (SNF) or sulfonated melamine formaldehyde (SMF) superplasticizer exhibits lower compressive strengths than the reference specimen containing no superplasticizer [2]. Ninety day compressive strengths were reduced by an average of 12.8% with the addition of the superplasticizer, ranging from a minimum difference of 7.5% to a maximum of 22.8% with the addition of an SMF superplasticizer at *w/c* 0.45 and 0.50, respectively. Such low strengths are not normally observed with superplasticized Type I cement concretes.

An attempt has been made to explain this anomalous behaviour of concrete made with ASTM Type V cement by carrying out physico-chemical investigations on cement paste samples. Type V cement paste samples were made both with and without the addition of 0.3% and 0.6% SMF superplasticizer (based upon weight of cement) at *w/c* 0.35. For comparative purposes, the effect of the superplasticizer on ASTM Type I cement was also investigated. In order to study the effect of superplasticizers on the hydration, microstructure and strength development of these pastes, conduction calorimetry, thermogravimetric analysis, mercury intrusion porosimetry and compressive strength tests were carried out at various times during the hydration.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Cements

ASTM C150-89 Types I and V Portland cements were used [3]. The physical properties and chemical analysis of the cements are given in Table 1.

2.1.2 *Superplasticizer*

A sulfonated melamine formaldehyde was used.

2.2 Sample preparation

The proportioning of the four cement paste mixtures containing 0.6% SMF is given in Table 2. Mixture 1 was a Type I reference mixture containing no superplasticizer. Mixture 2 contained Type I cement and superplasticizer (SP). Mixtures 3 and 4 both contained Type V cement, but without and with superplasticizer, respectively. The

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Table 1 Chemical analysis and physical properties of ASTM Types I and V cements

Cement oxide composition (%)			Bogue's compound composition (%)[a]		
	Type I	Type V		Type I	Type V
SiO_2	20.05	21.90	Tricalcium silicate (C_3S)	54.29	54.25
Al_2O_3	4.60	3.32	Dicalcium silicate (C_2S)	16.53	21.86
TiO_2	0.20	—	Tricalcium aluminate (C_3A)	8.01	3.11
P_2O_5	0.19	—	Tetracalcium aluminoferrite (C_4AF)	7.52	10.22
Fe_2O_3	2.47	3.36	Total	86.35	89.44
CaO	61.88	63.30			
SrO	0.14	—			
MgO	2.37	3.09			
Na_2O	0.19	0.18	*Physical properties*		
K_2O	0.94	0.30	Blaine fineness ($m^2\ kg^{-1}$)	348	316
SO_3	3.79	3.47			
LOI	2.44	0.98			
Total	99.26	99.90			

[a] Cement nomenclature: C = CaO; S = SiO_2; A = Al_2O_3; F = Fe_2O_3.

Table 2 Proportioning of cement paste mixtures

Mixture	*w/c*	Water (g)	Cement (g)	SP. solution (g)
1 Type I	0.35	1750.5	5000.4	0
2 Superplasticized Type I	0.35	1674.7	5000.1	75.3
3 Type V	0.35	1750.5	5000.0	0
4 Superplasticized Type V	0.35	1674.9	5000.0	75.1

w/c was 0.35 for all four mixtures. The superplasticizer was a 40% solution and the dosage rate used for mixtures 2 and 4 was 0.6% (solid/cement ratio). In addition, a fifth mixture containing Type V cement (5000.4 g), water (1712.5 g) and 0.3% SMF solution (38.3 g) was also prepared. For each mixture, twelve 50 mm cube specimens were cast which provided triplicate samples for each hydration period tested. All the specimens were left covered in moulds for 24 h, and then were demoulded and kept in the moist curing room at 100% RH and 23°C until the date of testing. Samples were cured for 1, 3, 7, and 28 days before testing.

2.3 Techniques

2.3.1 *Compressive strength determination*

Samples were tested at each of the four hydration intervals (1,3,7, and 28 days) following the ASTM C109-86 procedure [4]. The broken cube from each test was placed in a desiccator and, upon completion of an entire set of samples, a sample from the core was taken from each cube and was vacuum dried at 100°C for a minimum of 24 h for TGA and porosimetry determinations.

2.3.2 *Thermogravimetric analysis*

The thermogravimetric analyser (TA Instruments) consists of a furnace which surrounds a balance and a thermocouple. The balance supports an aluminium pan containing the sample. Thermal Analyst 2100 was used to control the heating of the sample and record data every 3 s. The vacuum-dried sample of each replicate was ground to a fine powder and then approximately 50 mg of the sample was used. The sample was heated from room temperature to 900°C at 10°C min^{-1} in a continuous flow of nitrogen (100 ml min^{-1}). Data were recorded both as the differential weight loss and the total weight loss of the sample as a function of temperature. The amount of calcium hydroxide (CH) in the cement paste could be determined by the weight loss due to the decomposition of CH.

2.3.3 *Porosimetry*

Porosity and pore size distributions were obtained by mercury intrusion porosimetry employing American Instrument Company equipment. The vacuum dried samples were broken into smaller pieces and further dried at 105°C under vacuum for 24 h. A maximum pressure of 207 MPa was applied to determine pore size diameter

down to 0.0058 μm. A contact angle of 130° was used in the calculation of pore size from the pressure measurement. The volume of mercury intruded at the maximum pressure was considered to be the total porosity.

2.3.4 *Conduction calorimetry*

Isothermal conduction calorimetry was used to measure the heat evolved during cement hydration as a function of time. Most of the heat was released during the first 72 h of hydration. The calorimeter from the Institute of Applied Physics, TNO-TU Delft, contained 6 cells mounted on a metal base plate surrounded by foam insulation. A thermopile located under each cell measured the heat production. Each cell contained a Teflon-coated aluminium specimen holder into which was placed a polyurethane insert holding the sample. An aluminium cover, surrounded by a rubber O ring, was securely fastened to the base plate to keep the vessel watertight. The calorimeter was placed in an isothermal water bath. Voltage signals from each thermopile were recorded by a Datataker DT100 Data Logger (Data Electronics, Australia), and converted to calories using a formula that considered sample weights and cell sensitivities. Data were calculated as the rate of hydration (cal g^{-1} h^{-1}) or integral heat (cal g^{-1}).

A volume of 3.5 ml of distilled, deionized water or an aqueous solution containing the required amount of superplasticizer (0.3% or 0.6% solid/cement ratio) was added to 10.000 g of cement. Averaged millivolt signals for each sample were collected every 10 min for up to 72 h by the Datataker at a constant temperature of 25.0 ± 0.5°C.

3. RESULTS AND DISCUSSION

Table 3 shows data obtained by RamezanianPour and Malhotra [2] on strength development in concretes made with ASTM Type V cement with and without SMF superplasticizer at different *w/c* and various hydration ages. Higher compressive strengths were obtained at lower *w/c* for both types of concrete mixture. Although all 1 day old superplasticized concrete exhibited slightly higher compressive strengths than the reference samples at the same *w/c*, this difference gradually decreased by 3 days and remained below the reference values up to 90 days of hydration.

Figs 1–4 contain the results for the ASTM Types I and V cements containing 0.6% superplasticizer. Fig. 1 shows the strength development in Types I and V cement pastes without and in the presence of the superplasticizer. Type I cement reference samples and superplasticized Type I cement samples exhibited virtually identical strength development up to 28 days. The Type V cement (reference) indicates much lower strengths than the Type I cement (reference). The differences were greatest after 1 day of hydration (20.83 MPa or 46.6%), but gradually the Type V cement strength values increased with a difference in 28 day strength levels of only 9.10 MPa or 10.6%.

Table 3 Compressive strength development for both non-superplasticized and superplasticized concrete containing ASTM Type V cement at different *w/c*[a]

Compressive strengths (MPa)					
w/c	1 day	3 days	7 days	28 days	90 days
Reference concrete					
0.40	15.2	24.5	30.4	40.6	52.1
0.45	10.4	18.2	24.5	34.8	42.5
0.50	7.2	13.4	18.9	29.0	36.0
Superplasticized concrete					
0.40	15.9	22.3	27.3	36.0	44.6
0.45	11.8	18.3	22.7	30.5	39.3
0.50	7.7	11.8	15.4	22.4	27.8

[a] From reference [2].

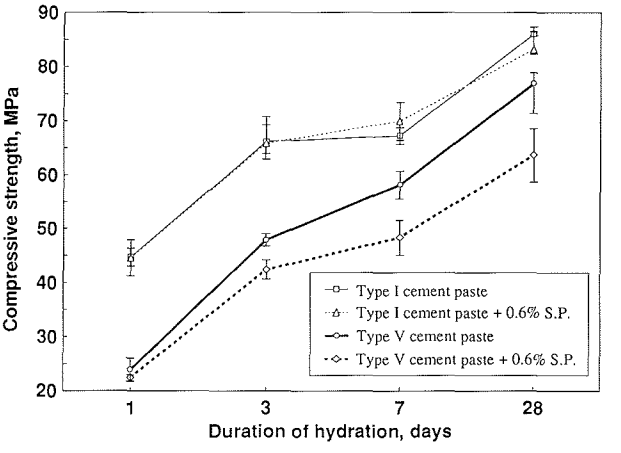

Fig. 1 Effect of a sulfonated melamine formaldehyde superplasticizer on the compressive strength development in ASTM Types I and V cement pastes.

There appears to be a significant difference between the compressive strength of Type V reference cement paste and the superplasticized Type V cement paste samples. The superplasticized pastes exhibited consistently lower compressive strengths than the references after 1 day of hydration, with a 28 day compressive strength reduction of 17.2%. These findings were consistent with the data by RamezanianPour and Malhotra [2], who reported strength reductions of 11.3–22.8% for concrete samples (Table 3).

Fig. 2 represents the conduction calorimetric curves for the hydrating Types I and V cements with and without the superplasticizer. The rate (A) as well as the amount of heat (B) developed up to 72 h are shown. Normal Portland Type I cement (Fig. 2A) exhibits an initial exotherm within the first 10 min of hydration and this is attributed to a combination of reactions such as the hydration of free lime, heat of wetting and the formation of ettringite of formula $3CaO(Al_2O_3, Fe_2O_3)\cdot 3CaSO_4\cdot 31\text{–}32H_2O$. Only a small inflection is registered in the

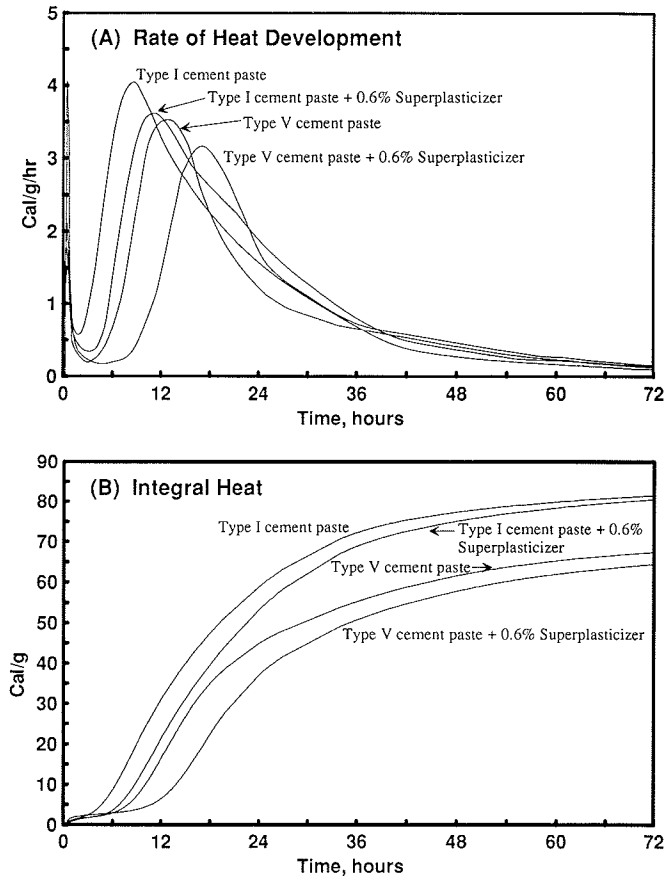

Fig. 2 Conduction calorimetric curves of ASTM Types I and V cement pastes treated with a sulfonated melamine formaldehyde superplasticizer ($w/c = 0.35$).

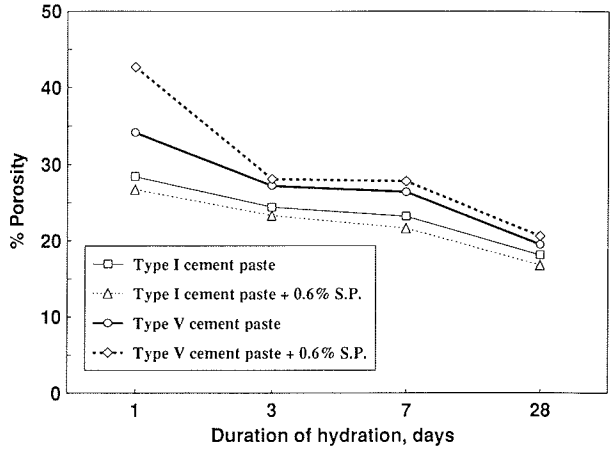

Fig. 3 Porosity development in ASTM Types I and V cement pastes treated with a sulfonated melamine formaldehyde superplasticizer.

figure because the cement was placed in the calorimeter a few minutes after it had been pre-mixed with water outside the calorimeter. This effect is followed by a period of relatively low chemical reactivity from about 30 min to 2.0 h, known as the 'induction' or 'dormant' period. At the end of this period an increase in heat evolution occurs with a peak of 4.04 cal g^{-1} h^{-1} at about 8.3 h and this is due to the hydration of the tricalcium silicate component of cement that yields calcium silicate hydrate and calcium hydroxide. After this peak, there is a gradual diminution in the evolution of heat, with the attainment of a steady state after about 50 h.

The addition of the superplasticizer had a retarding effect on the hydration of the Type I cement. The induction period was increased to 3.2 h, the exothermic peak was delayed until 11.0 h and the maximum thermal peak value was decreased to 3.62 cal g^{-1} h^{-1}. Similar observations have been reported by Ramachandran [5].

The hydration of Type V cement was retarded with respect to Type I cement; an increase in the induction period to 3.2 h, a delay in the exothermic peak until 13.3 h, and a decrease in the maximum thermal peak value to 3.52 cal g^{-1} h^{-1} were observed. A more efficient retardation effect was noted with the addition of the superplasticizer to the Type V cement than with a Type I cement. The induction period was increased to 4.8 h, the exothermic peak was delayed until 18.1 h, and the maximum thermal peak value was decreased to 3.17 cal g^{-1} h^{-1}.

Fig. 2B was obtained by integrating, at different times, the curves in Fig. 2A. The total amount of heat developed at different times may be used to estimate the degree of hydration of the silicate phases in the cement. The total heat generated by the hydration of the Type I cement after 72 h was 81.43 cal g^{-1}. Even after 3 days of hydration, the effects of the Type V cement and the superplasticizer were apparent. The 72 h total heat values were 80.45, 67.30, and 64.34 cal g^{-1} for the superplasticized Type I cement, Type V cement and superplasticized Type V cement, respectively. These values correspond to 1.20, 17.35, 20.99% reductions in the heat of hydration with respect to Type I cement.

Total porosity of the cement pastes after different hydration periods is shown in Fig. 3. After 1 day of hydration, Type V cement with the superplasticizer exhibited the highest porosity, and it continued to be higher than the other pastes up to 28 days of hydration.

The lower strength development in the pastes containing Type V cement and the superplasticizer may be due to the following factors. Type V cement contains a lower amount of C_3A, which is responsible for early strength development. The Type I cement having a much higher Blaine surface area (Table 1) than the Type V cement should exhibit an acceleration of the strength development in the Type I cement pastes. There is a possibility that in the hydration of Type V cement the Fe and Al hydroxide gels are formed that could retard the hydration of silicate phases, and thus retard the strength development.

In cement pastes it is generally observed that log porosity versus compressive strength bears a linear relationship [6]. All conditions being similar, the larger the porosity the lower is the compressive strength. Fig. 3 indicates the Type I cement pastes (with and without superplasticizer) exhibited much lower porosities than Type V cement pastes, indicating the strengths of the

Type V cements should be lower than those containing Type I pastes. In Type V cement pastes the incorporation of the superplasticizer results in a much higher porosity and reduced strength. It appears that the microstructure of the Type V cement is modified in the presence of the superplasticizer.

In Type V cement paste, the low strength development in the presence of the superplasticizer, especially at earlier times, is evident from the delayed induction period and lower degrees of hydration. Superplasticizers are adsorbed to different extents by the cement minerals. It has been reported that the C_3A phase not only adsorbs substantial amounts of a superplasticizer, but also at a very rapid rate [7]. The Type V cement contains only 3.11% C_3A compared with the Type I cement which contains 8.01% C_3A. Thus, lower amounts of the superplasticizer would be adsorbed by the C_3A component of the type V cement paste. Consequently, a larger amount of the superplasticizer is available in the solution phase to affect the hydration of the C_3S phase. It may not only disperse the C_3S particles but also will be adsorbed strongly and affect efficient hydration at earlier times of curing.

The degree of hydration of the cement pastes was estimated by determining the percent $Ca(OH)_2$ produced based on ignited weights by TGA [8]. The superplasticizer-treated cement pastes (Type I and V) exhibited lower amounts of CH than the corresponding reference samples (Fig. 4). These samples also showed lower compressive strengths in relation to the corresponding reference specimens. However, although Type V cement containing the superplasticizer showed the lowest compressive strength compared with other specimens, it exhibited the same degree of hydration as the Type I cement containing the superplasticizer after 3 days of curing. The porosity results showed significant differences, indicating that the microstructure rather than the degree of hydration played a major role in the strength development. There is also a possibility of more CH

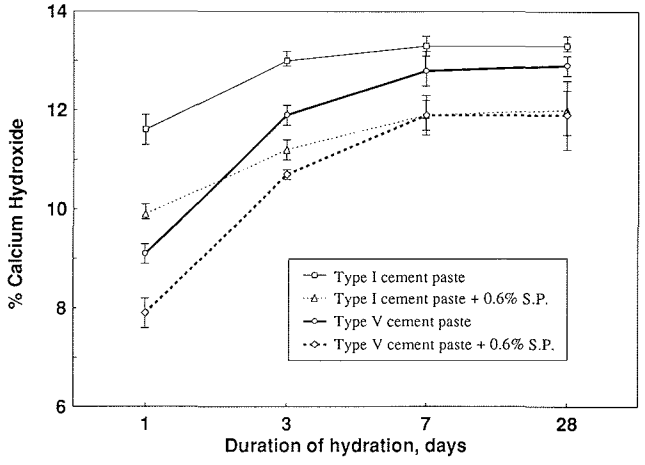

Fig. 4 Amount of calcium hydroxide formed at different curing ages in ASTM Types I and V cement pastes containing a sulfonated melamine formaldehyde superplasticizer.

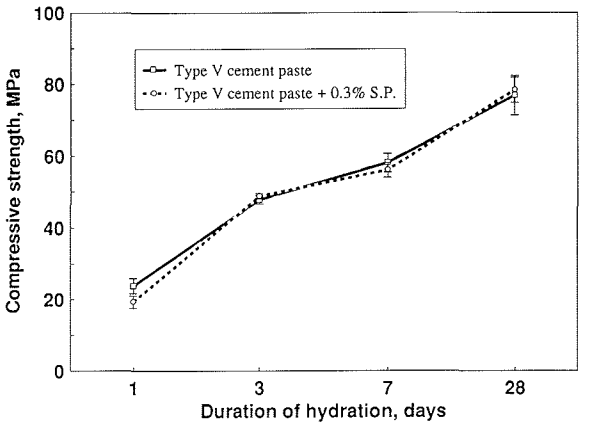

Fig. 5 The effect of a sulfonated melamine formaldehyde superplasticizer on compressive strength development in ASTM Types V cement paste.

present as a complex with the superplasticizer in Type I rather than in Type V cement. Thus a portion of $Ca(OH)_2$ will be undetected.

Fig. 5 represents the strength development in ASTM Type V cement pastes with 0.3% SMF. Contrary to the results obtained at 0.6% SMF (Fig. 1) the addition of 0.3% SMF does not result in retrogression of strength development. This would indicate the microstructure of the paste is not changed to any significant extent. The rate of hydration as well as the adsorption of SMF on C_3S would not be altered significantly [5,7].

4. CONCLUSIONS

The addition of 0.6% sulfonated melamine formaldehyde to ASTM Type V cement results in lowering of the compressive strength development. The superplasticizer, however, does not affect the strength development in ASTM Normal Portland Type I cement pastes. The lower strength development in Type V cement pastes in the presence of SMF is caused by the change in the microstructure, as evidenced from higher porosity values. The rate of hydration is also decreased because of the higher adsorption of the superplasticizer on the C_3S phase in Type V cement pastes. The strength difference may be attributed partly to the difference in surface area of cements and a higher than normal dosage of the superplasticizer. The degree of hydration determined by the estimates of $Ca(OH)_2$ reveals lower amounts of hydration with the superplasticized Type V cement pastes and the same levels for the SMF-treated Type I cement pastes. It is thus concluded that microstructure rather than the degree of hydration dominated the strength development at later ages. At a dosage of 0.3% superplasticizer, the strengths in Type V cement pastes were not affected. The low retardation effect, as well as the lower amounts of adsorption of superplasticizer, do not seem to influence the microstructure of the paste.

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RESUME

Comportement de ciment de type ASTM V hydraté en présence de mélamine-formaldéhyde sulfonée

Des ciments Portland de types ASTM I et V ont été hydratés pendant un maximum de 28 jours en présence de 0,3% et de 0,6% de mélamine-formaldéhyde sulfonée (SMF), suivant un rapport eau-ciment de 0,35. L'hydratation a été étudiée à l'aide de la calorimétrie à conduction et de l'analyse thermogravimétrique. La quantité de $Ca(OH)_2$ produite, la résistance à la compression et la porosité ont été déterminées après 1, 3, 7 et 28 jours de cure. La résistance à la compression de toutes les éprouvettes a augmenté avec la période de cure. Au cours de la période étudiée, les valeurs ont diminué dans cet ordre: ciment de type I (référence) = ciment de type I + SMF > ciment de type V (référence) ⩾ ciment de type V + SMF. L'ajout de superplastifiant a retardé la production de chaleur dans les ciments, et davantage dans les ciments de type V. La porosité était généralement plus grande dans le cas des éprouvettes qui avaient une faible résistance à la compression. En présence de 0,6% de SMF, la faible résistance initiale des mélanges de ciment de type V pourrait être attribuée au degré peu élevé d'hydratation. Aux âges plus avancés, c'est la microstructure plutôt que le degré d'hydratation qui a déterminé le degré de résistance atteint. Cependant, l'incorporation de 0,3% de SMF dans le ciment de type V n'a pas eu d'effet sur le degré de résistance qu'il a atteint.