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SPECIFIC SURFACE OF TWO HYDRATED CEMENTS DIFFERING IN STRENGTH

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Abstract

Specific surface, *S*, of CSH-gel particles of disordered layered structure, was studied by water sorption/retention in two cement pastes differing in strength, i.e. C-33 (weaker) and C-43 (stronger), w/c=0.4. Hydration time in liquid phase was t_h=1 and 6 months, followed by hydration in water vapour either on increasing stepwise the relative humidity, RH=0.5→0.95→1.0 (WS) or on its lowering in an inverse order (WR). Specific surface was estimated from evaporable (sorbed) water content, *EV* (110°C), assuming a bi- and three-molecular sorbed water layer at RH=0.5 or 0.95, respectively (WS). On WR it was three- and three- to four-molecular (50 to 75%), respectively, causing a hysteresis of sorption isotherm.

At RH=0.5 the *S* increased with cement strength from 146 $m^2 g^{-1}$ (C-33, 1 m) to 166 $m^2 g^{-1}$ (C-43, 1 m) and with hydration time to 163 (C-33, 6 m) and to 204 $m^2 g^{-1}$ (C-43, 6 m). At RH=1.0 (and 0.95), higher *S*-value were measured but these differences were smaller: *S* amounted to 190–200 $m^2 g^{-1}$ in C-33 (1 and 6 m) and 198–210 $m^2 g^{-1}$ in C-43 (1 and 6 m). Thus no collapse occurred on air drying of paste C-43 (6 m).

Keywords: cement hydration, CSH-gel, hydration time, specific surface, water sorption/desorption

Introduction

The simple method based on water sorption and static heating was derived for clays [1] and it was applied previously to study the cement hydration products [2]. Its simplicity and economy is its primary value, considering extensive informations derived from its interpretation. It may be applied in any basic chemical laboratory, obtaining numerous results and thus deriving standard deviation. It does not need any sample preparation, which could cause a change in its properties. The background of this method was discussed elsewhere [2]; here only the assumptions will be presented and some highlights outlined.

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The mass of cement increases on hydration to ΔM_o (as air dry) and this increase is divided into the evaporable at 110°C (*EV*) and non-evaporable water content. The non-EV and the hydration products estimated therefrom are discussed elsewhere [3].

The evaporable water, which covers uniformly the surface of the CSH-gel layered particles is bound by physical interactions of the energy about 1 kcal mol^{-1}. This is derived from the thermal kinetic energy of water molecules: E_k=3/2 RT=1.15 kcal mol^{-1}, with R=2 cal mol^{-1} K^{-1} and T=383 K; CSH represents calcium silicate hydrate. Sorption is an equilibrium kinetic process and if its energy is exceeded by E_k, the dipolar water molecules escape from the charged particle surfaces. Their electrokinetic ζ potential was measured as –1.8 mV [4].

Thus the quantity of the evaporable sorbed water (*EV*) is proportional to the specific surface area, *S* of the hydrated particles of the gel, forming a bimolecular layer at *RH*=0.5 (and on air drying if *RH* is about 0.5) and three-to-four molecular layer on full hydration (*RH*=0.95 to 1.0 [4–5]). *S* may be calculated, dividing the respective water content by the thickness of the molecular water layer, i.e. 0.6 or 0.9 nm for bi-molecular (*RH*=0.5) or three-molecular layer (*RH*=0.95 and 1.0), respectively, or 1.2 nm in case of four-molecular sorbed water layer. The diameter of a water molecule is about 0.3 nm, exactly 0.273 nm but in liquid water it occupies more space, resulting in the density 1 g cm^{-3}. The density of the sorbed water is probably increased by about 10% due to strong adhesive forces [5].

The poorly crystalline CSH-gel of disordered layered structure and of a given specific surface *S*, is the main product of cement hydration. Most of the layers represent structurally imperfect jennite [$Ca_9Si_6O_{32}H_{22}$], the others belong to the 1.4 nm tobermorite [$Ca_5Si_6O_{26}H_{18}$]; in both cases some of the silica tetrahedra are missing [6]. It is polymerized with the Arrhenius energy calculated as 35 and 100 kJ mol^{-1} for dimer and polymer, respectively [NMR, [7]].

The AFm phase, ideally monosulfoaluminate ($[Ca_2Al(OH)_6]_2{\cdot}SO_4.6H_2O$) may also contribute to the specific surface, which is considered here jointly with CSH-gel. Other hydration products are not discussed here, either being not abundant or indicating a low specific surface.

Here the hydration products of two cement pastes were studied to contribute to understanding the hydration mechanism and to check the suitability of a very simple testing method. The variable parameters were: (i) the standard strength of the hydrated paste, (ii) hydration time, t_h, (iii) hydration in liquid water, followed by hydration in water vapour at decreasing or increasing relative humidity *RH*, in WR and WS, respectively, and by static heating, SH. The change in mass was measured gravimetrically and the specific surface, *S*, was estimated from the sorbed water content. This was done to find the correlations between the parameters mentioned above.

Experimental

Materials

Ordinary portland cement of the grade 33 and 43 (Indian Standards, IS: 8112-1989) was supplied by the National Council for Cement and Building Materials (NCB, New Delhi, India). It indicated the chemical composition shown in Table 1, as measured by standard methods at NCB (Table 1a) and as estimated by SEM equipped with EDX (Table 1b).

Table 1a Chemical composition of the cements C-33 and C-43/mass%

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3	Na_2O	LOI
C-33	61.8	21.4	5.6	3.0	1.8	0.77	2.2	0.25	2.3
C-43	61.0	20.9	5.3	3.1	3.6	0.89	1.5	0.45	2.7

Table 1b Chemical composition of the cement pastes C-33 and C-43 as measured by EDX at magnification ×500 (hydrated for 1 month, acetone treated)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Photo
C-33	60.9	27.6	5.7	4.1	1.1	0.64	386
	60.7	29.2	4.8	3.2	1.7	0.37	–
C-43	59.6	28.5	4.7	3.9	2.6	0.68	381
C-43*	53.4	32.5	5.9	4.0	3.6	0.71	385

*Selected surface not containing portlandite crystals

Methods

Hydration in liquid water

Cement paste was prepared at the tap water/cement ratio *w*/*c*=0.4, it was formed into standard cubes at NCB and stored at room temperature in the water submerged state for the hydration time t_h=1 and 6 months. Sample fragments were air dried.

Hydrated cement paste was investigated either directly by static heating, SH, at 110°C and higher as discussed in [3] or after the subsequent hydration in water vapour.

Hydration in water vapour

Samples of the hydrated cement paste (5 g in triplicate) were put into aluminium containers and stored in desiccators over suitable solutions, at the given relative humidity, *RH* (relative water vapour pressure, p/p_o), at 30°C = const. and at atmospheric pressure.

RH was either increasing successively, defined as WS (RH=0.5→0.95→1.0) or decreasing successively in WR (RH=1.0→0.95→0.5). Storing time was 2 weeks in each case. Change in mass was measured gravimetrically.

The respective *RH* conditions were achieved over (i) saturated $Mg(NO_3)_2$ solution, *RH*=0.5, (ii) 10% H_2SO_4 solution, *RH*=0.95 and (iii) distilled water, *RH*=1.0.

Static heating

The hydrated paste samples were heated statically both before (defined as SH) and after the water sorption test (defined as WS and WR if studied at increasing or decreasing *RH*, respectively). The heating temperature discussed here was 110°C overnight.

The water content (W, escaping at 110°C as *EV*) was calculated in mass percent related to the sample mass at 800°C, i.e. ΔM(800°C)=0 and ΔM(110°C)=non-EV.

The standard deviation, σ, was in case of paste hydrated for 1 month (1 m): for W: ±0.02 to 0.3%, for *RH*=0.5±0.005 to 0.07, for *RH*=0.95±0.1 to 0.3, for *RH*=1.0±0.5 %. It was on heating at 110°C: ±0.02 to 0.1%. For 6 months hydration (6 m) it was somewhat higher, i.e. maximum up to 0.8, 0.9, 1.0, 0.9 and 0.9% respectively.

The sorption test and the heating test were derived for clays to estimate the specific surface (proportional to sorbed water content) and the content of accessory minerals; it was applied successfully to cement ([8]).

Additional tests

Selected samples were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), High resolution transmission electron microscopy (HRTEM) and discussed in [3].

Results

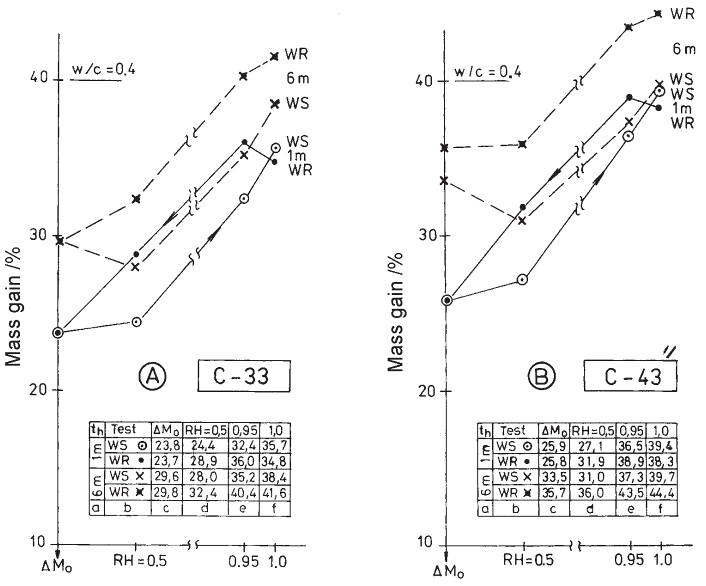
Sorption test

Total ΔM in water sorption

On hydration of cement the water is bound in CSH-gel (this gel was observed in TEM, [3]) and in other hydration products thus the mass increases by ΔM (air dry, related to mass after heating at 800°C for 1 h). This value was higher in the stronger paste, i.e. ΔM(C-43)>ΔM(C-33) and after the longer hydration time, i.e. ΔM(6 m)> ΔM(1 m), Fig. 1.

The hydration process was not terminated after 1 month and the ΔM of both pastes (1 m) stored at *RH*=0.5 indicated a slight increase, as compared to ΔM_o of the hydrated and air dry paste, Fig. 1. The ΔM (*RH*=0.5) of both pastes (6 m) was lowered as compared to the ΔM_o, and the same was found when analyzing the *EV* (Fig. 2). This indicates collapse either in the thickness of the hydrated cement particles or in the thickness of the sorbed water layer (more probable).

The extent of hydration, ΔM, was much higher after 6 months than after 1 month and the respective curves were more elevated in the first case. It is interesting to note that the curve for WR(*RH*) at t_h=1 month almost coincides with that for WS(*RH*) at t_h=6 months, Fig. 1.



t_h	Test	ΔM_0	RH=0,5	0,95	1,0
1m	WS ⊙	23,8	24,4	32,4	35,7
	WR ●	23,7	28,9	36,0	34,8
6m	WS ×	29,6	28,0	35,2	38,4
	WR ✖	29,8	32,4	40,4	41,6
a	b	c	d	e	f

t_h	Test	ΔM_0	RH=0,5	0,95	1,0
1m	WS ⊙	25,9	27,1	36,5	39,4
	WR ●	25,8	31,9	38,9	38,3
6m	WS ×	33,5	31,0	37,3	39,7
	WR ✖	35,7	36,0	43,5	44,4
a	b	c	d	e	f

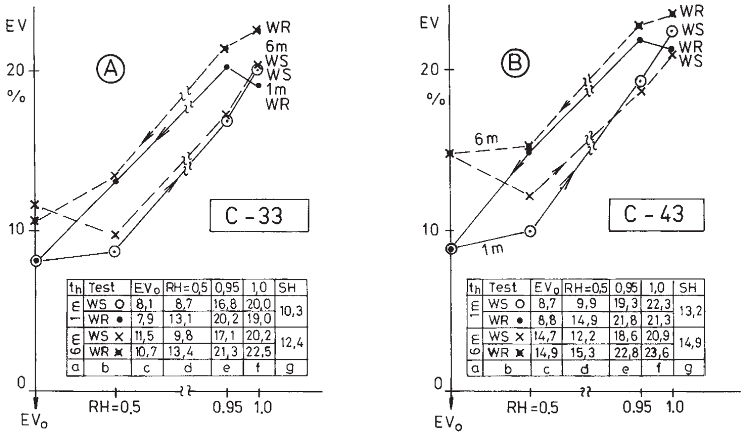
Fig. 1 Change in mass (%) of the pastes prehydrated in liquid water and subsequently hydrated in water vapour at definite *RH*

A hysteresis was found in all the pastes thus more water was retained on decreasing *RH* in WR than sorbed on its increasing in WS. Exceptional were both pastes hydrated for 1 month and stored at *RH*=1.0 as their Δ*M*(*RH*=1.0) were higher in WS- than in WR-test (Fig. 1). Thus some geometrical hindrances prevented full hydration on WR, e.g. the surface tension at the saturated water vapour pressure [compare [4]]. In case of (6 m) paste the hysteresis was observed within the entire *RH*-range.

Both pastes hydrated for 6 months indicated the Δ*M*(*RH*=1.0) exceeding the initial water content at *w*/*c*=0.4, i.e. W=40%: WR at *RH*=0.95 to 1.0 was 40.4 to 41.6% and 43.5 to 44.4% for C-33 and C-43, respectively (Fig. 1). Thus at t_h=6 months the liquid water available at *w*/*c*=0.4 was not sufficient for full hydration.

EV water content

EV-water content (110°C, SH) was also higher in the stronger paste. [*EV*(C-43)> *EV*(C-33)] and was slightly higher after a longer hydration time. [*EV*(1 m)< *EV*(6 m)], Fig. 2. The differences between pastes (1 m) and (6 m) are though much smaller than those presented in Fig. 1 for the total mass change Δ*M*. At the high *RH*=0.95 (WR) this difference is 1% only and the graphs almost overlap, whereas the difference in water sorption at *RH*=0.5 and in EV_0 is important. The increase in the Δ*M* with hydration time, as presented in Fig. 1, concerns thus rather the hydration products, than the sorbed water content and the specific surface, which is discussed below. The lack of hysteresis of pastes (1 m) at *RH*=1.0, Fig. 2, is similar to that presented in Fig. 1 thus it concerns the sorbed water content.



t_h	Test	EV_0	RH=0,5	0,95	1,0	SH
1m	WS ○	8,1	8,7	16,8	20,0	10,3
	WR ●	7,9	13,1	20,2	19,0	
6m	WS ×	11,5	9,8	17,1	20,2	12,4
	WR ✖	10,7	13,4	21,3	22,5	
a	b	c	d	e	f	g

t_h	Test	EV_0	RH=0,5	0,95	1,0	SH
1m	WS ○	8,7	9,9	19,3	22,3	13,2
	WR ●	8,8	14,9	21,8	21,3	
6m	WS ×	14,7	12,2	18,6	20,9	14,9
	WR ✖	14,9	15,3	22,8	23,6	
a	b	c	d	e	f	g

Fig. 2 Change in evaporable water content (%), *EV*(110°C) of the pastes prehydrated in liquid water and subsequently hydrated in water vapour at the *RH* indicated

The similarity of the shape of the graphs obtained for C-33 and C-43 (Figs 1 and 2) indicates that the results obtained have some physical meaning, which is interpreted below.

Discussion

The comparison of *EV* values at *RH*=0.5 with the respective EV_0 indicates that the hydration proceeded in water vapour in the pastes studied in WR: the *EV*(WR, 0.5)>EV_0, Fig. 2. The same is true also for the pastes (1 m) studied in WS. An exceptional behaviour indicated the pastes (6 m, WS) showing some collapse and a lower value of *EV* than that of EV_0 i.e. *EV*(6 m, WS)<EV_0, Fig. 2. Thus a part of the high hydration achieved after 6 months was reversible : storage at *RH*=0.5 for a prolonged time caused a lowering of the high sorbed water content to an equilibrium state. An analogous behaviour is shown in Fig. 1, concerning the values of ΔM and ΔM_0.

Hydration was not completed even at 6 months and it proceeded in water vapour at a high relative humidity. Unhydrated alite and belite (XRD) were found in pastes (1 m), decreasing slightly after 6 months hydration; unhydrated klinker grains were observed by SEM in C-33 (1 m) [3]. Water availability at *w*/*c*=0.4 was not sufficient for full hydration, which proceeded in pastes (6 m) in water vapour, ΔM exceeding finally this value of 40% (Fig. 1).

The hysteresis of the *EV* water content on sorption (WS) and desorption (retention, WR) may be due either to (i) a different thickness of the molecular sorbed water layer, *th*, higher on WR than on WS and/or (ii) a different *S*, thus a different thickness, δ of the layered particles of the hydrated CSH-gel. Both these values will be analysed.

In analogy to clay particles the specific surface, *S*, of the CSH-gel was estimated assuming at WS : (i) a bimolecular sorbed water layer at *RH*=0.5 (of the thickness *th*=0.6 nm), (ii) a three-molecular layer at *RH*=0.95, *th*=0.9 nm [1, 2, 5], see Introduction. Dividing the respective values of *EV* by the respective thickness *th*, the specific surface was calculated. These assumptions are approximately valid for clay minerals [1] and for platy particles of CSH-gel. In both cases the value calculated for *RH*=0.95 seems to be the more adequate for the final hydration state: the salts dissolved in the pore water cause a lowering of *RH*. For the air dry state the adequate *S* is that estimated for *RH*=0.5, which is usually close to the relative humidity of the laboratory air.

There is a small difference only in the values of EV between pastes (1 m) and (6 m), Fig. 2. Thus it is not probable that the increased hydration time or change in hydration conditions (WR *vs.* WS) resulted in an important change of particle thickness. Accordingly for WR the thickness *th* (i) was chosen such as to obtain at the given *RH*, the *S*-values similar in WR and in WS test. The possible *th*-values are presented in Table 2, corresponding to the given contribution of particular molecular layers. In the Table 3 there is presented the assumed *th* and the specific surface *S* calculated therefrom.

Table 2 Thickness, *th* of the sorbed water layer at the given contribution of molecular layers: bi-molecular, *th*=0.6 nm; three-molecular, *th*=0.9 nm; four-molecular, *th*=1.2 nm

Contribution bi- + three-molecular		*th*/nm	Contribution three-+four-molecular		*th*/nm
100%+0%	1:0	0.60	100%+0%	1:0	0.90
50%+50%	1:1	0.75	50%+50%	1:1	1.05
25%+75%	1:3	0.825	25%+75%	1:3	1.125
0%+100%	0:1	0.90	0%+100%	0:1	1.20

Table 3 The assumed thickness of the sorbed water layer, *th* and the estimated therefrom specific surface, *S*

Paste	Test	*RH*=05		*RH*=0.95		*RH*=1.0	
		th/nm	*S*/m^2 g^{-1}	*th*/nm	*S*/m^2 g^{-1}	*th*/nm	*S*/m^2 g^{-1}
C-33	WS	0.6	146	0.9	187	1.05	190
1 month	WR	0.9	145	1.05	193	1.05	181
C-33	WS	0.6	163	0.9	190	1.05	191
6 months	WR	0.825	163	1.05	192	1.125	200
C-43	WS	0.6	166	0.9	190	1.125	198
1 month	WR	0.9	165	1.125	194	1.125	189
C-43	WS	0.6	204	0.9	206	1.05	200
6 months	WR	0.75	204	1.125	202	1.125	210
a	b	c		d		e	

The values of *th* used in estimation of *S* from WR test results are reasonable: in both pastes (1 m) a three-molecular water layer may be retained on the particle surfaces at

RH=0.5 in WR (bi-molecular in WS, Table 3, column c). In the (6 m) pastes of a higher hydration (higher *S*) only a part of the sorbed layer is three-molecular at these conditions, i.e. 50 to 75% in C-43 and C-33, respectively, thus the assumed *th* is 0.75 to 0.825 nm. Otherwise *S* would be lower in WR than in WS, which would be illogical.

In C-33, at *RH*=0.95 and WR, the four-molecular sorbed water layer occupies 50% of the specific surface (*th*=1.05 nm), the rest hosting a three-molecular layer (Table 3, column d). In the hydrated paste C-43 this value is 75%, thus the average *th*=1.125 nm and it was assumed also in most cases at *RH*=1.0 (Table 3, column e).

The estimate of the specific surface at *RH*=0.5 was higher in stronger paste and on longer hydration time (Table 3, column c); at a high *RH* these differences are much smaller (Table 3, column d and e). The most important difference is in the reversibility of hydration: the decrease in *S* on drying at *RH*=0.5 was more important in paste C-33 than in paste C-43 in which case no collapse was found after 6 months hydration and *S*(0.5) was approximately equal *S*(0.95), Table 3, compare column d and c. The reversibility of hydration was similar in case of paste C-33 (6 m) and C-43 (1 m).

As it was mentioned above the *EV* of pastes (6 m) decreased on prolonged storage in WS at *RH*=0.5 and constant temperature as compared to EV_o, which is attributed here to a change in number of sorbed molecular water layers. This was not the case either in WR or in (1 m) pastes (Fig. 2).

At a high *RH* an important increase in sorbed water content occurred. The above considerations indicate that both processes took place, i.e. the specific surface increased with hydration time and with the *RH* of the environment and simultaneously the number of molecular sorbed water layers *th* was changed. These processes are interrelated: a tendency was observed of an increase in *th* with the increase in specific surface on hydration. It is also possible that the surface charge of cement particles increases with the decrease of particle thickness as it was observed in clays [1]. This problem is worth checking.

Table 4 Most probable specific surface *S* ($m^2 g^{-1}$), from WS

RH=	ΔM_o/%		0.5		0.95		1.0	
	1 m	6 m	1 m	6 m	1 m	6 m	1 m	6 m
C-33	25.6	30.6	146	163	187	190	190	191
C-43	28.8	34.1	166	204	190	206	198	200

Conclusions

- The total change in mass on hydration (ΔM_o) was observed to increase with the paste strength and with hydration time.
- It is composed of the evaporable sorbed water, *EV*(110°C), which content is proportional to the specific surface *S*, and of water bound in the hydration products, included in non-*EV*(110°C). The increase in hydration time influenced rather the non-*EV* than the *EV* water content.

- The specific surface, *S*, was calculated from *EV* assuming that it covers uniformly this surface by a water layer of a given thickness, *th*=0.3 nm if monomolecular. On water sorption, WS: (i) at *RH*=0.5 a bi-molecular water layer is 0.6 nm thick, (ii) at *RH*=0.95 a three-molecular layer has *th*=0.9 nm and (iii) at *RH*=1.0 the *th* increases to an incomplete four-molecular layer: 50% in C-33 and 75% in C-43 resulting in the average *th*=1.05 and 1.125 nm, respectively.
- On water desorption, WR, from a full hydration (*RH*=1.0): (i) at *RH*=0.5 there remains a three-molecular layer of *th*=0.9 nm, incomplete after a long hydration time of 6 months (50–75%) and (ii) at *RH*=0.95 to 1.0 a three-to-four molecular layer forms of *th*=1.05–1.125 nm (50–75% of the four-molecular layer).
- The specific surface, *S*, as calculated from *EV* at *RH*=0.5, increased with cement strength and with hydration time. It was lowered from *S*=190–210 $m^2\ g^{-1}$ on full hydration at *RH*=1.0 to *S*=145–165 $m^2\ g^{-1}$ on air drying (*RH*=0.5). Only in the stronger paste C-43 at t_h=6 months, the particle collapse did not occur and *S*=204 $m^2\ g^{-1}$.

The influence of these factors on cement strength needs a more extensive discussion.

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References

1 E. T. Stepkowska, Engineering Geology, 28 (1990) 249.
2 E. T. Stepkowska, J. M. Bijen, J. L. Perez-Rodriguez, A. Justo, P. J. Sanchez-Soto and M. A. Aviles, J. Thermal Anal., 42 (1994) 41.
3 E. T. Stepkowska, J. L. Perez-Rodriguez, M. A. Aviles, M. J. Jimenez de Haro and M. J. Sayagues, J. Therm. Anal. Cal., 69 (2002) 187.
4 H. Uchikawa, S. Hanehara and D. Sawaki, Proc. 10th ICCC, Gothenburg 1997, V. 3, p. 8.
5 T. C. Powers, Cement and Concrete Ass., London 1968, p. 319.
6 H. F. W.Taylor, J. Am. Ceram. Soc., 69 (1986) 464.
7 A. R. Brough, C. M. Dobson, I. G. Richardson and G. W. Groves, J. Mater. Sci., 30 (1994) 1671.
8 E. T. Stepkowska, A. K. Mullick, S. K. Handoo, J. L. Perez-Rodriguez, M. A. Aviles and E. Gomez, Proc. 10th ICCC, Gothenburg 1997, V. 3, p. 4.