Study of the hydration of cement with high slag content

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ABSTRACT

The physico-chemical properties of cementitious materials, such as transport properties or porosity are established during the hydration process. The latter which involves dissolution and precipitation reactions, is characterized by the mineralogical and structural changes associated to water state (evolution from evaporable water to chemically bound water and physically absorbed water) and chemical shrinkage. These physico-chemical properties are modified by the addition of supplementary cementitious materials like slag. Powers' model, based on the water state repartition, was initially developed to describe the hydration of Portland cement. This work aims to apply this model to slag blended cements hydration. Commercial cements with a variable amount of slag, ranging from 0% to 80% (% weight) are used in this study. First, the water state repartition was experimentally studied from 7 days to 1 year. The measurements of chemical shrinkage and bound water content show clearly the slowdown of the hydration with the presence of slag. The determination of the degree of hydration, by thermogravimetry analysis and by ^{29}Si MAS NMR, is a crucial point which is discussed. Then Powers' model is applied to slag blended cements and the results are compare to experimental measurements.

1. INTRODUCTION

Blast furnace slag is a byproduct which is increasingly used for replacing part of clinker in cement. Slag addition modifies the physico-chemical properties of cementitious material. These properties evolve during the hydration process which depends on the anhydrous composition and their dissolution kinetic. Slag and clinker are composed of the same main oxides. But slag is mainly a glassy material so that its hydration kinetic is slow compared to the one of clinker. It is therefore necessary to activate slag hydration. It is commonly admitted than clinker hydration activates slag dissolution by increasing the pH value [1,2].

Powers develops an empirical model for the hydration of Portland cement [3]. The latter is based on the repartition of water state (capillary water, gel water and chemically bound water) according to a global degree of hydration. The equations used to apply the model have been recently described by Jensen et al. [4]. The aim of this work is to apply Powers' model for slag blended cements (until 80 % of slag).

First part of this work is devoted to the acquisition of the model's parameters (chemical shrinkage and bound water content) and to the determination of the degree of hydration (based on bound water content and ^{29}Si MAS NMR measurements). Then, the adapted model is applied to slag blended system and the results are discussed.

2. MATERIALS AND METHODS

2.1 Materials

Four commercial cements from Calcia with different slag content were studied with the compositions given in Table 1. All cements come from the same factory.

The cement pastes were prepared according to the standard procedure EN 196-6 [5]. The water/binder mass ratio was calculated for each cement in order to have the same ratio in volume. The samples were cured in solution where the concentrations of calcium, potassium and sodium were fixed to be equal to that of the pore solution. These concentrations were measured after extraction of the poral solution at 1 month of hydration.

Samples were characterized after 7, 28 days, 6 months and 1 year of hydration.

Table 1. Cements composition and properties

	CEM I 52.5 N	CEM II/A 42.5 N	CEM III/A 52.5 N	CEM III/C 32.5 N
Clinker [%w]	92.2	76.8	34.54	14.2
Slag [%w]	0	14.2	61.1	80.1
$CaCO_3$ [%w]	1.9	3.8	0	0
Calcium sulfate [%w]	5.6	4.7	3.8	5.2
Specific gravity [g/cm^3]	3.06	3.07	2.96	2.91
Blaine surface [cm²/g]	4000	3400	4600	4800
w/b	0.41	0.41	0.42	0.43

2.2 Methods

The chemical shrinkage was measured by casting 20 g of paste in a 50 ml bottle filled with water and connected to a pipette (0.5 ml). The surface of exchange was 12 cm² and the paste thickness was 1 cm. The temperature is regulated through immersion of the device in a water bath at 25 °C.

Thermogravimetric analysis (STA 409 PC LUXX, Netzsch) was used to estimate the quantities of portlandite and chemically bound water. The protocol used was similar to the one described in [6]. The mass losses measured between 105 °C to 550°C and 420 °C to 550 °C were respectively associated to the bound water [7] and portlandite [6] content. The mass losses were normalized to the mass at 550 °C. Based on water bound content, a global degree of hydration can be defined:

$$\alpha_{global}^w = w_b^t / w_b^\infty \qquad (Eq\ 1)$$

Where w_b^t and w_b^∞ are respectively the bound water content at time t and at the complete hydration (ml/g of cement). w_b^∞ is estimated considering the cement composition [8,9].

^{29}Si magic-angle spinning (MAS) NMR experiments were performed in order to determine the quantity of unhydrated clinker and slag [10]. Before crushing the sample, the hydration was stopped by the freeze drying method. Spectra were collected on a Bruker Avance 300 WB (7.05 T) spectrometer using a Bruker CPMAS probe of 4 mm at a spinning frequency of 12.5 kHz. Recycle delay of 2 s was employed. The spectra were fitted using an in-house made software developed by Charpentier [11]. The fitting procedure are detailed in [10]. The specific degree of hydration (of clinker and slag) was deduced from the estimated remaining anhydrous content. We can note that two hypothesis are made to determine the degree of hydration of clinker; C$_3$A is fully hydrated whereas C$_4$AF hasn't reacted [12].

3 Experimental measurements

The global degree of hydration, based on the bound water content, is given in Table 2.

Table. 2. Portlandite content (CH), bound water content (w$_b$) and global degree of hydration (α_{global}) at 7, 28, 180 and 365 days of hydration.

Day	Parameter	CEM I	CEM II/A	CEM III/A	CEM III/C
7	w_b^t (ml/g)	0.168	0.132	0.113	0.075
	CH (g/g)	0.236	0.180	0.108	0.045
	α_{global} (%)	67	53	42	28
28	w_b^t (ml/g)	0.185	0.148	0.116	0.087
	CH (g/g)	0.251	0.185	0.109	0.05
	α_{global} (%)	74	59	43	32
180	w_b^t (ml/g)	0.193	0.174	0.144	0.094
	CH (g/g)	0.262	0.216	0.126	0.057
	α_{global} (%)	77	69	53	35
365	w_b^t (ml/g)	0.199	0.182	0.156	0.105
	CH (g/g)	0.275	0.222	0.124	0.065
	α_{global} (%)	79	73	58	39
∞	w_b^∞ (ml/g)	0.25 [8]	0.25 [8,13]	0.27 [8,13]	0.27 [8,13]

The bound water content increases with the hydration time due to hydrates formation. On the opposite, the addition of slag has a negative effect on the bound water content. In literature, the bound water content, estimated at 180 days of hydration, is comparable for a Portland cement (0.18 ml/g [9] and 0.21 ml/g [12]) and for a slag blended cements (0.19 ml/g for a cement with 42 % and 70 % of slag [9]). The bound water content measured at 180 days for our CEM III/A cement is lower (0.14 ml/g). The low reactivity of the incorporated slag is underlined by this observation and by the quantity of portlandite (no consumption observed in slag blended cement – Table 2).

The global degree of hydration (α_{global}) could be estimated by the specific degree of hydration of clinker ($\alpha_{clinker}$) and slag (α_{slag}) determined by ^{29}Si MAS NMR experiment:

$$\alpha_{global} = u_{slag}\,\alpha_{slag} + \alpha_{clinker}\,u_{clinker} \qquad (Eq\ 2)$$

With u the initial volume fraction of clinker and slag.

The results are given in the Table 3 with an error of 5 %.

Table 3. Degree of hydration of Clinker (Cl), slag (S) and cement (Ce) in %w.

	7 days			180 days			365 days		
	Cl	S	Ce	Cl	S	Ce	Cl	S	Ce
CEM I	61		61	81		81	80		80
CEM II/A	51	26	47	75	43	70	71	44	67
CEM III/A	53	13	27	64	45	52	68	46	54
CEM III/C	70	10	19	74	19	27	76	26	33

The percentage of reacted slag increases with the clinker content. This observation can be related to the fact that clinker dissolution activates the slag hydration [1]. There is a difference of 5 – 15 % between the two methods

(bound water and ^{29}Si MAS NMR). The quantity of the bound water content at complete hydration must be determined accurately to improve the determination of the global degree of hydration based on bound water content. We also expect that intermediate time of hydration will better constraint deconvolution of the ^{29}Si MAS NMR spectra (in progress).

The chemical shrinkage at complete hydration could be estimated from experimental measurements. The chemical shrinkage evolution results are shown in Figure 1.
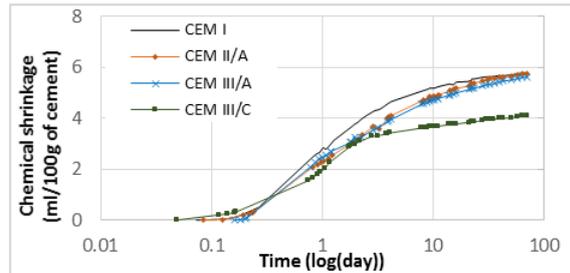

Figure 1. Chemical shrinkage evolution of each cement.

The chemical shrinkage evolves quickly during the first days and strongly slowdowns after some tens of days. We can notice that the hydration of slag blended cements is still uncomplete whatever the slag content (Table 3). Compared to other cements, the CEM III/C cement (80 % of slag) is characterized by a lower chemical shrinkage after 3 days. For lower content of slag (CEM II/A and CEM III/A cements), the chemical shrinkage, achieved at about 100 days, is close to that of the CEM I cement paste. This similar behavior could be related to their Blaine surface. We can note that Guillon *et al.* [14] measured a chemical shrinkage of 5.5 ml/100g after 100 days of hydration of a mix of CEM I cement with 60 % of slag.

5. Hydration model

The parameters introduced in the Powers' model are given in Table 4.

Table 4: Parameters used for applying the hydration model

At complete hydration	CEM I	CEM II/A	CEM III/A	CEM III/C
Chemical shrinkage (ml/g)	0.08	0.1	0.17	0.19
Water bound (ml/g)	0.25	0.27	0.29	0.32
Adsorbed water (ml/g)	0.17	0.17	0.16	0.15

The chemical shrinkage and the bound water content at complete hydration are deduced from experimental data at respectively 7 days and 1 year considering the global degree of hydration achieved. The absorbed water are calculated based on data reported in literature (0.19 ml/g of clinker [3] and 0.15 ml/g of slag

[9]). Besides, the specific degrees of hydration are determined by ^{29}Si MAS NMR experiments and the same method is used for the global degree of hydration to be coherent.

The Powers' model was applied to all cement but only the results associated to CEM I, CEM III/A and CEM III/C cements are displayed (Figure 2).
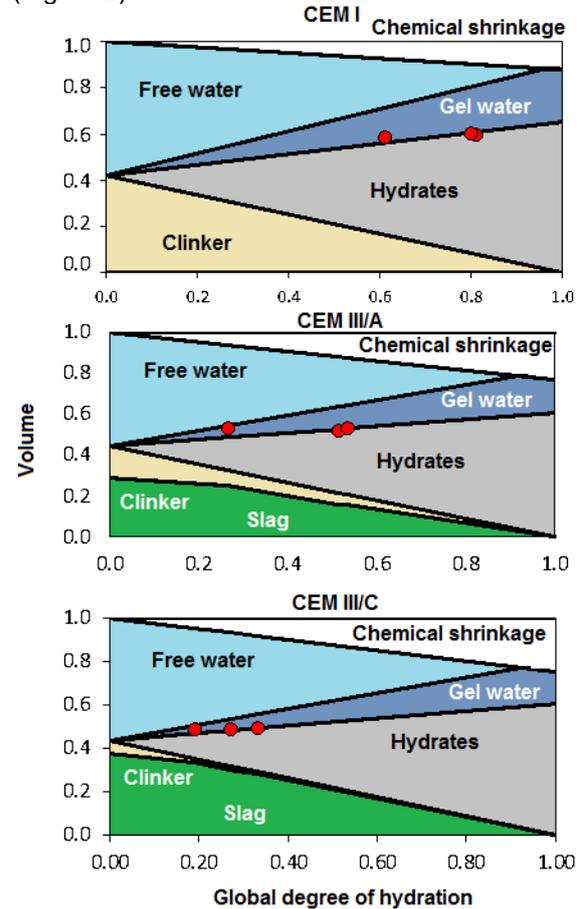

Figure 2. CEM I, CEM III/A and CEM III/C (80%w of slag) cement evolution (in volume) according to the degree of hydration. The volume of hydrates, deduced from the experimental measurements of water bound content (Table 2), is represented by Red dots.

Bound water content (Table 2) is used to compare the Powers' model with experimental measurements (red dots in Figure 2). The difference between the model's results and the experimental data don't exceed 0.02 ml/g for all cements expect for CEM III/A cement. In this case, this difference is about 0.04 ml/g after 7 days of hydration. It is noteworthy that the deviation of the experimental measurement is about 0.004 ml/g.

These discrepancies could be linked to the difficulty to determine accurately the water state repartition at complete hydration. We can notice that the bound water content at complete hydration presented in Table 4 are higher than the ones defined in Table 2 for the slag blended cements. The highest difference is obtained for the CEM III/C cement. The estimation of the

bound water content at complete hydration is especially difficult for blended cements with high slag content. Indeed, the maximal global degree of hydration achieved at one year is low (0.33 for a CEM III/C cement). The possible error induced by extrapolation of the chemical shrinkage between 7 days to complete hydration should be even greater.

Based on these data (Table 4), it is possible to estimate the quantity of bound water and the value of chemical shrinkage (of slag) at complete hydration. The chemical shrinkage deduced for all slag blended cements ranges from 0.22 ml/g of slag to 0.23 ml/g of slag. A significant difference is obtained for the bound water content associated to CEM II/A cement (0.43 ml/g of slag) compared to the other slag blended cements: 0.32 -0.35 ml/g of slag cements. We can note that Maekawa et al. [13] estimated a value of $V_{bw}^{\infty} = 0.3$ ml/g; in accordance with these results. The probable overestimation of bound water content at complete hydration of CEM II/A is probably associated to the deconvolution difficulties of the ^{29}Si MAS NMR spectra. Without further data, it is supposed to be related to the low slag content.

All these remarks underline the necessity to characterize samples at intermediate time of hydration as well as at higher degree of hydration to improve the definition of the parameter of Powers' model. Significantly higher degrees of hydration could be achieved using accelerated hydration experiments.

Another point that has to be mentioned is the known mutual interaction between the hydration of clinker and slag [1]. The different variation of clinker and slag consumption in CEM III/A (Figure 2) underlines undoubtedly the complex relation between slag and clinker hydration. A detailed description of the hydrated samples seems to be necessary.

4. CONCLUSION

The Powers' model was applied to describe the hydration of slag blended cements. The chemical shrinkage and the bound water content at complete hydration are determined by extrapolating experimental data.

The bound water contents measured experimentally are compared with the model results. The difference obtained is one order of magnitude higher than the deviation of the experimental measurements.

Samples with higher degree of hydration are needed to determine accurately the chemical shrinkage and the bound water content at complete hydration. This is especially crucial for CEM III/C cement where the degree of hydration is about 33 % after one year.

This difference could also be related to the determination of the global degree of hydration. Intermediate times of hydration are necessary to improve the estimation of this parameter. Indeed, these additional points will allow better constraint deconvolution of the ^{29}Si MAS NMR spectra.

A detailed description of hydrated samples, from few days to several years of hydration, seems to be necessary to develop a model taking into account the contribution of clinker and slag as well as their mutual interaction. A kinetic law of hydration could be coupled to the model.

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